1990

The Effect of Structure and Geometry on the Spectroscopy of Beta-Diketones.

Steven Eugene Arnold

Louisiana State University and Agricultural & Mechanical College

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The effect of structure and geometry on the spectroscopy of beta-diketones

Arnold, Steven Eugene, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1990
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THE EFFECT OF STRUCTURE AND GEOMETRY ON THE SPECTROSCOPY OF BETA-DIKETONES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Steven Eugene Arnold
B.S. Louisiana State University, 1985
December, 1990
DEDICATION

to my parents
and

to my wife
Donna
ACKNOWLEDGMENT

The author wishes to thank his major professor Dr. Robert V. Nauman for his scientific guidance and for his many other teachings as well.

The other members of Dr. Nauman's research group, Dr. Timothy Fillingim, Dr. Jerry Lewis, Dr. Cristian Franco, Dr. Claudina Veas, Elizabeth Wilhite, and Vestal Shirley are gratefully acknowledged for their assistance, helpful discussion, and friendship.

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The author would like to thank Marcus Nauman for his kind assistance in the collection of the $^{19}$F NMR spectra.

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FOREWORD

"We can imagine that this complicated array of moving things which constitutes 'the world' is something like a great chess game being played by the gods, and we are observers of the game. We do not know what the rules of the game are; all we are allowed to do is to watch the playing. Of course, if we watch long enough, we may eventually catch on to a few of the rules. The rules of the game are what we mean by fundamental physics. Even if we know every rule, however... what we really can explain in terms of those rules is very limited, because almost all situations are so enormously complicated that we cannot follow the plays of the game using the rules, much less tell what is going to happen next. We must, therefore, limit ourselves to the more basic question of the rules of the game. If we know all the rules, we consider that we 'understand' the world."

Richard Feynman

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ABBREVIATIONS AND SYMBOLS

+, - ......... a superscript plus or minus indicates a positive or negative ion of the species to which it is appended

ACAC ......... acetylacetone
TFACAC ....... trifluoroacetylacetone
HFACAC ....... hexafluoroacetylacetone
BA ........... benzoylaceton
BZTFAC ........ benzoyl trifluoroacetone
DBM ........... dibenzoylmethane
α-ME-ACAC .... 3-methyl-acetylacetone
1,3-PENT ...... 1,3-cyclopentanedione
1,3-HEX ...... 1,3-cyclohexanediode
2-ME-1,3-HEX . 2-methyl-1,3-cyclohexanediode
2-AC-HEX ...... 2-acetylcyclohexanone
c ............ molar absorptivity
3MP .......... 3-methylpentane
DMSO .......... dimethylsulfoxide
MEOH .......... methanol
TMS .......... tetramethylsilane
K ............ unit of absolute temperature, the Kelvin
RT, kT ....... thermal energy
conc. ......... concentrated
MNDO ......... modified neglect of differential overlap
The following terms, when used as suffixes, refer to the species indicated.

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ABSTRACT

In this work the ultraviolet (UV) absorption and the \(^1\)H and \(^{19}\)F nuclear magnetic resonance spectra of \(\beta\)-diketones were studied. Potential energy curves for various geometries of the compounds were calculated by means of the MNDO method. The compounds included in the work were acetylacetone, trifluoro- and hexafluoro-acetylacetone, benzoylacetone, dibenzoylmethane, benzoyltrifluoroacetone, 3-methyl-acetylacetone, 1,3-cyclopentanediione, 1,3-cyclohexanediione, 2-methyl-1,3-cyclohexanediione and 2-acetyl-cyclohexanone. The spectra of the neutral enolic, anionic and cationic species were investigated. In addition, the spectra of the reaction products of the compounds with boron trifluoride which were formed in polar and nonpolar solvents were studied.

The results were interpreted in terms of the geometries of the molecules. It is hypothesized that the presence of an electron withdrawing substituent on the opposite side of the conjugated system from an electron donating substituent leads to a more nearly planar molecule. The spectra of the anionic species and the potential energy calculations indicate that the predominant geometries of the aliphatic anions are nonplanar and that there are multiple geometries of the
anion of hexafluoroacetylacetone. The UV absorption spectra indicate that the phenyl rings of the aromatic diketones rotate out of the molecular plane upon anion formation and rotate to a more nearly planar conformation upon cation formation. The spectra indicate that the reaction of boron trifluoride with the fluorinated diketones results in formation of two types of nonchelated monodentate $\text{BF}_3$ adducts that are dependent upon the solvent polarity.
INTRODUCTION

The goal of this research is to determine the effect of geometry on the spectroscopy of β-diketones and to determine how the geometry and the structure are interrelated. I will use structure in this dissertation to mean the identity of the molecule as defined by its molecular formula and geometry to mean the shape of the molecule. Often, unfortunately, the geometry of a molecule is neglected when its spectra are considered. It has been shown previously by other members of this research group\textsuperscript{2-8} that geometry is a very important factor in interpreting the spectroscopy of a molecule. This work is a continuation of that research. It is hoped that by observing trends in the spectroscopy of β-diketones, one’s ability to predict and interpret the spectroscopy of other conjugated molecules will be extended.

Knowledge of the geometry of molecules, particularly conjugated ones, is important for many reasons. The positions of spectral bands are affected by the geometry of the molecule. If a molecule exists in more than one geometric form, there may be many unexpected bands in the spectra of that molecule. The UV-visible absorption spectrum of a molecule depends on the geometry of the molecule because the geometry of a molecule affects the electronic structure. In turn, the electronic structure
determines the bonding between the atoms or groups of atoms and determines the vibrational frequencies. The vibrational frequencies affect the infrared, Raman, and UV-visible spectra. The splittings, chemical shifts and number of peaks in the NMR spectra are also affected by the geometry. These examples indicate that these and other spectroscopic techniques may be useful probes for determining the geometry of molecules.

Due to the effect on the electronic structure, the geometry of a molecule also affects the reactions of that molecule. Particular molecular sites may be more or less reactive in a given reaction because of the geometry of the molecule. In addition to the electronic effects on the reactivity there are steric effects. Reaction at certain molecular sites may be enhanced or hindered by the spatial characteristics of a particular geometry. The attacking reagent must be able to reach the reactive site in order to react. Knowledge of the likely geometries of a molecule may allow one to design more efficient and specific reactions. In addition to reaction at specific sites, it is increasingly required that the reaction also be stereospecific and produce products that have a particular stereochemistry. Knowledge of the molecular geometries of potential reactants would help the design of stereospecific reactions.
In the following portions of the Introduction, I will present the compounds that were studied in this research, define some of the nomenclature that will be used in the discussion of them, introduce the types of data to be considered and discuss the methods and principles that will be used in the interpretation of the data. In the Experimental section, the sources and purification of compounds and reagents will be presented, the apparatus and instrumentation will be described, the computer programs and theoretical computations that were used will be discussed, and the preparation of sample solutions will be described.

The Results and Discussion section will be divided into sections covering the various types of species that were studied in this work. The discussion of the neutral enol forms will be presented first, and the influence of the hydrogen bonds will be discussed. The influence of the structure and geometry of the compounds will be discussed in all sections. In particular, the effects of charge and the conjugation effects of aromatic rings will be important. The neutral enol section contains some material which overlaps a later section which will deal with the reactions of the diketones with boron trifluoride. Some of the data and interpretations for the later section are presented in the neutral enol section because the results are useful in the
interpretation of the enol data.

The next section covers the anionic forms of the diketones. The anion section contains most of the potential energy calculations that were performed and are used in the discussion of the likely geometries of the ions of the diketones. Some supplementary NMR data relevant to this section are presented later in a section that covers the reactions of the anions of the diketones with boron trifluoride.

The next section in the discussion covers the spectroscopy of the cations. Again, the influence of the geometry on the spectroscopy is discussed, and the changes in the geometry that accompany ionization are rationalized.

In the next two sections, the reactions of diketones with boron trifluoride in polar and nonpolar solvent, respectively, are covered. In particular, evidence that the fluorinated diketones may form nonchelated BF$_3$ addition products is presented. In addition, the changes in the geometry and electronic structure upon reaction with BF$_3$ are discussed. The UV absorption data in these two sections are supplemented by $^{19}$F NMR data collected as part of this research. As mentioned previously, the data and interpretations in these sections have some overlap with previous sections.

The Conclusion contains a summary of the results and
the principles that were developed to explain the observed trends and the individual cases.

Appendix one contains output from the molecular orbital calculations for selected geometries.

Appendix two contain printouts of some of the computer programs that were written and used in this work.

The β-diketones are useful for a spectroscopic study of geometry because they are conjugated molecules that have many possible geometrical and structural forms available to them. In this research a series containing aliphatic, aromatic, acyclic and cyclic β-diketones and their fluoro derivatives has been investigated. Figure 1 shows the structures of the enol form of the compounds. The neutral molecules and their anionic and cationic forms have been studied. The spectroscopy of organic ions is in general less well known than that of the neutral species. The addition products of reactions of β-diketones with boron trifluoride are also considered. Some metal chelates have also been prepared and studied. The major use of the β-diketones is chelation of metals, and their importance and versatility in this area are shown by acetylacetone, which is reported to have been coordinated to every naturally occurring metal.⁹

In addition to the enol form of the β-diketones shown in Figure 1 there is the keto form, shown below on
Figure 1

acetylacetone (2,4-pentanedione)  trifluoroacetylacetone

hexafluoroacetylacetone  benzoylaceton

benzoyltrifluoroacetone  dibenzoylmethane (1,3-diphenyl-1,3-propanedione)
Figure 1 (cont.)

**dimedone**  
(5,5-dimethyl-1,3-cyclohexanedione)

2-methyl-1,3-cyclohexanedione

1,3-cyclohexanedione

2-acetyl-cyclohexanone

α-methyl-acetylacetone

4-methyl-1,8-decalindione
the right, that is in equilibrium with the enol form on the left.

Because in the keto forms there is little electron delocalization, the electronic transitions occur in isolated parts of the molecules and are less affected by geometric changes; consequently, although the keto-enol equilibrium is a complication the spectroscopy of the keto forms is not important in this work. The equilibrium is not a major problem because the diketones that were studied are all essentially 100% enolized in non-aqueous solution.

The geometrical variations will now be considered. There are three extreme limits of geometrical forms into which the compounds are often grouped. These limiting forms are named for the resemblance of the backbone of the molecules to letters of the alphabet. Thus, as shown below, there may be U, S, and W forms.

These limiting forms are planar molecules, but there is
the possibility of rotation about bonds to produce similar molecules that are nonplanar. It is this nonplanarity which is a major concern of this work.

It must be understood that the various geometries discussed in this work can be experimentally distinguished because they have not only different electronic wavefunctions but also different nuclear positions. The forms are not merely different resonance structures of the same compound; the forms have different geometries. In the case of the Kekulé structures of benzene, all the structures have the same geometry.

The aim of this work was to determine the geometries of the various structures and to uncover some set of "rules" that would relate the types of geometries with the spectra of a relatively large set of compounds and their derivatives. The role of the hydrogen bond and the effect of charge, both positive and negative, were also studied. The primary method of analysis was ultraviolet absorption spectroscopy. The structures of the various species and their properties were further investigated by means of nuclear magnetic resonance spectroscopy. Both $^1H$ and $^{19}F$ NMR spectroscopy have been used. Computer calculations have been carried out; emphasis was put on the calculation of potential energy curves relevant to the formation of nonplanar geometries. The calculations were performed by means of the MNDO method (modified
neglect of differential overlap) because this method has been used successfully for the treatment of rotations about bonds in conjugated molecules. The MNDO method will be discussed later in the experimental section.

The basic concept in the interpretation of the UV data is that the more planar the molecule, the lower the transition energy will be. This correlation may be understood by analogy with the one-dimensional particle in a box problem. The transition energy decreases as the box becomes longer. A textbook example of the redshifting effect with increasing chain (i.e. box) length is given by the polymethine dyes. As the conjugated chain becomes longer, the absorption wavelength becomes longer. If one were to begin to introduce a twist at some point in the chain, however, the result would be that the spectrum would appear more and more like a spectrum of a mixture of two independent molecules as the amount of twist increased. These two molecules would correspond approximately to the two sections of chain, one on each side of the twist. The spectrum would blue shift because of the shortening of the effective chain length until the two sections were independent and essentially noninteracting.

The change of the spectrum from that of the entire molecule to that of the two sections is a gradual one. The gradual shift occurs because the overlap of the pi
orbitals gradually decreases as the twist increases; the resonance is not destroyed until there is no more overlap of the pi orbitals. The overlap of p orbitals to form a pi bond is depicted on the left in the diagram below. The darkened area, in which the space is covered by both orbitals, is the region of overlap. If one of the orbitals is rotated by 90° as shown on the right, the orbitals no longer overlap and the pi bond is destroyed.

In quantum mechanical terms, as discussed in the book by Jaffé and Orchin\(^1\), the overlap integral between orbitals \( \phi \) on adjacent atoms \( r \) and \( s \) is given by:

\[
S = \int \phi_r \phi_s \, d\tau
\]

which varies from 1 to 0 as the angle of rotation between the two orbitals varies from 0° to 90°. If the twist angle between the orbitals is \( \theta \) and the maximum value of the overlap integral (at \( \theta=0^\circ \)) is \( S_{rs}^0 \), then the overlap between \( \phi_r \) and \( \phi_s \) varies according to the equation:

\[
S_{rs}^\theta = S_{rs}^0 \cos \theta
\]

It will prove useful to make a slight extension of this equation to include a third atom, \( t \), attached to atom \( s \), and to calculate the total overlap between atoms \( r \) and \( s \).
and atoms s and t:

\[ S_{rst} \theta_1, \theta_2 = S_{rs}^0 \cos \theta_1 + S_{st}^0 \cos \theta_2 \]

in which \( \theta_1 \) is the angle of rotation between orbitals on atoms r and s, and \( \theta_2 \) is the angle of rotation between orbitals on atoms s and t. Assuming that atoms r, s, and t are all carbon atoms that have the same bond lengths between them, the values of \( S_{rs}^0 \) and \( S_{st}^0 \) should be equal, and may be set equal to 1. The equation simplifies to:

\[ S_{rst} \theta_1, \theta_2 = \cos \theta_1 + \cos \theta_2 \]

The total overlap for three atoms bonded in a straight chain as a function of the two twist angles is plotted in Figure 2. The total overlap varies from a maximum of 2 for the planar configurations (\( \theta_1 = \theta_2 = 0^\circ \)) to 0 for the totally perpendicular configuration (\( \theta_1 = \theta_2 = 90^\circ \)). The equation developed in this section will be used in a later section to compare the relative amounts of overlap present in various geometries of the \( \beta \)-diketones.

The above equation may be used to illustrate that even though the total twist over the length of the molecule may be quite large, the resonance may still extend over the length of the molecule because the total twist may be distributed among all the p orbitals of the pi system. The distribution of the twist may be visualized to be like fanning a deck of cards. Each card overlaps the cards behind and in front of it.
Figure 2

Total overlap for three atoms bonded in a straight chain
is not new and is the basis for the hypothesis that aromatic compounds in which there is a Möbius twist may some day be discovered.\textsuperscript{11}

A shortcoming of the foregoing treatment is that the overlap is only a portion of the total quantum mechanical treatment of a molecule and does not completely determine the resonance. For example, on the basis of overlap alone, one could not distinguish between the various planar U, S, and W forms of the β-diketones. All of these planar forms have the maximum possible overlap. It is the other portions of the complete quantum mechanical description of the molecules, such as electron repulsion, that must be used to explain the differences between forms that have the same overlap. Rather than attempting a full quantum mechanical treatment for those cases I will use an approach based on experimental data.

Considering planar forms of the β-diketones, I hypothesize that the U forms have the longest wavelength absorptions and the absorptions of the S and W forms would lie to the blue of that of the U forms. The hypothesis that the U form has the lowest transition energy may be supported by considering the spectra of simple cis-trans isomer pairs. The transitions of planar compounds that have cis conformations about double bonds lie to the red of those of their trans isomers. This statement may seem to be in disagreement with popular
belief because in many familiar cases the cis isomers are not completely planar due to steric interactions. Perhaps the most studied system of this kind is stilbene. The trans isomer of stilbene under most conditions absorbs to the red of the cis isomer. However, when the molecule is constrained to be more nearly planar by placing it into a dibenzyl crystal matrix, the cis isomer absorbs farther to the red. Since the U form of the $\beta$-diketones has a cis configuration about its carbon-carbon double bond and the S and W forms have a trans configuration, the U should absorb farther to the red than the S and W forms if all are planar. The transitions of nonplanar geometries will be considered throughout this work.

At this point it is necessary to refute a statement made in the literature (1965) that it is not possible for the enol forms of the diketones to exist in a nonplanar geometry. The evidence (1963) given in support of this statement is that bicyclo-[2.2.2]-octanetrione, illustrated below, exists entirely in the keto form.

The authors of the 1965 paper reasoned that this bicyclic molecule could not attain a planar geometry that would
make it able to enolize. However, an examination of the structure of the enol form of the compound makes the reason for its existence in the keto form immediately apparent. In the enol form, bicyclo-[2.2.2]-octanetrione would be required to have a bridgehead double bond. That is, the carbon-carbon double bond in the enol form would have excessive angle strain due to the geometric constraints of the bicyclic system. The orbitals that must overlap to form the double bond are constrained to be essentially perpendicular to one another; consequently, their overlap is minimized. It is well known that double bonds are extremely rare when overlap is hindered. Thus, the enol form of bicyclo-[2.2.2]-octanetrione is greatly destabilized relative to the keto form. The nonplanar geometries suggested for the diketones studied in this work require only moderate twists about essential single bonds, and minimal angle strain is introduced. Therefore, the statement that the β-diketones cannot exist in the enol form in nonplanar geometries is not valid.

The principles outlined in this section will be used to infer geometries for various species throughout this work. Since the 0-0 band cannot be determined, the \( \lambda_{\text{max}} \) of a UV absorption band will be used as an indication of the energy of the transition and consequently as a probe of the geometry of the molecule. The assignment of most
of the UV bands to absorptions of entire molecules or to specific portions of the molecules has been made previously by other members of this research group. These assignments have been made largely on the basis of comparison of the spectra of the β-diketones with the spectra of simpler model compounds.

In the preceding paragraph it was stated that the $\lambda_{\text{max}}$'s of the UV absorption bands will be used as an indication of the energy of the transition. The energy of the purely electronic transition is the energy of the 0-0 transition, in which there is no change in the vibrational energy upon excitation. However, the $\lambda_{\text{max}}$ of an absorption band does not necessarily correspond to the wavelength of the 0-0 transition. Therefore, the energy corresponding to the wavelength of maximum absorption is not necessarily an exact measure of the energy of the purely electronic transition. However, because the readily available experimental quantity is the $\lambda_{\text{max}}$ and because the transition giving the $\lambda_{\text{max}}$ generally terminates in only lowly excited vibrational levels, the $\lambda_{\text{max}}$ is used. The use of the $\lambda_{\text{max}}$ as an indication of the energy of the electronic transitions is therefore a potential source of error, but unfortunately there is no simple way to determine the wavelength of the 0-0 transition. As long as the amount of vibrational excitation accompanying the electronic excitation is not
too great and is fairly consistent from one species to another, the approximation should not be too severe.

The geometries of a species are deduced from comparisons of its spectra with those of related compounds about which some geometrical information is known. For example, the compound 1,8-decalindione is confined by its structure to exist in a nearly planar U conformation. Likewise, 1,3-cyclohexanedione must exist in a W conformation as a consequence of its structure. Other \( \beta \)-diketones may be classified as belonging to the U or W classes by comparison of their spectra with the spectra of these reference compounds. The geometries may be further deduced to be more or less nearly planar than one another by comparison of their \( \lambda_{\text{max}} \)'s. Two compounds of the U type, for example, that have similar structures and have nearly the same \( \lambda_{\text{max}} \) (for comparable transitions) should have similar geometries. However, if one compound has a \( \lambda_{\text{max}} \) further to the red than another, it is likely that the first compound is more nearly planar than the second.

The study of the spectra of different forms of the same molecule can be very useful. The changes in the spectra that accompany ionization are extensively studied in this work. The changes in the \( \lambda_{\text{max}} \)'s between the neutral and ionic forms may be used as a guide to the changes in geometry that occur upon ionization. Other
chemical modifications such as chelation also provide useful results. The trends in the spectral properties of \( \beta \)-diketones will be interpreted in terms of known trends in their chemical properties. Hydrogen bond strength and electron density are two chemical properties that I will use in this manner.

The NMR spectra of the compounds will be used to determine the structures of the compounds when that information is not known and to investigate the geometries of the molecules as well. The number of peaks in the NMR spectrum of a compound is useful for the determination of the geometries of a molecule. For example, two groups may appear to be equivalent when the molecule is drawn on paper but appear to give different signals in the NMR spectrum. It is possible that the real shape of the molecule causes the two groups to be chemically inequivalent. Another possibility in the example cited above is that the groups within a single molecule are equivalent but the molecule is present in more than one form. The resonances of the group in each form are different.

Molecular orbital calculations have been performed; these calculations focus on the evaluation of the most energetically favorable geometries of the various species studied. These computational results are combined with the experimental results to decide the number of
observable geometries that may be present. The calculations are also used to give more specific estimates of the geometries of some of the species than are possible from the experimental data alone. A brief comparison of several molecular orbital methods is given in a later part of this section.

For convenience, I will now define a system of notation that will be used in the discussion of some of the various geometries. The torsional angles about the bonds in the $\beta$-diketones will be designated $\phi_1$ and $\phi_2$ as depicted below. The planar U geometry defines $\phi_1 = \phi_2 = 0^\circ$.

\[ \begin{array}{c}
\text{R}_1 \\
\text{R}_2
\end{array} \]

The planar W geometry defines $\phi_1 = \phi_2 = 180^\circ$. The two possible planar S geometries are given by $\phi_1 = 0^\circ$, $\phi_2 = 180^\circ$ and vice versa. In the symmetric diketones the two S forms are identical. The arrows in the illustration above indicate that the directions of increasing $\phi_1$ and $\phi_2$ correspond to rotation in opposite directions.

The geometries of the planar U, S, and W forms may be used to define a coordinate system which is shown in Figure 3. Potential energy calculations have been performed to give results along paths corresponding to distortion from the planar U to the planar S and W forms. Distortion of the planar U geometry along the axes from U
Figure 3
Coordinate system for torsion angles that were used to define geometries
to either of the S geometries will be termed S
distortion, and distortion along the dotted path from U
to W will be termed W distortion. With energy as a third
axis, a potential energy surface may be constructed for a
particular compound. The distinction between the
directions of increasing $\phi_1$ and $\phi_2$ is unimportant except
in the case of W distortion. As mentioned, the direction
of increasing $\phi$ is for rotation in opposite directions,
such that the oxygens will be twisted away from one
another. Any geometry in the coordinate system may now
be defined in terms of the torsion angle and the type of
distortion. For example, the point marked "a" in the
figure, which has $\phi_1=140^\circ$, $\phi_2=0^\circ$, will be designated
140-S$_1$ to indicate that it has 140° of distortion of the
S$_1$ type. For symmetric diketones, the notation for this
point would be shortened to 140-S, because the two S
distortions are identical. The point labeled "b" in the
figure has $\phi_1=45^\circ$, $\phi_2=45^\circ$ and will be designated 45-W.
Only one angle need be specified for points along the
three paths between the U and the S and W geometries
because the other angle is understood to be either equal
to the first or zero. In the event that a point not on
one of these paths is considered, the values of $\phi_1$ and $\phi_2$
should both be specified.
EXPERIMENTAL

Compounds

The pure diketones were commercial products, and the metal chelates and salts were synthesized from these compounds in the laboratory. The acetylacetone was that of Matheson, Coleman, and Bell. Trifluoroacetylacetone, hexafluoroacetylacetone, and benzoylacacetone were those of Peninsular ChemResearch, Inc. Some trifluoroacetylacetone from Columbia Organic Chemicals Co. Inc. was used as well. The \( \alpha \)-methyl-acetylacetone was a product of K & K Laboratories, Inc.. The cyclic compounds 1,3-cyclopentanedione, 1,3-cyclohexanedione, and 2-methyl-1,3-cyclohexanedione were products of Aldrich Chemical Co.. The other cyclic compound, 5,5-dimethyl-1,3-cyclohexanedione, was that of Eastman Kodak Chemicals.

The \( \beta \)-diketones were purified prior to use. The liquid diketones were purified by distillation and the solids by sublimation. The cyclic diketones are thermally unstable over time and were stored in a freezer. Most compounds were stored in the dark.

The compounds benzalacetone, trans-1,2-dibenzylethylene, and acetonylacetone, all products of Aldrich Chemical Co., and benzophenone, a product of City Chemical Corporation (New York) were used for general comparison purposes and were not purified.
The spectra agree with those obtained previously with purified samples by other members of this group.

Solvents were normally purified prior to use. Absolute methanol (Mallincrodt) was distilled over magnesium powder to remove water and was stored over 4Å molecular sieves. Absolute ethanol and 2-propanol (Mallincrodt) were treated in a similar manner. Cyclohexane (Baker) and 3-methylpentane (Phillips) were washed several times with aliquots of concentrated sulfuric acid, washed with several aliquots of distilled water, dried over anhydrous sodium carbonate, distilled, and stored over metallic sodium. Concentrated sulfuric acid (Mallincrodt) was taken straight from the bottle with no purification. Carbon tetrachloride (Mallincrodt) was purified by passing it twice through a column of silica gel.

Sodium hydride 50% oil dispersion from Alfa Products was used without purification or removal of the oil. Boron trifluoride ethyl etherate from Aldrich Chemical Co. was taken from a new bottle and was used without purification.

Sodium acetylacetonate was prepared by the method described by Cheng\textsuperscript{2} from acetylacetone and sodium hydroxide. Metal chelates were prepared from the diketones by the method of Charles and Pawlikowski.\textsuperscript{15} In that method, an aqueous solution of the metal salt

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(usually the acetate) and an aqueous solution of sodium acetate are mixed with a solution of the diketone in methanol. The metal chelate precipitated immediately or upon gentle heating. The complexes were filtered, washed thoroughly with cold water and cold methanol, and recrystallized from a methanol/water mixture.

**Apparatus**

The UV spectra were recorded by means of a Cary 14 spectrophotometer operated in double beam mode. Room temperature spectra were recorded with the sample and solvent contained in matched 1.0 cm silica cells. The NMR spectra were recorded by means of a 100 MHz Bruker FT-NMR system. For $^1$H spectra, TMS was used as an internal standard, and the tubes were spun during data acquisition. For $^{19}$F spectra, an external standard spectrum of freon (CCl$_3$F) was used, and the sample tubes were not spun.

All computations were carried out by means of a Leading Edge Model D computer that has 640 K memory. The 8088 microprocessor was supplemented by an 8086 math coprocessor. Internal storage was supplied by a 30 megabyte hard disk card. All UV spectra were digitized on a Genius digitizing tablet, and the data from the tablet were collected and stored by software programs which I wrote and which are listed in an appendix. The UV spectra were plotted by means of a program written by
myself which is also listed in an appendix. I have also written simple but convenient molecule viewing and plotting programs which were very useful for checking input coordinates for the molecular orbital calculations. The main advantage of these programs over some other programs of this type is that they use ASCII data input files which may be clipped from the geometry-checking output files of the MNDO program. Clipping the data in this manner eliminates the need to type in the coordinates and the associated typographical errors and tedious, time-consuming work. Gaussian bandfits of some UV spectra were performed by means of the program BANDIT. The BANDIT program is discussed later in this section.

The MNDO method, not to be confused with the MINDO method, was used for the molecular orbital calculations in this work. The MNDO method, developed by Dewar and Thiel, is a semiempirical SCF-LCAO-MO (self-consistent field, linear combination of atomic orbitals, molecular orbital) treatment based on the NDDO (neglect of diatomic differential overlap) approximation. The differences among a few semiempirical methods will now be discussed. The basic differences are in the types of electron repulsions that are ignored by the calculations. The descriptions given here of the repulsion integrals neglected and considered at each
level is adapted from Levine, Quantum Chemistry, Third Edition and from the MNDO reference papers listed above.

Most of the previous molecular orbital calculations performed on these compounds by former members of this research group have been at the CNDO (complete neglect of differential overlap) level. Under the CNDO approximation, which is covered in some detail by Davis, electron repulsion integrals containing product terms for electrons in different atomic orbitals (AO's) on the same atom are neglected. The two electron repulsion integral is defined by:

\[(rs|tu) = \int \int \phi_r(1)\phi_s(1)\left(\frac{e^2}{r_{12}}\right)\phi_t(2)\phi_u(2)\,d\tau_1\,d\tau_2\]

in which the \(\phi's\) are atomic orbitals, \(e\) is the electronic charge and \(r_{12}\) is the interelectron separation. If orbitals \(\phi_r\) and \(\phi_s\) are centered on atom A and orbitals \(\phi_t\) and \(\phi_u\) are centered on atom B, the integral is a two-center integral. Under the CNDO approximation, the only nonzero two-center repulsion integrals are of the form \((rr|tt)\).

In the INDO (intermediate neglect of differential overlap) method, differential overlap between different AO's on the same atom are not neglected in the one-center repulsion integrals, but in the manner of CNDO all other electron repulsions are neglected. The INDO
approximation thus considers one-center integrals of the form \((rs|rs)\), in which both sets of orbitals are on the same atom. Both the CNDO and INDO treatments assign the same value to all two-center repulsion integrals regardless of the types of atomic orbitals occurring in the integral. That is, the \(s\), \(p_\sigma\), and \(p_\pi\) orbitals are treated alike. The parameter sets used by CNDO and INDO for some integrals have been adjusted to make the results agree as closely as possible with the results of ab-initio calculations. The spectroscopic version of CNDO, CNDO/S, was parameterized to give agreement with the experimental spectra of a set of compounds.

The MINDO (modified intermediate neglect of differential overlap) method uses the same repulsions as the INDO method, but it is parameterized to make the calculated heats of formation agree with the experimental values for the compounds in the parameterization set as closely as possible.

The NDDO (neglect of differential diatomic overlap) approximation includes all two-center electron repulsions. As in the other treatments, all three and four-center integrals are neglected. In the NDDO approximation, however, different values of the repulsion integrals are assigned for the different types \((s, p_\sigma, p_\pi)\) of orbitals occurring in the integrals. The MNDO (modified neglect of diatomic overlap) method is a
parameterized application of the NDDO approximation and thus includes more electron repulsion integrals than the CNDO, INDO and MINDO methods. The MNDO program is parameterized to give agreement with experimental heats of formation and has been shown to give good agreement with experiment in the calculation of many rotations about conjugated bonds. The significant increase in the number of electron repulsions considered in the MNDO method is the reason for the improvement of the results over those of the other methods in the calculation of molecular geometries.

The geometric parameters used in the MNDO program input for the calculations performed in this work are given in Table 1.

All of the potential energies calculated in this work were those of the ground state molecules. In some of the previous work done by other members of this group, calculations were made for excited state energies and those excited state calculations should not be confused with these ground state calculations. In addition, many spectroscopic calculations were made previously by means of the CNDO/S program. The transitions predicted by the CNDO/S method for planar forms of the β-diketones have been somewhat useful to those previous workers. However, the CNDO/S calculations that I have carried out for nonplanar forms of the β-diketones do not give reasonable
Table 1

Geometric parameters used in MNDO calculations

**Bond lengths** (Å)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-CH₃, C-CF₃</td>
<td>1.540</td>
</tr>
<tr>
<td>C-C (all other)</td>
<td>1.390</td>
</tr>
<tr>
<td>C-O</td>
<td>1.280</td>
</tr>
<tr>
<td>C-H</td>
<td>1.060</td>
</tr>
<tr>
<td>C-F</td>
<td>1.320</td>
</tr>
<tr>
<td>O-H</td>
<td>1.190</td>
</tr>
<tr>
<td>O-B</td>
<td>1.487</td>
</tr>
<tr>
<td>B-F</td>
<td>1.372</td>
</tr>
</tbody>
</table>

**Bond angles** (degrees)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C-C, C-C-O</td>
<td>120.0</td>
</tr>
<tr>
<td>C-C-H</td>
<td>109.5</td>
</tr>
<tr>
<td>C-C-F</td>
<td>109.5</td>
</tr>
<tr>
<td>C-O-H</td>
<td>102.0</td>
</tr>
<tr>
<td>O-B-F</td>
<td>108.6</td>
</tr>
</tbody>
</table>

Torsional angles were defined previously in the introduction.
results for the trends in the spectroscopy and I have abandoned calculations of that type. Unfortunately, no better spectroscopic molecular orbital program is available.

Several of the UV spectra obtained in this research contain overlapping bands. Because the overlap of bands causes the apparent band maxima to be shifted from their true values it is desirable to resolve the spectrum into individual bands which reflect the actual transition wavelengths. In this work the resolution of bands in this manner was performed by means of the BANDIT computer program. The BANDIT program performs the resolution by an iterative least-squares procedure. Bands may be assumed to be either gaussian or lorentzian in shape and because UV absorption bands are normally gaussian in shape, that shape was chosen. The digitized experimental spectra were put into the computer program and resolved into a user-specified number of gaussian bands. The program requires that the user also input a pair of walls for each band which define the range of data to be used for determining each band. In addition the user may also specify initial guesses for the band maxima, widths and areas. In order not to influence the fit by a possibly prejudiced guess, in this work only the walls were specified. The program reports the band maxima, widths, and areas it obtains from each iteration of the fitting
procedure, and the best fit is chosen on the basis of the root-mean-square (rms) error between the fitted spectrum and the experimental spectrum. In all procedures of this type, there is an element of error inherent in the assumptions of the bandshape, number of peaks, and choice of walls; other selections could give a similar or better fit. The results are used as a guide to the interpretation of the experimental results and are not assumed to be totally accurate accounts of the number or positions of the actual transitions.

Preparation of Solutions

Because aging has been observed to decrease the absorptivity of some solutions of the β-diketones, stock solutions were not made; new solutions were prepared and used immediately. Solutions of liquid compounds for UV analysis were prepared by taking a sample from the bottle with a microliter syringe and diluting with solvent to the approximate concentration desired for the experiment. Solutions of the solid compounds were likewise prepared from small amounts of the solid that were diluted to the desired concentration. The concentrations normally used for the UV studies were on the order of $10^{-5}$ M. Because the cyclic diketones are extremely insoluble in nonpolar solvents, it was necessary to first dissolve a small sample in a drop of methanol and then dilute with the nonpolar solvent. This procedure produced spectra in
agreement with those obtained by previous members of this research group. However, care must be taken not to use more than a drop of alcohol per 10ml of nonpolar solvent or a significant amount of the cyclic diketone will be present in the final solution as the anion. In some cases that situation was observed to occur in the course of this work.

Solutions prepared for NMR analysis were generally prepared by dissolving the compounds in CCl$_4$ for $^1$H spectra and CCl$_4$ or methanol for $^{19}$F spectra. Concentrations of solutions for NMR were usually on the order of 10% by volume of the diketone.

The addition of sodium hydride to solutions of the diketones was normally done by adding a small amount of the solid 50% NaH oil dispersion directly to the UV sample cell. The volume change was assumed to be negligible, and because there is a negligible absorbance due to the small amounts a compensating amount of reagent in the reference cell was not necessary. In many cases drops of the BF$_3$ reagent were added directly to the sample cell. The volume change for addition of these small amounts was again assumed to be negligible. There is a negligible absorbance of small amounts of the BF$_3$ etherate dissolved in polar solvents and again the reagent was added only to the sample cell in those cases. However, in nonpolar solvents the BF$_3$ etherate causes
significant scattering due to turbidity of the solution. In those cases, the reagent was added to the reference cell as well as the sample cell to compensate for the scattering. Some residual scattering is still evident in some cases because of differences in the turbidities. In other cases, solutions of approximately 1.5% and 20% by volume of the BF$_3$ etherate in methanol were prepared. The resulting solutions were used as the solvent and were also placed in the reference cell.

The UV spectra in this work are presented in two slightly different forms. Because the concentrations of the solutions are not known, except in order of magnitude, most spectra have been normalized to an absorbance of one at the $\lambda_{\text{max}}$. This procedure makes it easier to compare the $\lambda_{\text{max}}$'s, which is in almost all cases all that is necessary. Normalization also prevents the comparison of intensities among spectra obtained at different sample concentrations, for which no such comparison should be made. Spectra for which the normalization has been performed have the title "Normalized Absorbance" for the vertical axis. In cases for which the concentration is known to be the same for two or more spectra, the normalization was not performed, and the vertical axis is titled "Absorbance". The absorbance values are those of the spectrum as recorded.
RESULTS AND DISCUSSION

In this section, the discussion will generally be divided into sections in which the spectroscopy of the neutral molecules, anionic forms, cationic forms, and the products of reaction with boron trifluoride will be discussed. Within these sections, the acyclic aliphatic compounds will be discussed first, and sections on the aromatics, the cyclics, and a group of compounds, 2-acetylcyclohexanone, α-methyl-acetylacetone and 4-methyl-1,8-decalindione will follow.

Neutral Molecules

An important question regarding the neutral enol species is that of the role of the hydrogen bond in determining the spectra. It is well documented that as electron withdrawing groups are added to a β-diketone in the enol form the strength of the hydrogen bond decreases. As electron donating groups are added the hydrogen bond strength increases. These trends are revealed by the acidities, the NMR chemical shift of the enol protons,\textsuperscript{21,22} the vibrational frequency of the O-H stretches,\textsuperscript{23,24} and molecular orbital calculations performed in this work.

There is much evidence to support the statement that the enolic proton of the β-diketones exists in a double well potential.\textsuperscript{25} Figure 4 illustrates a double well potential for a generalized case. There are two
Figure 4

Generalized double well hydrogen bond potential
structures for the diketones, differing only in the positions of the enol proton. If the molecule is not symmetrical there may be a preference of the enol proton for one oxygen over the other, or in other words the two wells of the potential do not have equal depths. The proton will prefer attachment to the oxygen on the side that has the deepest potential well. It has been suggested, as would be expected, that the deepest well is on the side of the most electron-rich oxygen. For example, structure 1 for benzoylacetone is favored over structure 2.

\[ \text{structure 1} \quad \text{structure 2} \]

In most cases, however, the barrier between the two wells of the potential is quite low and has a magnitude equal to only a few vibrational quanta.

It is important to be specific about the meaning of the term hydrogen bond. In this discussion I will use the definition that the hydrogen bond is that bond which binds the hydrogen to the molecule. The strength of the hydrogen bond is therefore the sum of the strengths of the two bonds to the hydrogen. In most cases, the hydrogen bond strength as defined herein is difficult to assess accurately because of the difficulty of separating the results of different effects. For example, the
hydrogen bond strength is not merely the difference in energy between the hydrogen bonded form and the anion, because of the electronic and steric changes that accompany ionization.

The accepted computational method for estimation of hydrogen bond strengths is to compare the differences in energy between the hydrogen bonded forms and the neutral forms which are not hydrogen bonded but to which the proton is still attached. The energy difference between a non-hydrogen bonded form and the corresponding hydrogen bonded form is the depth of one well of the potential. In Figure 4, the two energy differences are labeled $\Delta E_1$ and $\Delta E_2$. The total hydrogen bond strength is then estimated to be the weighted average of the depths of the two wells. The weighting factors are the percent populations in the two wells that are given by the Boltzmann equation.

Most molecular orbital programs have difficulty with hydrogen bonding, and MNDO is no exception; the problem has been confirmed by the authors of the program. The authors of MNDO have stated that the calculation sometimes predicts repulsive or attractive forces between atoms that may be hydrogen bonded. From my results it appears that the preceeding statement is true if the program is allowed to minimize the energy by changing the geometry of the hydrogen bond, which is the method of
choice from the program author's perspective. I have observed the calculated energy to be minimized for non-hydrogen bonded structures for the β-diketones under those circumstances. However, if the position of the proton in the hydrogen bond is fixed at a value close enough for the program to see an interaction, at least for the compounds studied in this work an attractive potential is predicted. The hydrogen bond energies calculated in this work were obtained for fixed positions of the proton in the hydrogen bonded and non-hydrogen bonded cases. It appears that the MNDO method in this case is sufficient at least to predict the ordering of a series of hydrogen bond strengths and gives somewhat reasonable values for those strengths.

The results of several calculations of this type for the β-diketones are listed in Table 2. The energies were calculated by means of the MNDO method as part of this research. The calculation for dibenzoylmethane could not be carried out because of the size limitations of the MNDO program.

In the series acetylacetone (ACAC), trifluoroacetylacetone (TFACAC), hexafluoroacetylacetone (HFACAC) the hydrogen bond strength decreases. If the hydrogen bond strength determined the planarity of the molecule, it could be expected that the stronger the hydrogen bond the lower the transition energy would be.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>H-BOND STRENGTH (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexafluoroacetylacetone</td>
<td>4.04863</td>
</tr>
<tr>
<td>trifluoroacetylacetone</td>
<td>4.93554</td>
</tr>
<tr>
<td>acetylacetone</td>
<td>6.53852</td>
</tr>
<tr>
<td>α-methylacetylacetone</td>
<td>6.84189</td>
</tr>
<tr>
<td>benzoylacetone</td>
<td>16.62664</td>
</tr>
<tr>
<td>dibenzoylmethane</td>
<td>unable to calculate</td>
</tr>
</tbody>
</table>
However, the $\lambda_{\text{max}}$'s of the neutral enols of these compounds are 270, 282, and 272 nm, respectively, from ACAC to HFACAC. The UV spectra of these compounds are shown in Figure 5. Cheng\textsuperscript{2} observed weak vibrational structure in the spectra of these compounds at 77 K. The lack of a systematic trend of the $\lambda_{\text{max}}$'s as a function of hydrogen bond strength indicates that the hydrogen bond strength does not control the planarity of the molecules.

The UV transitions of the $\beta$-diketones have been assigned to be $\pi^* - \pi$ transitions. This assignment has been made on the basis of the $\epsilon$ values and the weakness of the solvent effect on the band positions. The characteristics of the absorption bands of these molecules in general are extremely solvent insensitive, and this slight sensitivity leads to the conclusion that any charge-transfer character in the transitions is extremely small. While it is true that there is a significant shift of the transitions of the $\beta$-diketones in solution compared to their vapor absorptions, the shift may be attributed to a difference in the character of the hydrogen bond between the two sets of conditions. Experimental evidence points to the presence of a nearly linear hydrogen bond in the vapor phase\textsuperscript{27} and a bent hydrogen bond in the solution phase.\textsuperscript{24} Another strong argument that may be made against significant charge transfer character in the transitions is that the
Figure 5
Absorption spectra of
a. ACAC in 3MP
b. TFACAC in 3MP
c. HFACAC in 3MP
absorption spectra of the neutral, anionic, and cationic forms of the diketones studied all have the same general appearance. If the transitions had significant charge transfer character, it would be highly unlikely that the spectra of three species that have such different charge distributions would be similar.

Considering all of the above factors, one concludes that the long wavelength of the TFACAC transition relative to the positions of the transitions of ACAC and HFACAC must be due to an effect other than the charge-transfer character of the transition or the hydrogen bond strength. I believe that the presence of an electron withdrawing substituent on one side of the conjugated system and an electron donating substituent on the other side causes a higher degree of planarity of the enol ring and leads to the longer $\lambda_{\text{max}}$ of TFACAC relative to those of ACAC and HFACAC.

The effect of conjugation of phenyl groups in the aromatic $\beta$-diketones is seen in the series acetylacetone (ACAC), benzoylaceton (BA) and dibenzoylmethane (DBM). The H-bond strength as well as the conjugation increases in the order ACAC, BA, DBM. The $\lambda_{\text{max}}$'s are 270, 307 and 337 nm respectively. Vibrational structure in the room temperature spectra of BA and DBM is evident on the long wavelength side of the most intense transitions. The spectra of these compounds are shown in Figure 6.
Figure 6
Absorption spectra of
a. DBM in 3MP
b. BA in 3MP
spectra of the aromatic compounds contain bands attributable to the entire molecule (those listed above) as well as ones at shorter wavelengths attributable to the benzoyl groups and the styryl groups. The assignment of the short wavelength transitions to the benzoyl and styryl groups was made by Kuo and others of this group by comparison with the transitions of benzalacetone, chalcone and the other reference compounds listed in the experimental section. For comparison, the spectra of benzalacetone and chalcone are presented in Figure 7. The short wavelength portion of the spectrum of benzalacetone shows the double-humped peak that has been assigned to a styryl type absorption. Notice that because benzalacetone has no benzoyl group, there is no benzoyl transition. The short wavelength region of the chalcone spectrum shows a broader band, slightly redshifted to approximately 230 nm which probably corresponds to a combination of the benzoyl and styryl transitions. It is likely that the phenyl rings in chalcone are not held in a particular geometry relative to the rest of the molecule as rigidly as they are in the diketones. The lesser rigidity probably explains the lack of separation of the benzoyl and styryl transitions into separate bands.

In addition to the transitions listed above, DBM has another weak transition that has not been assigned in the
Figure 7

Absorption spectra of

a. benzalacetone in MEOH

b. chalcone in MEOH
previous work of members of our group. That transition is at approximately 295 nm and varies in appearance from a small hump to a flat portion in the spectra in various reports. In my spectra, it appears as a small hump. It does not disappear after the DBM has been purified by sublimation and does appear in literature reports of the spectra. By comparison with the spectrum of benzalacetone, I attribute it to a transition of the cinnamoyl group of the DBM molecule. The corresponding weak transition should also be present in the spectra of the other aromatic diketones. In BA, the transition is concealed within the main band, but it is observed in the spectrum of benzoyltrifluoroacetone.

A theoretical treatment of the transitions of BA and DBM has been reported, and the spectra reported in that reference generally agree with those reported here. However, the assignment of the transitions is based on the theoretical treatment, and though many of the interpretations may be reconcilable with those here, they do not seem to me to be wholly justifiable. For example, the two peaks for DBM and BA that we have attributed to styryl transitions are attributed by these workers to charge transfer from the phenyl rings of DBM to the enol ring. If the transitions were due to charge transfer from the phenyl to the enol ring, then they should not be observed in benzalacetone, which has no enol ring.
Moreover, there are also the same two transitions present in the spectra of BA and benzalacetone, which have only one phenyl ring. Both peaks are present in the BA spectrum in the literature article, though they acknowledge the presence of only one.

The angle of rotation of the phenyl rings of aromatic diketones relative to the plane of the enol rings is a major factor in determining the spectroscopy. The rotational angle affects the extent of overlap of the orbitals of the two rings. The crystal structure of DBM shown in Figure 8 indicates that the two phenyl rings are not completely coplanar with the enol ring and are not equivalent. One phenyl ring is nearly coplanar with the enol ring; there is only approximately four degrees difference between the planes of the phenyl and enol rings. The other phenyl ring lies approximately thirteen degrees out of the plane of the enol ring. The crystal structure of BA shown in Figure 9 indicates that the phenyl and enol rings are within approximately 6° of planarity.

A comparison of the short wavelength transitions of DBM, BA, and benzoyltrifluoroacetone (BZTFAC) is shown in Figure 10. It can be seen that the benzoyl bands of BA (~245 nm) and BZTFAC (~260 nm) are separated by several nanometers, with that of BZTFAC to the red. The fact that the benzoyl transition of BZTFAC lies to the red of
Figure 8

Two views of the DBM crystal structure
Figure 9

Two views of the BA crystal structure
Figure 10
Absorption spectra of benzoyl transitions of aromatic diketones in 3MP
a. BA
b. DBM
c. BZTFAC
that of BA suggests that the phenyl ring in BZTFAC is more nearly coplanar with the enol ring than is the phenyl ring in BA. Recall that the crystal structure of BA indicates that the phenyl ring is in fact not completely coplanar with the enol ring. The benzoyl band of DBM (270-235 nm) is broader and more flat-topped than those of BZTFAC and BA and covers the absorption range of both of them. The conclusion is that the DBM benzoyl transition is made up of one benzoyl transition of each of the types exhibited by BA and BZTFAC. The two phenyl rings in DBM are nonequivalent in their UV absorptions. The UV spectra of BA and BZTFAC indicate that there is only one transition of the phenyl rings in each spectrum.

It has long been known that \( \beta \)-diketones can react with BF\(_3\) to produce a chelated BF\(_2\) structure and a release of HF.\(^{31}\) That reaction occurs in the cases of BA and DBM and is shown below.

\[
\begin{align*}
O & \quad O \\
R_1 & \quad R_2 \\
+ \quad BF_3 & \quad \rightarrow \\
F \quad F & \quad + \quad HF
\end{align*}
\]

To my knowledge, BABF\(_2\) is the only BF\(_2\) chelate of the diketones for which the crystal structure has been determined.\(^{32}\) The crystal structure in Figure 11 shows that the chelated "enol" ring and the phenyl ring are completely coplanar. The UV spectra of BABF\(_2\) support the
Figure 11

Two views of the BABF$_2$ crystal structure
hypothesis that the geometry of BABF₂ in solution is essentially planar. The UV spectrum of BABF₂ exhibits red shifts of the main and benzoyl transitions relative to those of BA. The spectra are shown in Figure 12.

It should be clearly understood that the arguments presented here do not rely on the assumption that the crystal structure geometries of the compounds are the same as the geometries of the molecules in solution. The UV data do support the conclusion that the geometries of the solvated molecules are similar to the geometries of the compounds in the crystalline forms.

The nonequivalence of the phenyl rings in DBM affects the most intense transition (that of the entire molecule) as well as the benzoyl transitions. The work of Kuo and Pascal on DBM at 77 K shows a red shift of the $\lambda_{\text{max}}$ relative to that at room temperature. Pascal's spectrum has peaks for DBM at 77 K at approximately 345, 360, and 380 nm. The 360 and 380 nm peaks have approximately equal intensity, but the 345 nm peak is less intense. From my work, the most intense band in the UV spectrum of the DBMBF₂ chelate occurs at 360 nm and has shoulders at 345 and 380 nm. The UV spectra of DBM and the BF₂ chelate are shown in Figure 13. The chelation of BF₂ by DBM has produced a spectrum in which the main features are similar to those of DBM at low temperature. This similarity is interpreted to be the
Figure 12
Absorption spectra of

a. BA in 3MP

b. BA in 3MP with BF$_3$
Figure 13

Absorption spectra of

a. DBM in 3MP

b. DBM in 3MP with BF$_3$
result of the formation of a more nearly planar molecule; increased planarity leads to the redshift along with an increase in the structure of the spectrum because of the more rigid geometry. Further evidence that the phenyl rings in DBMBF$_2$ are equivalent and more nearly coplanar with the enol ring is given by the fact that the benzoyl transition of DBMBF$_2$ is sharper at the top and lies farther to the red than those of pure DBM.

A portion of the $^1$H NMR spectrum of DBM is shown in Figure 14. The single peak at approximately 6.8 ppm is due to the proton on the central carbon of the enol ring. The set of peaks in the 7.4 ppm region is due to the phenyl ring protons which are furthest from the carbonyl groups. The set of peaks in the 8.0 ppm region is due to the phenyl ring protons which are adjacent to the carbonyl groups. After addition of BF$_3$, the spectrum shown in Figure 15 is obtained. All of the peaks are shifted to higher chemical shift values due to the electron withdrawing nature of the BF$_2$ group in the chelate. The splittings of the central set of peaks is clarified, which suggests that the molecule is more rigid. Very similar results are obtained for BA. The NMR spectra of BA in CCl$_4$ and with BF$_3$ are shown in Figures 16 and 17.

The calculational treatment$^{28}$ of the UV transitions of BA and DBM mentioned earlier does lend some support to
Figure 14

A portion of the $^1$H NMR spectrum of DBM in CCl$_4$. 
Figure 15

A portion of the $^1$H NMR spectrum of DBM in CCl$_4$ in the presence of BF$_3$.
Figure 16

A portion of the $^1$H NMR spectrum of BA in CCl$_4$.
Figure 17

A portion of the $^1H$ NMR spectrum of BA in CCl$_4$ in the presence of BF$_3$. 

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the general statements made here, even if the detailed assignments do not agree. The calculations by those workers indicate the redshift of the transitions with increasing planarity of the enol and phenyl rings and the presence of multiple transitions arising from the two phenyl rings in DBM.

Because BZTFAC has both a phenyl and a trifluoromethyl substituent it is important to note the effect of the opposing influences of these groups on the hydrogen bond strength. The NMR signal of the enol proton and the acidity indicate that the H-bond of BZTFAC is somewhat weaker than that of ACAC. The $\lambda_{\text{max}}$ of BZTFAC occurs at 325 nm, to the red of that of BA. The spectrum is shown in Figure 18. As in the case of TFACAC, there are electron donating and electron withdrawing groups on opposite ends of the conjugated system of BZTFAC and planarity is favored even though the hydrogen bond strength is decreased. As already stated, the high degree of planarity of BZTFAC is also indicated by the peak position of its benzoyl transition. In BA the benzoyl transition occurs at roughly 246 nm. In BZTFAC the benzoyl transition occurs at 260 nm. By comparison with the benzoyl transitions of DBM, the phenyl ring in BZTFAC should be nearly coplanar with the enol ring. Recall that the crystal structure of DBM indicates that one phenyl ring may out of the plane of the enol ring by
Figure 18

Absorption spectrum of BZTFAC in 3MP
approximately 4°, and the other by approximately 13°. The data indicate that the angle of rotation of the phenyl ring in BZTFAC is nearer the lower value. The foregoing statement assumes that the two different enol rings affect the conjugation in a similar way. It was mentioned earlier that the weak 295 nm transition attributed to the cinnamoyl group is observed in the spectra of BZTFAC in nonpolar solvents.

The β-diketones that have 5 and 6 membered rings may be taken to be representative of molecules that have W conformations. The work of Pascal\(^3\) established that cyclic diketones that have larger and larger rings eventually reach a point where they are able to form U conformations. The compounds in the W conformation are incapable of forming intramolecular hydrogen bonds; however, they have been shown by NMR and X-ray crystallography to form intermolecular H-bonds.\(^{33,34}\) It is also immediately evident from an examination of the \(^1\)H NMR spectra of cyclic diketones dissolved in nonpolar solvents that they also form intermolecular H-bonds in solution as well. For this reason, it is quite difficult to make unambiguous assignments of the peaks in the NMR spectra; consequently the usefulness of the NMR spectra of the cyclic β-diketones was extremely limited in this work. It has been suggested that because of the inability to form intramolecular H-bonds these cyclic
diketones have a higher equilibrium concentration of the keto form than the other diketones. This suggestion may be true, but the evidence still points to a predominance of the enol form. Experimental reports in the literature state that the cyclic diketones in nonpolar solvents are strongly enolized and dimerized.\textsuperscript{35,36} The intermolecular hydrogen bonding undoubtedly compensates for the lack of intramolecular hydrogen bonds and stabilizes the enol form.

The lack of intramolecular H-bonds also contributes to the acidity of the W compounds. The W diketones are stronger acids than the diketones which are capable of H-bonding. In polar solvents such as methanol, the intermolecular H-bonds are broken and the W diketones at low concentration are observed to be present to a great extent as the anion. In nonpolar solvents, the acidity of the neutral enols may still be higher than that for an analogous U diketone because intermolecular H-bonds are generally weaker than intramolecular ones.

The UV $\lambda_{max}$'s of the cyclic diketones in the enol form occur in the following order: 1,3-cyclopentanedione (1,3-PENT) 235 nm, 2-methyl-1,3-cyclohexanedione (2-ME-1,3-HEX) 247 nm, 1,3-cyclohexanedione (1,3-HEX) 249 nm and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) 255 nm. The spectra of all except dimedone are shown in Figure 19. Note that the absorption of 1,3-HEX is on the
Figure 19
Absorption spectra of
a. 1,3-PENT in 3MP
b. 1,3-HEX in 3MP
c. 2-ME-1,3-HEX in 3MP
order of 20 nm to the blue of that of ACAC. The spectra illustrate the blue shift of the spectrum of a W conformation relative to that of a U conformation. Although the structures of 1,3-HEX and ACAC are not the same, the substituent effect of the extra CH2 group of the cyclic compound should cause it to absorb even farther to the red than would a W ACAC geometry. The absorbances of all of the cyclic W diketones fall to the blue of the band of ACAC.

The relatively large difference in the absorption wavelengths of 1,3-PENT and 1,3-HEX is surely due in part to the angle strain at the C2 position. The ordering of the transition energies of the six-membered ring compounds may be explained on the basis of the effects of substitution in the different positions. The crystal structure of dimedone indicates that the carbon to which the two methyl groups are attached is out of the plane of the other carbon atoms. In the case of dimedone, that distortion does not affect the chromophore. However, in the case of 2-ME-1,3-HEX, if the methyl-substituted carbon is out of the plane, then the conjugation of the chromophore is reduced and the spectrum would be shifted to the blue. I believe that the foregoing statement is the reason that the methyl substitution in 2-ME-1,3-HEX does not lead to the red shift that would normally be attributed to such a substitution.
Unlike those of the acyclic diketones, the UV spectra of the cyclic diketones show no vibrational structure. This lack of structure points to at least a partial answer to the question of the effect of the H-bond on the spectroscopy. It has been shown here that the H-bond does not appear to be a major factor in determining the UV $\lambda_{\text{max}}$'s of the neutral enols. However, the absence of structure in the spectra of the W compounds which are incapable of H-bonding suggests that the H-bonds of the U diketones are involved in the vibrational mode(s) that cause the structure in their spectra.

It is well known that, in general, a molecule capable of forming an intramolecular hydrogen bond will tend to form that bond in the absence of strong steric factors that prevent or hinder the necessary geometry. The twisting of the large-ring cyclic diketones to the H-bonded U form demonstrated by Pascal is a good example.

It had been previously proposed that substitution of the acyclic diketones at the 3 (α) position could lead to steric hindrance and the formation of non H-bonded structures. The steric hindrance hypothesis is supported by the fact that the UV spectrum of α-methyl-acetylacetone (α-ME-ACAC) has two distinct peaks. The spectrum of α-ME-ACAC in 3MP has a $\lambda_{\text{max}}$ at
250 nm and a shoulder at approximately 300 nm.

The 300 nm shoulder is consistent with a band in the spectrum of a U H-bonded enol. The spectrum obtained with α-ME-ACAC dissolved in methanol has a $\lambda_{\text{max}}$ at 259 nm and a shoulder at approximately 300 nm. The spectra are shown in Figure 20. The difference in the wavelength of the maximum peak for α-ME-ACAC dissolved in methanol relative to that in 3MP is due to dissociation to the anion in the more polar solvent. The overlap of the bands may cause an apparent shift in the position of each band. The shift is especially severe for the shoulder. A gaussian fit of the spectrum (methanol solvent) was performed and a fit with a total rms error of .00491 absorbance units was achieved when peaks at 259 nm (the $\lambda_{\text{max}}$) and 295 nm (the shoulder) were used. The hypothesis that the shoulder corresponds to the U geometry is strongly supported by the fact that the reported $\lambda_{\text{max}}$ of 4-methyl-1,8-decalindione enol, which can be considered to be a derivative of α-ME-ACAC which must be in essentially a completely planar U geometry, occurs at 295 nm also.

The $\lambda_{\text{max}}$ peak for α-ME-ACAC in 3MP at 250 nm would be consistent with the absorption of either an S or a W geometry. Previous assignments of this band attribute it to the keto form, but this work and that of Davis indicate that that assignment is incorrect. Davis
Figure 20

Absorption spectra of
a. α-ME-ACAC in 3MP
b. α-ME-ACAC in MEOH
attributed it to the S form, but I have yet another interpretation. The absorption wavelength correlates well with the spectrum of 1,3-cycloheptanone, which has been shown by Pascal to have a geometry intermediate between those of a U and a W geometry but one that is closer to W. My MNDO calculations for α-ME-ACAC enol indicate that a twist of 140° of both acetyl groups away from one another leads to a near-W geometry that has a heat of formation within 5 Kcal/mol of that calculated for the U H-bonded enol. Because the energy differences in these calculations are the sums of the differences due to the geometric changes and the energy required to break the hydrogen bond, they are subject to large errors. Therefore, even though the energy difference of 5 kcal/mol is large compared to the thermal energy available at room temperature the presence of the near-W form should not be discounted as a possibility. In the nomenclature system defined in the introduction, the near-W geometry proposed for this α-ME-ACAC species is designated 140-W. The potential energy curve for twisting of α-ME-ACAC enol from a non hydrogen bonded U to a W geometry is shown in Figure 21.

Another indication that the non H-bonded conformer of α-ME-ACAC has a near-W geometry comes from a comparison with 2-acetylcyclohexanone (2-AC-HEX). The structure of 2-AC-HEX allows only U and S conformations.
Figure 21
Potential energy curve for distortion of the α-ME-ACAC enol from U - W
(0° = non H-bonded planar U enol)
Because 2-AC-HEX and \( \alpha \)-ME-ACAC are both substituted at the \( \alpha \) position they should have a similar type of steric effect as a result of that substitution. The spectrum of 2-AC-HEX shown in Figure 22, however, has only a single peak at 282 nm. The \( \lambda_{\text{max}} \) of 2-AC-HEX at 282 nm indicates that it is present as the U H-bonded enol. The fact that this compound has only this single peak in its spectrum means that even though it has a strong steric factor inhibiting the U H-bonded geometry, that geometry is more stable than any available S geometry. By analogy, the 250 nm peak of \( \alpha \)-ME-ACAC must belong to some form of a W geometry, and I believe that a twisted form close to 140-W is the most likely.

I stated that the 259 nm peak in the \( \alpha \)-ME-ACAC methanol spectrum is attributed to ionization to the anion. By analogy with the enol forms, the geometry of that anion should also be near-W. The potential energy curve for distortion of \( \alpha \)-ME-ACAC anion from U-W is shown in Figure 23. The minimal energy geometry occurs at the 140-W position, in support of the hypothesis.

The spectra of \( \alpha \)-ME-ACAC obtained by me and previous members of this research group do not agree with that published in a significant literature reference on this topic.\(^{37,38}\) On examination of the published spectra, it is apparent that the spectra are not those of pure \( \alpha \)-ME-ACAC but are dominated by the spectra of the anion.
Figure 22
Absorption spectrum of 2-AC-HEX in 3MP
Figure 23

Potential energy curve for distortion of α-ME-ACAC\(^-\)
from U – W
of ACAC, which was used in the synthesis attempt. The spectra obtained for α-ME-ACAC in this laboratory are in excellent agreement with the spectra reported for the other α-substituted compounds in that reference.
Anions

In general, the UV $\lambda_{\text{max}}$'s of the anions are several nanometers farther to the red than those of the neutral molecules. In addition, there is generally an increase in absorptivity ($c$) upon formation of the anions. An increase in $c$ often indicates an increase in the electron density of the chromophore; that is very likely the case in anion formation. The red shift is due to the added resonance caused by the electron delocalization that distributes the charge. Cheng stated that if one assumes that the change in delocalization energy upon removal or chelation of the enolic proton were essentially the same for all of the diketones, there should be a similar shift for all of the compounds in the absence of other effects. Perhaps at least a steady trend could be expected. He then pointed out that the shifts are not similar; there are significant irregularities. Having established that other effects are likely to be present, Cheng attributes the irregularities to charge transfer through the enolic proton. As I have already stated, I do not believe that there is significant charge transfer character in the transitions. At the least, I will point out that there is an alternative explanation for the deviations, and I believe that it is more likely that this alternative explanation is consistent with the larger body of data that I have considered.
One of the assumptions of the hypothesis that all of the red shifts observed upon formation of the anion should be alike is that the geometries of the molecules do not change upon ionization. The hypothesis that there should at least be a trend in the shifts assumes that the $\lambda_{\text{max}}$'s of the enol forms vary according to the strength of the hydrogen bond. In the previous section I pointed out that hydrogen bond strength does not determine the $\lambda_{\text{max}}$ of the enol and that it is not necessary to resort to charge transfer to explain the observations. In this section, I will discuss evidence that indicates that the geometries of the molecules do in fact change upon ionization.

One of the most important results obtained by Cheng was that the anion of hexafluoroacetylacetone (HFACAC\textsuperscript{−}) exhibits two emissions that have different excitation spectra. The evidence is very strong that there are multiple geometries for HFACAC\textsuperscript{−}. Cheng interprets the multiple geometries in terms of an "enol ion" and a "keto ion". Davis undertook many CNDO calculations that consider the rehybridization of the central carbon of HFACAC\textsuperscript{−} to sp\textsuperscript{3} to form the keto ion. My interpretation of the result is quite similar but retains the more "modern" view of the resonance delocalized charged ion. Rather than a rehybridization of the central carbon to sp\textsuperscript{3} that makes it tetrahedral to form a keto ion, I
believe that there is a twist of the two acetyl groups away from one another to form a W-distorted nonplanar geometry. This geometry, which has equal twist angles of both acetyl groups and sp² hybridization of the central carbon, would retain the C₂ᵥ symmetry of the planar anion. The cause of this twist would be repulsion of the two trifluoro groups for one another as well as the charge repulsion of the two oxygens.

The results of my MNDO calculations for the anions of ACAC (ACAC⁻), TFACAC (TFACAC⁻) and HFACAC (HFACAC⁻) show that for W distortion there is a minimal energy geometry at approximately the 30⁻W geometry. The potential energy curves for ACAC⁻ and TFACAC⁻ U-W distortion are shown in Figures 24 and 25. The minimum at -30° deepens as the methyl groups are replaced by trifluoromethyl groups. There is a second dip in the potential energy curves approximately at the 140⁻W geometry mentioned earlier in the discussion of α-ME-ACAC. In the case of α-ME-ACAC anion, that near-W geometry was assigned to give a peak in the 259 nm region. The UV spectra of ACAC⁻, TFACAC⁻, and HFACAC⁻, shown in Figure 26, have no absorbances in that region of the spectrum; this result indicates that these anions are not present in a near-W geometry. The λ_max’s are 293 nm for ACAC⁻, 292 nm for TFACAC⁻, and 303 nm for HFACAC⁻. The spectra of TFACAC and HFACAC in pure methanol (not
Figure 24

Potential energy curve for distortion of ACAC\textsuperscript{−}

from U - W
Figure 25

Potential energy curve for distortion of TFACAC$^-$ from U – W
Figure 26
Absorption spectra of
a. ACAC in MEOH with NaH
b. TFACAC in MEOH with NaH
c. HFACAC in MEOH with NaH
shown) indicate that at the low concentrations of these solutions they are largely dissociated to the anion. Addition of NaH to the solutions to give the spectra of the anions produces only a slight increase in the absorbance. The spectrum of HFACAC\(^-\) is the only one of the three that has structure in the form of shoulders at approximately 292 and 315 nm. These wavelengths correspond to the maxima in the two excitation spectra obtained by Cheng for the two emissions of HFACAC\(^-\) and indicate that they are attributable to two different geometries. Other strong evidence from the present work for the presence of multiple geometric forms of HFACAC\(^-\) comes from the \(^{19}\)F NMR spectrum of that anion formed in methanol solution to which NaH has been added. There are two strong peaks attributable to the anion at -78.5956 and -86.3130 ppm relative to that of CCl\(_3\)F. The spectrum indicates that there are two predominant forms of HFACAC\(^-\) but does not rule out the existence of more forms. For ease of comparison of spectra later, the spectrum is shown in Figure 52 in the section dealing with the reactions of BF\(_3\) with the diketones in polar solvent.

The minimum in the potential energy curve for ACAC\(^-\) at the 140-W geometry is approximately 5 kcal/mol higher in energy than that of the 30-W geometry; this difference indicates that the 140-W well should not be populated at room temperature if the calculations are correct. For
the reasons mentioned in the discussion of \( \alpha \)-ME-ACAC, however, it is important not to assume the accuracy of the calculated energies. In this case, the experimental evidence verifies that the potential well for the 140-W geometry is probably not occupied.

The MNDO calculations also seem to rule out the possibility that these anions could be in the planar S geometry. In all cases, the planar S geometry is calculated to be at an energy maximum that is not as high in energy as that of the planar W. The energies of the planar W anions are all extremely high due to the steric interaction of the methyl and/or trifluoromethyl groups in that geometry. The calculations and the examination of molecular models make it clear that these acyclic molecules cannot achieve the planar W geometry.

MNDO potential energy calculations for ACAC\(^-\) as a function of twist angle of a single acetyl group (S distortion) were also performed. Figure 27 shows the potential curve. The minimal energy geometry along this path occurs approximately at the 50-S geometry. The energy of the 50-S geometry is calculated to be approximately 0.7 kcal/mol higher than that of the 35-W geometry. If this value is accurate, then there should be a significant population of molecules in those two states at room temperature, because the difference is on the order of RT at 298 K, which is about 0.6 kcal/mol.
Figure 27
Potential energy curve for distortion of ACAC$^-$ from U - S
There is a second well in the U-S potential curve at approximately $140^\circ$ of twist (140-S), which has an energy of approximately 0.7 kcal/mol higher than the 50-S well. Being a factor of 2.5 RT higher in energy (at 298 K) than the 35-W geometry, there may also be a spectroscopically significant population in this well at room temperature if the relative energies and the shape of the potential are correct.

The potential curves for HFACAC$^-$ for W and S distortion are shown in Figures 28 and 29. The minimal energy geometry is the 30-W, the next lowest is 2.5 RT higher in energy, the 40-S geometry. The 40-S geometry may have some population at room temperature. The next well is at the 120-S geometry, 7.9 RT higher in energy than the 30-W geometry. The 120-S well should therefore not be significantly populated at room temperature. The difference in the shapes of the U-S potential energy curves for HFACAC$^-$ and ACAC$^-$ also suggests that some S-distorted HFACAC$^-$ may be present. The large peak in energy at low twist angles in the ACAC$^-$ curve is replaced by a shallow dip in the HFACAC$^-$ curve.

The $\lambda_{\text{max}}$ of the anion of 4-methyl-1,8-decalindione has been reported to be 315 nm.$^{13}$ The 1,8-decalindione anion may be considered to be an essentially planar U anion. The $\lambda_{\text{max}}$ of no aliphatic anion studied in this research exceeds that value. That none of the spectra of
Figure 28

Potential energy curve for distortion of HFACAC$^-$ from U - W
Figure 29
Potential energy curve for distortion of HFACAC$^-$ from U - S
the aliphatic anions have a $\lambda_{\text{max}}$ as far to the red as 315 nm suggests that the predominant geometries of ACAC$^-$, TFACAC$^-$ and HFACAC$^-$ are nonplanar. The presence of the distinct shoulders in the spectrum of HFACAC$^-$ and the apparent absence of structure in the spectra of ACAC$^-$ and TFACAC$^-$ may be attributable to multiple geometries for HFACAC$^-$ but not for the others. The calculations suggest that different results should be observed, that ACAC$^-$ should be present in at least two geometries and possibly three and that HFACAC$^-$ should be present in one or possibly two geometries. It is likely that there are multiple geometries of ACAC$^-$ and TFACAC$^-$ present in solution, but that some of them are present at low concentration or that their transitions are otherwise buried in the absorption band which is observed.

As I have emphasized, the results of the calculations are not to be considered to be totally reliable; at best the calculations provide only guidance for interpreting trends. In addition to the quantum mechanical approximations that are made in the calculations, they neglect solvation energy and the effects of ion pairing. These approximations are in addition to the assumption in the use of the results that the differences in the calculated heats of formation ($\Delta H_f$) are indications of the differences in Gibbs free energy ($\Delta G$) between the different geometries.
Because the anions ACAC\(^{-}\), TFACAC\(^{-}\) and HFACAC\(^{-}\) each have a band at 292 nm, it is probable that that band is attributable to similar geometries in all three cases. I assign the 292 nm bands in these three ions to the minimal energy geometry which has been calculated for each, which is approximately the 30-W geometry. There remain two bands in the spectrum of HFACAC\(^{-}\) to be assigned. The longest wavelength band of HFACAC\(^{-}\) at 315 nm falls on the \(\lambda_{\text{max}}\) of the anion of 4-methyl-1,8-decalindione, which must be in a nearly planar U geometry. Therefore, the 315 nm band in the HFACAC\(^{-}\) spectrum is attributable to a very nearly planar U geometry. It appears that in this case the molecular orbital program underestimates the stability of the very nearly planar forms. The \(\lambda_{\text{max}}\) band for HFACAC\(^{-}\) at 303 nm should be due to a geometry having an amount of overlap intermediate between those of the other two geometries. The calculations suggest that that geometry is likely to be approximately the 40-S geometry.

It may seem that the assignment of the 303 nm band of HFACAC\(^{-}\) to an S-distorted U geometry is inconsistent with previous arguments. Recall that the earlier predictions of the relative wavelengths of U and S transitions applied to their planar forms. Also recall that the more planar the molecule, the further the transition falls to the red. The maximum intensity
transition at 303 nm for HFACAC− was assigned to the 40-S geometry. The 292 nm shoulder was assigned to the 35-W geometry. From the definition of the geometries, the 35-W geometry has both trifluoroacetyl groups twisted 35° away from the plane of the molecule. The 40-S geometry has only one trifluoroacetyl group twisted by 40° from that plane. From the equation developed in the introduction the total overlap of the pi orbitals in the two forms is 1.638 for the 35-W geometry and 1.766 for the 40-S geometry. Therefore, the 40-S geometry is more nearly planar and has more overlap of its pi orbitals than does the 35-W geometry and thus absorbs farther to the red.

Several possible geometries for the HFACAC anion have been suggested; one is approximately as planar as those proposed for ACAC− and TFACAC−, and two are more nearly planar than those. It has been stated that the probable cause for the anions to be nonplanar is the core repulsions of the methyl and trifluoromethyl groups and the charge repulsion of the oxygens. What is the explanation for the evidence that there appears to be more nearly planar geometries for HFACAC− than that observed for ACAC− and TFACAC−? The explanation that I offer is that the electron withdrawing effect of the fluorines reduces the charge density on the oxygens, allowing more planar forms to be stable. The acidity of
the fluorinated diketones illustrates not only the weakness of their hydrogen bonds but also the stability of their anions; these effects may be attributed to the reduced charge on the oxygens of the anion.

There may be supporting evidence for the existence of multiple geometries of ACAC\(^{-}\) from a \(^1\)H NMR study reported in the literature\(^{39}\). However, those authors considered only the planar U, S, and W forms to be possible. They concluded from the presence of two methyl signals obtained for a solution of the Na(ACAC) salt in methanol that the ACAC anion is present in the planar S form. There may be severe problems with these experiments, however. I have observed that if a solution of Na(ACAC) in methanol is prepared, the UV spectrum of that solution is largely that of the neutral enol of ACAC. That is, there is an equilibrium between the anion and the neutral enol formed by reprotonation by the solvent in the absence of excess base. The UV spectrum of the same Na(ACAC) salt dissolved in the aprotic solvent DMSO contains only the absorption of the anion of ACAC. In the NMR study, dissolution of Na(ACAC) in deuterated methanol would lead to deuteration of the ACAC\(^{-}\) and would produce a spectrum that would have two sets of peaks, both of which would appear to be those of an anion.

In a related experiment, the authors of the NMR
paper added NaI to the solution and observed a change in the relative amounts of the two species; presumably this effect is caused by an increased amount of ion pairing. In my analogous UV experiment, addition of NaNO₃ (NaI was unavailable) to a solution of neutral ACAC produced a spectrum in which the absorbance of ACAC⁻ was evident. The experiment demonstrates that the NO₃⁻ ion in methanol is able to deprotonate ACAC. An equivalent statement is that HNO₃ is a weaker acid in methanol than is ACAC. It must be remembered that our normal ideas of the strengths of acids and bases are valid only for aqueous solutions. It is possible that the addition of NaI to the NMR sample caused a shift of the enol-anion equilibrium to favor the anion through formation of DI.

A verified example of the UV spectrum of a twisted anion of a β-diketone comes from the spectrum of a nickel complex of ACAC. It has been reported that the hydrated octahedral complex Ni(ACAC)₂ · 2H₂O when heated loses its water and forms oligomers; the most common oligomer is the trimer that has the formula [Ni(ACAC)₂]₃.⁴⁰,⁴¹ The X-ray crystal structures of the aquated monomer⁴² and the anhydrous trimer⁴³ have been determined. The diaquated monomer has an octahedral bonding arrangement about the Ni ion and a water molecule at each of the axial positions. The structure of the trimer consists of three Ni ions bound together by twisted ACAC anions which act
as bridges. There are two types of ACAC ligands in this species; one group consists of relatively planar ACAC anions, which are bound to only one Ni each, and the other group consists of twisted ACAC anions forming the bridges. The oligomers have a distorted octahedral bonding arrangement about each Ni ion. The UV absorption spectra of the hydrated complex and the anhydrous oligomer have been published and clearly show two bands in the ligand absorption region for the oligomer and only one for the monomer. The two bands are stated to be due to the bridging and nonbridging ligands, but the authors did not associate the bands with the change in geometry of the ligands that caused the difference in their absorptions. The monomer $\lambda_{\text{max}}$ at 295 nm is near the normal ACAC anion band position, and the oligomer band is blue shifted to the 260-270 nm region. Clearly, the twist present in the ACAC anions of the bridging ligands in the oligomer is the cause of the new band. I have synthesized the monomer complex and the oligomer and have successfully reproduced the results.

The UV spectra of the anions of BA ($\text{BA}^-$) and DBM ($\text{DBM}^-$) are shown in Figures 30 and 31. Again there is a red shift of the $\lambda_{\text{max}}$ of the anions relative to that of the neutral enol, and the transitions of the entire molecule and those of the benzoyl groups can be seen. The $\lambda_{\text{max}}$ of $\text{DBM}^-$ at 347 nm occurs to the red of that of
Figure 30

Absorption spectra of

a. BA in MEOH
b. BA in MEOH with NaH
Figure 31
Absorption spectra of
a. DBM in MEOH
b. DBM in MEOH with NaH

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BA\textsuperscript{-} at 325 nm as expected. The $c$ for DBM\textsuperscript{-} at the $\lambda_{\text{max}}$ is lower than that for the neutral enol; this phenomenon is unusual. The benzoyl transitions for both anions occur at approximately 242 nm which is to the blue of their positions in the enols and show an increase in intensity. The blue shift and increased intensity of the benzoyl bands suggests that the phenyl groups have rotated out of the plane of what was formerly the enol ring and are thereby less conjugated with it. The wavelength of 242 nm for the benzoyl transitions shows that they have approximately the same degree of resonance as does benzaldehyde which absorbs in that region of the spectrum. Thus, the conjugation of the phenyl and enol rings has been greatly reduced. The effect on the transitions of the whole molecules is to cause them to occur at a higher energy than that which would be observed if the anions were planar. The phenyl group rotation also probably causes the long wavelength bands to be less intense than they would be if the molecules were planar. In the case of DBM\textsuperscript{-} that decrease is enough to cause it to have a lower $c$ than the neutral enol.

The decrease in conjugation caused by the phenyl group rotation is most evident in the spectrum of the anion of BZTFAC (BZTFAC\textsuperscript{-}). The $\lambda_{\text{max}}$ of BZTFAC\textsuperscript{-} occurs at 322 nm, which is a position to the blue of that of the neutral enol. The benzoyl transition is again found at
242 nm. The spectra are shown in Figure 32.

Unfortunately, the blue shift is too small to be clearly seen in the figure. However, it is clear that there is no red shift. The BZTFAC anion is the only anion from this research to exhibit a blue shift of its anion relative to the position of the band of the neutral enol. It was stated previously that the neutral enol of BZTFAC is probably nearly planar and has the greatest degree of conjugation of its enol and phenyl rings of all the aromatic diketones in this study. Upon ionization that conjugation is dramatically reduced and the spectrum blue shifts.

It should be mentioned that the previous explanation of the blue shift of the BZTFAC$^-$ band relative to that of the neutral enol, given by Pascal, was that the presence of the trifluoromethyl substituent caused a reduction of the delocalization of the anion. If this explanation were correct, the same effect should be observed for TFACAC$^-$, and the effect is not observed. I believe that the evidence strongly supports my explanation.

The reason that the phenyl groups of the aromatic diketones rotate out of the plane of the enol ring upon ionization may be understood by considering the ionization to be a perturbation of the system; the system responds by seeking a means of minimizing the effect of the perturbation. If the perturbation is formation of
Figure 32
Absorption spectra of
a. BZTFAC in 3MP
b. BZTFAC in MEOH with NaH
the negative ion by removal of a proton, the result is an electron-rich system. The molecule seeks to minimize its high electron density and in the case of the aromatic diketones it is able to minimize the electron density by reducing its interaction with the electron-donating phenyl group(s). This interaction can only be reduced by rotating the phenyl group(s) to decrease the overlap of the pi orbitals of the enol and phenyl rings and consequently to reduce the electron donation by the phenyls through resonance. The phenyl groups are still able to donate (or accept) small amounts of charge by induction. The hypothesis proposed here and applied to the anions makes a prediction about the spectra of the cations. Because the change in the charge density upon cation formation (the "perturbation") is opposite to that of anion formation, the hypothesis predicts that the cations of the aromatic diketones will be more planar than the neutral enols and will absorb farther to the red.

The UV spectra of the anions of the cyclic diketones are illustrated in Figure 33. The $\lambda_{\text{max}}$'s are 260 nm for 1,3-PENT, 279 nm for 1,3-HEX, 282 nm for dimedone, and 292 nm for 2-ME-1,3-HEX. This order differs from that observed for the neutral enols and reflects the expected effects of alkyl substitution and ring size. Probably the need for electron delocalization has overcome the
Figure 32
Absorption spectra of
a. 1,3-PENT in MEOH with NaH
b. 1,3-HEX in MEOH with NaH
c. 2-ME-1,3-HEX in MEOH with NaH
steric barriers to planarity in the conjugated system of 2-ME-1,3-HEX. Note that the $\lambda_{\text{max}}$'s of none of these W anions is to the red of those of the U anions. The absorption of the anion of 2-ME-1,3-HEX, that has the large substituent effect of 2-methyl substitution, coincidentally occurs in the same region as the absorptions of ACAC$^-$ and TFACAC$^-$.

The general conclusion is that even a substantially planar W anion does not absorb as far to the red as does a U anion; this conclusion is in agreement with the proposed hypothesis that the W forms of the diketones absorb to the blue of the U forms.

The spectra of $\alpha$-ME-ACAC in methanol and of $\alpha$-ME-ACAC to which NaH was added are shown in Figure 34. As has already been mentioned, the spectrum of $\alpha$-ME-ACAC in methanol has a $\lambda_{\text{max}}$ at 259 nm and a shoulder at approximately 300 nm. Upon addition of NaH, the 259 nm band remains essentially unchanged and the lower energy band becomes the new $\lambda_{\text{max}}$ at approximately 302 nm. The lack of a change of the 259 nm band upon addition of base indicates that that band belongs to the anion of $\alpha$-ME-ACAC which is formed by dissociation in methanol. I have already further assigned that band to be the absorption of a near-W geometry of the $\alpha$-ME-ACAC anion having approximately a 140° twist of both acetyl groups away from one another. The 300 nm band is attributable
Figure 34

Absorption spectra of

a. $\alpha$-ME-ACAC in MEOH

b. $\alpha$-ME-ACAC in MEOH with NaH
to a U geometry. A gaussian fit analysis of the spectrum of this compound in NaH/Methanol gave a spectrum with a total rms error of .00928 absorbance units with peaks at 258.6 nm and 302.3 nm. The slight redshift of the 302 nm band in \( \alpha \)-ME-ACAC\(^-\) relative to the bands of the other aliphatic anions is probably due to the \( \alpha \)-methyl substitution rather than a more planar geometry. Recall that the \( \lambda_{\text{max}} \) expected for a nearly planar U group of this type is at 315 nm. Therefore, the 302 nm band of \( \alpha \)-ME-ACAC\(^-\) is attributable to a significantly nonplanar geometry. The MNDO calculations indicate that the minimal energy near-U geometry is at approximately the 45-W geometry, in support of the above conclusion.

The spectra of 2-acetylcyclohexanone (2-AC-HEX) in methanol and in the presence of NaH are presented in Figure 35. As in the case of \( \alpha \)-ME-ACAC, there is evidence of dissociation of the neutral molecule in methanol to form some of the anion, which gives a shoulder at approximately 310 nm. Upon addition of NaH, the \( \lambda_{\text{max}} \) of the 2-AC-HEX\(^-\) is seen at 308 nm. The slight shift to the red of the peak of this anion relative to that of the \( \alpha \)-ME-ACAC anion which gave the 302 nm peak is probably due in part to the substituent effect of the additional CH\(_2\) group present in 2-AC-HEX. The geometry of 2-AC-HEX is also more restricted than that of \( \alpha \)-ME-ACAC. The cyclic nature of 2-AC-HEX prohibits W
distortion but allows S distortion. The restriction to only S type distortion may also contribute to the red shift because it has been shown that W distortion leads to a larger blue shift than a similar amount of S distortion.
Figure 35
Absorption spectra of
a. 2-AC-HEX in MEOH
b. 2-AC-HEX in MEOH with NaH
The UV spectra of several cations of β-diketones have been reported in the literature. In the first reference the spectra of diketones dissolved in concentrated H\textsubscript{2}SO\textsubscript{4} were recorded. The spectra of β-diketones dissolved in concentrated H\textsubscript{2}SO\textsubscript{4} obtained in the present work are in agreement with those given in that report. In the second reference it is stated that the cations are formed in a 0.1 N HCl/alcohol solution and that the spectra show a similarity to the spectra of the anions. The general similarity of the spectra of the cations and anions is expected because the ions should have similar extents of electron delocalization. My attempts to repeat the experiments in which the β-diketones are dissolved in 0.1 N HCl revealed that the protonation in such dilute acid solutions cannot be complete. Incomplete protonation is very likely because the diketones themselves are weak acids and the hydrogen bond must be broken in order to form the cation. The spectra of the aliphatic compounds in dilute acid solution show evidence for equilibria between the neutral and cationic species. In most cases as more and more acid is added to the solution the λ\textsubscript{max} shifts farther to the red and approaches the λ\textsubscript{max} of the anion. Therefore, the spectra of the cations reported in the second literature reference cannot be definitive because of the
incomplete protonation. The exception to the rule of a red shift upon formation of the cation in HCl/alcohol occurs in the case of the aromatic diketones and will be discussed later. The spectra of most of the cations obtained in this work were those of samples dissolved in concentrated \( \text{H}_2\text{SO}_4 \) and show no appreciable evidence of incomplete protonation. That the cations formed in concentrated \( \text{H}_2\text{SO}_4 \) should be singly charged species to which a proton has been added to one of the oxygens is indicated by NMR studies reported in the literature.\(^{46,47}\) The structure is illustrated below.

![Structure](image)

The UV \( \lambda_{\text{max}} \)'s of the cations of the acyclic, aliphatic diketones are 287 nm for acetylacetone (ACAC\(^+\)), 287 nm for trifluoroacetylacetone (TFACAC\(^+\)), and 280 nm for hexafluoroacetylacetone (HFACAC\(^+\)). The spectra are shown in Figure 36. Note that in none of these cases does the \( \lambda_{\text{max}} \) of the cation fall as far to the red as the \( \lambda_{\text{max}} \) of the corresponding anion. The slight blue shift of the bands of the cations relative to those of the anions may indicate that the repulsion between the protons attached to the oxygens is causing the cations to have a greater twist away from planarity than the twist
Figure 36

Absorption spectra of
a. ACAC in conc. H$_2$SO$_4$

b. TFACAC in conc. H$_2$SO$_4$

c. HFACAC in conc. H$_2$SO$_4$
present in the anions. This increase in the twist was a result that I had predicted. It seems relatively certain that the cations do not absorb to the red of the \( \lambda_{\text{max}} \)'s of the neutral enols.

The probable reason that the repulsion of the ends of the "U" for the cations may normally be greater than that of the anions is that the protons of the cations are able to get much closer to one another than can the oxygens of the anions. That is, it is possible for the protons of the cations to have an eclipsing interaction which is not possible for the oxygens of the anions.

The basic factors that will determine the geometry of an ion are the same for cations and anions; they are the charge density on the coulombically interacting groups and the magnitudes of the purely steric repulsions between the other groups of the molecule. The results of these two effects may be seen in the spectrum of HFACAC\(^+\) when it is compared with those of ACAC\(^+\) and TFACAC\(^+\). The charge density on the protons in HFACAC\(^+\) is probably slightly higher than that in ACAC\(^+\). The extra repulsion of the two trifluoro groups in HFACAC\(^+\) combined with the coulombic repulsion causes HFACAC\(^+\) to be more nonplanar than ACAC\(^+\) and produces a \( \lambda_{\text{max}} \) farther to the blue and a larger blue shift relative to the band position of the anion than that of ACAC\(^+\). It is important to note that the trend in the \( \lambda_{\text{max}} \)'s of the cations is opposite to the
trend in the $\lambda_{\text{max}}$'s of the anions, in support of the charge density hypothesis.

Another important observation relative to the spectra of the ions of HFACAC is that the spectrum of HFACAC$^+$ is unstructured and has only a single smooth peak, while the spectrum of HFACAC$^-$ has the structure which has been attributed to the presence of several conformers. If the structure in the HFACAC$^-$ spectrum were vibrational, because of the similarity of the electronic structure of the ions it might be expected that the cation spectrum would be similarly structured. The lack of structure in the HFACAC$^+$ spectrum supports the hypothesis that there are different conformers observed for HFACAC$^-$, but only one conformer of HFACAC$^+$ is observed.

The results of computer calculations for some of the cations have been previously published. Ab-initio gaussian calculations of the ACAC cation have led to the conclusion that ACAC$^+$ has the structures shown below.

I feel that these structures are unacceptable and that the program is attempting to converge to an enol structure rather than a cationic one. The authors of the computational paper refer to the observed equivalence of
the $^{13}\text{C}$ chemical shifts of the carbonyl carbons$^{49,50}$ as evidence for equilibration between the two resonance forms. On the basis of the equivalence of the carbonyl carbon chemical shifts the authors of the NMR paper come to the same conclusion. Alternatively, it has been pointed out in the literature$^{46}$ that the NMR resonances of the cations of ACAC and other diketones are more reasonably explained by the presence of delocalized structures; this concept is my proposal as well. One must use caution in performing calculations on molecules that may have hydrogen bonding because many programs have difficulty with hydrogen bonds. Often the programs will predict the presence of hydrogen bonds that should not exist or predict the absence of hydrogen bonds that should exist. I stated previously that I believe that the most likely structure for the cations involves protonation of an oxygen to yield a non-hydrogen bonded open structure, and this conclusion seems to be supported by the data.

The results of my own MNDO calculations for the cations tends to support my hypothesis about the structure and geometry for those species. The calculations are complicated by the need to specify the positions of the protons attached to the oxygens. In reality, these protons are probably quite free to rotate in a conical fashion around the carbon-oxygen axis. The
calculations thus give only an estimate of the instantaneous energy of the cations in a particular configuration. I have computed several potential curves for distortion of the planar U cations toward the W conformation for various angles of rotation of the protons toward or away from one another; examples are depicted by the following structures.

As expected, the potential energy curve for a configuration in which the protons are oriented toward one another has a minimum at a larger twist angle than that for the anion. However, the position of this minimum depends strongly on the relative orientations of the protons, and consequently it is unrealistic to estimate the actual degree of distortion from any set of calculations for an assumed orientation of the protons. The calculations do support the hypothesis that the protons are significantly interacting and are causing an increase in the distortion of the geometry away from planarity. I believe that the minimal energy configuration of the cations is one in which there is some degree of distortion toward a W geometry. Especially for the cations, distortion toward a W
geometry gives the largest separation of the interacting groups. Because of the greater effective volume required by the rotating protons of the cations compared with that of the oxygens of the anions, I believe that S distortion is not favorable for the cations. The observed lack of structure in the HFACAC\textsuperscript+ spectrum indicates that only one type of geometry is present, and I believe that that geometry has W type distortion.

The spectra of the cations of BA, DBM, and BZTFAC, (BA\textsuperscript{+}, DBM\textsuperscript{+}, and BZTFAC\textsuperscript{+}, respectively) formed in concentrated H\textsubscript{2}SO\textsubscript{4} are shown in Figure 37. The \(\lambda_{\text{max}}\)'s of all of these cations fall to the red of those of their respective anions. The longest wavelength bands are due to transitions of the whole molecule in each case. Recall that I hypothesized that in order to reduce the charge density in the aromatic anions the phenyl rings were rotated out of the plane of the rest of the molecule. In the cations that situation is reversed and the phenyl rings are pulled into the plane. The added resonance effect of the phenyl rings enhances the electron donation by induction. The increased planarity of the molecule also results in a larger red shift of the band of the cation relative to that of the neutral enol than that observed for the anions.

The small peak in the 300 nm region of the DBM\textsuperscript{+} spectrum and the shoulder in the BA\textsuperscript{+} spectrum are
Figure 37
Absorption spectra of
a. BA in conc. $\text{H}_2\text{SO}_4$

b. DBM in conc. $\text{H}_2\text{SO}_4$

c. BZTFAC in conc. $\text{H}_2\text{SO}_4$
attributable to a transition of a protonated benzoyl group. The spectrum of benzaldehyde in concentrated H$_2$SO$_4$, shown in Figure 38, has a $\lambda_{\text{max}}$ in that region due to a $\pi^* \rightarrow \pi$ transition.

There are many more possible resonance structures that may be drawn for the cations of the aromatic $\beta$-diketones than for the aliphatic ones. Those resonance structures for DBM$^+$ are illustrated in Figure 39. Structures of this type for these cations were also proposed in one of the previous literature references. The analogous structures for the other compounds may be easily deduced from those in the figure. Remember that a molecule cannot be fully described by any single one of these structures but only by consideration of the group as a whole. The presence of structures that have double bonds to the phenyl rings strongly supports the idea that the phenyl rings of the cations are in the plane of the rest of the molecule.

The spectra of the cations of BA, DBM, and BZTFAC formed in approximately 5 M HCl/MeOH differ considerably from the spectra described for the cations formed in concentrated H$_2$SO$_4$. Protonation of BA and DBM in HCl/MeOH causes the $\lambda_{\text{max}}$’s to change from those of the neutral enols at 307 and 337 nm respectively, to the $\lambda_{\text{max}}$’s of the cations at 260 and 250 nm, respectively, after approximately two days. The spectra are shown in
Figure 38
Absorption spectra of
a. benzaldehyde in MEOH
b. benzaldehyde in HCl/MEOH
c. benzaldehyde in conc. $\text{H}_2\text{SO}_4$
Figure 39

Resonance structures for DBM$^+$
Figures 40 and 41.

The spectra of the cations of BA and DBM in HCl/MEOH are attributable to transitions of benzaldehyde protonated under those conditions. The spectra are consistent with the interpretation that the absorbing species are the dications of those diketones. The dications of β-diketones have been observed in several NMR experiments reported in the literature. The structures of the dications, shown below, may be described as diprotonated keto forms.

These structures for the dications have been confirmed by their $^1$H NMR spectra, in which a peak for two protons, one attached to each oxygen, and a peak for two protons on the central carbon are present.

The conversion to the dication is nearly complete after approximately two days under the conditions specified. It is probable that the somewhat slow rate of formation of the dication is due to its formation by diprotonation of the fraction of the compound that is present in the keto form rather than a conversion of the protonated enol form to the diprotonated keto form. The hypothesis that the major pathway for formation of the
Figure 40
Absorption spectra of
a. BA in HCl/MEOH (fresh solution)
b. BA in HCl/MEOH (solution aged two days)
Figure 41
Absorption spectra of
a. DBM in HCl/MEOH (fresh solution)
b. DBM in HCl/MEOH (solution aged two days)
dication is through the keto tautomer is further supported by two other observations. The first observation is that the dication is a major protonation product only in solutions that contain water. It has been observed that the proportion of the keto form of the β-diketones is larger in aqueous solutions than in non-aqueous solutions. The HCl/MEOH solutions were all prepared by dilution of 12 M aqueous HCl and thus contain water. The second observation is that in the HCl/MEOH solutions of DBM there does not appear to be any evidence of the monocation absorbances of DBM in the concentrated H₂SO₄ solutions. There must be an equilibrium between a monocation and the dication and the equilibrium should be observable under the conditions of the experiment. The most likely explanation for the apparent absence of a monocation peak is that there are two forms of monocation; one is a monoprotonated enol form and the other is a monoprotonated keto form that is illustrated below.

![Chemical Structure](image)

The enol monocation gives rise to the absorption in the 400 nm region when the solvent is concentrated H₂SO₄. The apparent absence of a band due to the enol monocation in the HCl/MEOH solutions is probably due to the
inability of these acid conditions to break the strong hydrogen bond of the DBM enol. Protonation of the keto tautomer has no such barrier to overcome and diprotonation should be almost as likely as monoprotonation. The keto monocation should have much less of a change in its absorption spectrum relative to the parent ketone upon protonation (as seen in the case of benzaldehyde in HCl/MEOH). Therefore, the keto monocation is probably not distinguishable as a distinct species in the "dication" spectra. When DBM was dissolved in a ~9 M aqueous solution of H$_2$SO$_4$, in contrast to the case of concentrated H$_2$SO$_4$, an equilibrium between the neutral enol, the enol monocation, and the dication was observed. The spectrum is shown in Figure 42. Thus, under these acid conditions, protonation of both the enol and the keto forms of DBM in the presence of water is observed. In the case of BA in HCl/MEOH, the spectrum of a small amount of the enol monocation is observed. It is likely that both the enol and keto forms of BA are protonated in HCl/MEOH because the hydrogen bond of BA is weaker than that of DBM.

The presence of the CH$_2$ group in the keto cations destroys the conjugation of the pi system over the length of the molecule and insulates the two ends from one another. There is no longer a transition of the molecule
Figure 42

Absorption spectrum of DBM in 9M aqueous $\text{H}_2\text{SO}_4$
as a whole but one due to the ends acting independently. The band is shifted to the blue because of the shortening of the box in the particle in the box analogy.

Strong support for the interpretation of the BA and DBM dication spectra is given by a set of experiments performed by previous members of this research group; the most recent one was that of Pascal. The experiment involved the irradiation of DBM in 3-methylpentane glass at 77 K. The source of the irradiation was a 1000 watt high pressure mercury arc. This irradiation was observed to cause cleavage of the hydrogen bond of DBM to produce a non-hydrogen bonded enol, which was trapped by the glass. The new species has an absorption to the blue of that of the hydrogen-bonded enol. In addition to the new absorption, a new emission attributable to this species was also observed. The phosphorescence of the H-bonded DBM enol is green and the phosphorescence of the new non-H-bonded species is blue and benzaldehyde-like. The excitation spectrum for the blue phosphorescence had a maximum at approximately 250 nm. These results were interpreted to indicate that a rotation of the two benzoyl groups by approximately 90° had taken place, leaving two essentially noninteracting benzoyl groups. The similarity of the results of these irradiation experiments and those in which the DBM and BA dications are formed is consistent with the hypothesis that upon
breaking the hydrogen bond of BA and DBM by irradiation with UV light and upon diprotonation, there is a loss of conjugation between the two halves of the molecule which results in benzaldehyde-like spectra.

It seems likely that the electron donation of the phenyl ring(s) of these molecules is able to compensate extensively for the positive charge in the cation. The greater basicity of these compounds and their ability to stabilize a larger positive charge allows them to be stable in the diprotonated keto form. The presence of water in the solution is also likely to stabilize the more highly charged dications. The aliphatic diketones show no evidence of dication formation in HCl/MEOH solution because of their lower electron density which makes them weaker bases and less stable as cations.

The conclusions presented above are supported by the spectra of BZTFAC in HCl/MEOH and in concentrated H₂SO₄ solution, shown in Figure 43. The HCl/MEOH spectrum recorded immediately after mixing the solution is essentially the same as that of a solution that is several days old. The HCl/MEOH spectra show evidence of the presence of the neutral enol, the enol monocation, and the keto dication. The long wavelength absorption is red-shifted by the presence of a shoulder which is due to the enol monocation. The presence of both types of cation in a rapidly established equilibrium in this case
Figure 43
Absorption spectra of
a. BZTFAC in HCL/MEOH
b. BZTFAC in conc. H$_2$SO$_4$
may be attributed to two factors. The ability of the HCl/MEOH to protonate the enol form of BZTFAC is probably due to the weaker hydrogen bond of the enol form. Recall that the hydrogen bond strength of BZTFAC is weaker than that of ACAC. The observation of a stable equilibrium between the neutral enol, the enol monocation and the keto dication is attributable to the lower electron density of BZTFAC caused by the electron withdrawing CF$_3$ group. The basicity is lowered, and the lower basicity may explain the incompleteness of the protonation. The conversion to the dication is incomplete because the dication is destabilized relative to the monocation also because of the lower electron density.

The BZTFAC enol monocation is apparently nearly planar, and the planarity is probably due to the aforementioned tendency of the electron donating and electron withdrawing groups to prefer to be coplanar in addition to the need for electron delocalization for charge stabilization.

The spectra of the cations of the cyclic diketones in concentrated H$_2$SO$_4$ are shown in Figure 44. Like those of the acyclic aliphatic diketones, all of these cations exhibit a blue shift relative to the absorption of the anions. Because these compounds must be present in a W geometry, the protons on the oxygens cannot get as close to one another as they can in the U case. However, there
Figure 44

Absorption spectra of

a. 1,3-PENT in conc. \( \text{H}_2\text{SO}_4 \)
b. 1,3-HEX in conc. \( \text{H}_2\text{SO}_4 \)
c. 2-ME-1,3-HEX in conc. \( \text{H}_2\text{SO}_4 \)
still are repulsive interactions of these protons with the proton attached to the central carbon or with the methyl group in 2-ME-HEX. These interactions are likely to produce nonplanar geometries of the "crown" or "envelope" type, which can explain the blue shifts. The cyclic diketones, like the other aliphatic diketones, show no evidence for dication formation. The published NMR studies report that even under superacid conditions, no formation of dications from the cyclic diketones was observed.

The spectra of the cations of α-ME-ACAC (α-ME-ACAC⁺), 2-AC-HEX, and 2-ME-1,3-HEX in concentrated H₂SO₄ are shown in Figure 45. Recall that these three compounds are structurally similar. Note that the spectrum of α-ME-ACAC⁺ is structured and has a λ_max at 292 nm and a shoulder at approximately 315 nm. A gaussian fit of the spectrum was performed and a fit that has a total rms error of 0.01948 absorbance units for peaks at 298 and 319 nm was obtained. The spectrum of α-ME-ACAC⁺ is the only one of the spectra of the cations studied in this work to have structure. The structure is very probably the result of the presence of two geometries of enol monocation; recall that there are two anions of α-ME-ACAC, one of a near-U type and another of the near-W type. Thus, it is logical to assign the 319 nm band to a near-U cation and the 298 nm band to a
Figure 45

Absorption spectra of

a. $\alpha$-ME-ACAC in conc. $\text{H}_2\text{SO}_4$

b. 2-AC-HEX in conc. $\text{H}_2\text{SO}_4$

c. 2-ME-1,3-HEX in conc. $\text{H}_2\text{SO}_4$
The structures of the cations of α-ME-ACAC are illustrated below.

A comparison of the α-ME-ACAC\(^+\) spectrum with the spectra of the cations of 2-AC-HEX (which will be shown to be a U cation) and 2-ME-1,3-HEX (which must be a W cation) strongly supports the conclusion that there are both U and W cationic forms of α-ME-ACAC.

The α-ME-ACAC cations are unusual in that they both absorb to the red of the positions of the bands of their corresponding anions. The red shift leads one to the conclusion that the cations are more nearly planar than the anions in this case. The significant nonplanarity of the anions must not be forgotten in the evaluation of the difference in the positions of the anion and cation absorptions.

That the cations of α-ME-ACAC are somewhat more planar than might be expected is likely to be due to the electron donating ability of the α-methyl group. That methyl group is able to contribute electron density to both sides of the molecule simultaneously and reduces the effective charge on both protons. The reduced coulombic
interaction of the protons allows more nearly planar geometries for both the near-U and near-W cations. The stabilization of the more nearly planar forms due to reduction of the coulombic interaction in this case is analogous to that effect proposed for HFACAC\(^-\) in which the electron withdrawing fluorines reduce the coulombic repulsion between the oxygens.

Another useful comparison is that of the ions of \(\alpha\)-ME-ACAC and the ions of 2-ME-1,3-HEX, which are structurally similar. The bands of \(\alpha\)-ME-ACAC\(^+\) at 298 and 319 nm are to the red of both the anion and the cation bands of 2-ME-1,3-HEX at 292 and 287 nm, respectively. I attribute the difference to the ability of the \(\alpha\)-ME-ACAC species to flex in a scissorlike fashion which allows it to reduce steric repulsion while remaining nearly planar. The cyclic compounds are unable to flex in this manner because the ring structure more rigidly fixes the bond angles.

The last cation to be considered is that of 2-AC-HEX (2-AC-HEX\(^+\)). The spectrum of 2-AC-HEX\(^+\) was shown in Figure 45. The \(\lambda_{\text{max}}\) of this cation is the same as the \(\lambda_{\text{max}}\) of its anion; both occur at 308 nm. That both these ions absorb at 308 nm indicates that both are nearly planar. Recall that the 2-AC-HEX species are comparable to the \(\alpha\)-ME-ACAC species because they can be considered to have similar substitutional and steric effects. By
comparison it is therefore not surprising that 2-AC-HEX$^+$
approaches planarity to approximately the same degree as
does the anion because of the electron donating effect of
the extra methylene group.

Because only a single band attributable to a U form
is observed in the spectrum of 2-AC-HEX$^+$ and because this
species cannot have W distortion, it seems likely that
there is no significant population of molecules that are
S distorted. Because 2-AC-HEX and $\alpha$-ME-ACAC are
structurally similar, by comparison it seems likely that
the $\alpha$-ME-ACAC species also should not have significant
populations of S-distorted molecules. These observations
strongly support the assignments of some of the bands of
the $\alpha$-ME-ACAC species to W-distorted and not S-distorted
forms.
REACTIONS WITH BORON TRIFLUORIDE IN POLAR SOLVENT

The order of discussion of the compounds in the next two sections will be different from that of previous sections so that similar results may be discussed as a group.

It is well documented in the literature that reaction of BF$_3$ with $\beta$-diketones produces chelated BF$_2$ products by the general reaction:

$$\text{R}_1\text{C(=O)C(=O)}\text{R}_2 + BF_3 \rightarrow \text{R}_1\text{C(=O)}\text{BF(=C(=O)BF_2)} + HF$$

The proposed mechanism of the reaction is one in which the boron trifluoride attacks one oxygen and subsequently attacks the other to eliminate HF.

$$\begin{align*}
\text{BF}_3 & \text{R}_1\text{C(=O)C(=O)}\text{R}_2 \\
& \text{R}_1\text{C(=O)}\text{BF(=C(=O)BF_2)} + HF
\end{align*}$$

It was desirable to study the reaction of BF$_3$ with the diketones in order to observe and study the changes in the spectra and geometries. In order to simplify the evaluation of the changes in the spectra upon addition of BF$_3$ in the polar solvent, the reaction with BF$_3$ was often carried out after addition of NaH to form the anion of the diketone. Addition of base removed the complication of beginning with an equilibrium enol/anion mixture. The presence of the base does not alter the reaction or the
spectrum of the final product. It has been experimentally observed that the result does not depend upon whether the initial form of the diketone is neutral or anionic.

The UV absorption spectra of the BF$_2$ chelates of acetylacetone (ACACBF$_2$), benzoylaceton (BABF$_2$), and dibenzoylmethane (DBMBF$_2$) are shown in Figure 46. The spectrum of ACACBF$_2$ has a $\lambda_{\text{max}}$ at 287 nm, redshifted from that of the neutral enol $\lambda_{\text{max}}$ at 270 nm. The red shift is probably attributable to a slight increase in planarity. The $\lambda_{\text{max}}$ of the ACACBF$_2$ chelate is comparable to the $\lambda_{\text{max}}$ of the TFACAC enol which I have also proposed to be quite nearly planar. The ACACBF$_2$ spectrum has the essential features of the ACAC enol spectrum, and it appears that the BF$_2$ group differs from the hydrogen of the enol only in its ability to hold the molecule in a planar geometry. The BF$_2$ group is a stronger Lewis acid than the proton and makes the BF$_2$ bridge appear to be a "super" hydrogen bond.

Most of the discussion of the aromatic diketone BF$_2$ chelates has already been covered in the discussion of those neutral molecules. Refer to that section for discussion of the effects of chelation of BF$_2$ on the UV spectra and geometry of BA and DBM. The conclusions will be briefly reviewed here.

Results similar to those for ACACBF$_2$ are obtained
Figure 46
Absorption spectra of
a. ACAC in 20% BF$_3$/MEOH
b. BA in 20% BF$_3$/MEOH
c. DBM in 20% BF$_3$/MEOH
for BABF₂, which has a redshift of the λ_max from the neutral enol peak at 307 nm to 330 nm for the BF₂ chelate. The redshift has been attributed to the induced coplanarity of the phenyl and enol rings. That the two rings are more nearly coplanar in the BF₂ chelate than in the BA enol is also indicated by the redshift of the benzoyl transition as well as by the crystal structures of these compounds. Let it again be emphasized that the spectra support the hypothesis that the molecules in solution and in the crystal share similar geometries and that a similarity has not been merely assumed.

The spectra of DBM enol and the DBMBF₂ chelate also show great similarities and lead to the same conclusions. The redshifts of the λ_max and the benzoyl transition indicate that the chelation of BF₂ has produced a more nearly planar compound. The two benzoyl transitions of the enol have merged into a single peak in the DBMBF₂ spectrum; this result was described in the neutral molecule section. The increase in structure of the spectra indicates that the molecules are more nearly rigid and contributes to the view of the BF₂ bridge being a "super" hydrogen bond. The marked trend in the degree of structure in the spectra in Figure 46 clearly shows that even with a "super" hydrogen bond, the more electron-rich molecules are more nearly rigid.

The probable reason for the induced planarity of the
aromatic diketones upon chelation of BF2 is the electron withdrawing effect of the fluorines. The fluoro groups cause the enol ring to be electron poor, and the molecule "responds" by adding the extra electron density that the phenyl groups are able to deliver when they are coplanar with the enol ring. The spectra of these chelates should be similar to those that would be obtained from a planar neutral enol.

The spectra observed for the BF2 chelates discussed above are in excellent agreement with the transitions reported in the literature,\textsuperscript{51} although that reference does not cover changes in geometry brought about by the chelation of BF2. In addition, that reference does not cover the reactions of the fluorinated or cyclic diketones with BF3.

In contrast to the reactions of the above compounds, the reaction of BF3 with the anions of the cyclic diketones obviously cannot lead to chelated structures. The spectra are shown in Figure 47. The common factor observed in all of the spectra of the BF3 adducts of the cyclic diketones is that the spectra all have \( \lambda_{\text{max}} \)'s that approximately correspond to the neutral enol \( \lambda_{\text{max}} \) of the parent compound. The structure I propose for the reaction products is the following.
Figure 47

Absorption spectra of

a. 1,3-PENT in 1.5% BF₃/MEOH
b. 1,3-HEX in 1.5% BF₃/MEOH
c. 2-ME-1,3-HEX in 1.5% BF₃/MEOH
In this structure the BF₃ group has taken up the bulk of the negative charge and has left the electronic structure of the rest of the molecule similar to that of the neutral enol. The similarity of the electronic structure of the BF₃ adduct to that of the neutral enol is the origin of the similarity of their spectra. Note that once again a BFₓ group is observed to have the same spectroscopic properties as a proton in these compounds.

Considering the mechanism by which the chelation of BF₂ is postulated to occur, i.e. a double attack, I predicted that perhaps it would be possible to form monodentate adducts of BF₃ with a β-diketone in the U form if the electron density on one side of the molecule were too low to attract the second attack. The assumption is that the BF₃ first attaches to the most electron-rich oxygen and then attacks the second oxygen to eliminate HF (or F⁻ if reacted with the anion). I predicted that the reaction of the fluorinated diketones with BF₃ would produce monodentate adducts analogous to the products from the cyclic diketones above.

The UV spectra for the reactions of HFACAC⁻ with BF₃ are shown in Figures 48-50. I began with HFACAC because there are fewer possibilities for the structure of the BF₃ adduct due to the symmetry of HFACAC. The initial spectrum shown in Figure 48 is that of the anion of HFACAC that has a concentration on the order of 10⁻⁵ M.
Figure 48
Absorption spectra of
a. HFACAC (low conc.) in MEOH with NaH
b. HFACAC (low conc.) in MEOH with NaH and one drop of BF$_3$ etherate
Upon addition of 1 drop of BF$_3$ etherate to the 1-cm square cell, the essentially flat-line spectrum was obtained. The decrease in the absorption intensity indicates that the product of the reaction has a much smaller absorptivity ($\epsilon$) than that of the HFACAC anion. The volume change upon addition of the BF$_3$ is negligible. The experiment was repeated with a very much higher concentration of HFACAC anion, and several drops of BF$_3$ etherate were added to the cell in several aliquots. The spectra are shown in Figure 49. The spectra show two peaks, one at 305 nm and the other at approximately 270 nm. As more BF$_3$ is added, the 305 nm peak decreases and the 270 nm peak slowly increases. There is an isosbestic point at approximately 275 nm. The inversion of intensity of the two peaks and particularly the observation of an isosbestic point is unequivocal evidence for an equilibrium between the HFACAC anion (305 nm) and a BF$_3$ adduct (270 nm). I emphasize that the concentration of HFACAC in this experiment is very much higher than that of the previous experiment. Therefore, if the equilibrium were between the HFACAC anion and the neutral enol, the absorbance of that solution for a 1-cm pathlength would be unmeasurable. It is clear that the $\epsilon$ of the BF$_3$ adduct is very much lower than that of the HFACAC anion, and that the equilibrium lies strongly on the side of the adduct.
Figure 49

Absorption spectra of

a. HFACAC (high conc.) in MEOH with NaH
   and one aliquot of BF$_3$

b. solution (a) with one additional
   aliquot of BF$_3$

c. solution (b) with one additional
   aliquot of BF$_3$
The equilibrium that I propose is shown below.

\[
\begin{array}{cc}
\text{CF}_3 & \text{CF}_3 \\
\text{O} & \text{O} \\
\end{array}
+ \text{BF}_3 & \text{BF}_3^- \\
\text{CF}_3 & \text{CF}_3 \\
\text{O} & \text{O} \\
\end{array}
\]

A definitive spectrum of the BF\(_3\) adduct formed in \(-20\%\) BF\(_3\)/MEOH is shown in Figure 50. The \(\lambda_{\text{max}}\) of the BF\(_3\) adduct at 265 nm is in excellent agreement with the predicted behavior of a species that has the proposed structure; the \(\lambda_{\text{max}}\) is nearly the same as that of the neutral enol. The low \(\varepsilon\) value for the adduct also supports the proposed structure. The intensity of an electronic transition is dependent upon the electron density in the chromophore. The addition of a BF\(_3\) group to form the structure shown above effectively removes one electron from the chromophore and greatly reduces the \(\varepsilon\). It has been suggested\(^{52}\) that there may be loss of F\(^-\) from the product shown above to form a neutral species. Such a species would also produce spectra in excellent agreement with the observed results. The HFACAC molecule is already electron poor due to the presence of the trifluoro groups, and there is no electron well from which that the molecule can make up the deficiency. The cyclic diketones do not undergo such a large reduction in \(\varepsilon\) upon addition of BF\(_3\) probably because they have greater electron density and can draw on the electron donating alkyl substituents to compensate for the electron density.
Figure 50
Absorption spectrum of HFACAC in 20% BF$_3$/MEOH
placed on the BF$_3$.

The reaction of HFACAC$^-$ with BF$_3$ was further investigated by means of $^{19}$F NMR spectroscopy. The spectra are grouped together for ease of comparison. The spectrum of HFACAC in methanol is shown in Figure 51. There are two sets of major peaks, each set consisting of two peaks at approximately -85 and -90 ppm relative to CCl$_3$F. The spectrum of TFACAC in methanol (Figure 56) has only two major peaks, one at approximately -85 and the other at approximately -90 ppm. By comparison, it is clear that the peaks at -90.4126 and -85.2811 ppm in the HFACAC spectrum belong to the same molecule, and that the peaks at -90.1269 and -85.1269 belong to another form of the HFACAC molecule. Thus, there are two forms of the HFACAC enol present in methanol solution at this concentration of the diketone. It should be remembered that the concentration of the diketones in the solutions studied by NMR are much higher than those in the UV experiments, and dissociation to the anion is far from complete in the more concentrated solutions. What then are the two forms of HFACAC enol in methanol? It will be shown in the next section that the $^{19}$F NMR spectrum of TFACAC in CCl$_4$ has only a single peak. Therefore, the two peaks in the TFACAC spectrum recorded with methanol as the solvent cannot arise from the two possible tautomeric structures differing only in the position of
Figure 51

$^{19}\text{F NMR spectrum of HFACAC in ME0H}$

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Figure 52

$^{19}_F$ NMR spectrum of HFACAC in MEOH with NaH
Figure 53

$^{19}_F$ NMR spectrum of HFACAC in MEOH with NaH and BF$_3$
the hydrogen bonded enolic proton. However, if the hydrogen bond is broken, i.e. if the enol form is unchelated, then it may be possible to observe different chemical shifts for the fluorines in the two structures shown below.

I believe that the two peaks in the $^{19}$F NMR spectrum of TFACAC in methanol are attributable to the presence of the two unchelated enolic structures shown above. In the case of HFACAC the unchelated enol may have two peaks, one for each set of trifluoro groups. However, the two tautomeric enols for HFACAC are identical. Therefore, the presence of four peaks in the HFACAC spectrum cannot be explained on the basis of tautomeric pairs. I believe that the four peaks arise from the presence of two geometries of unchelated HFACAC in the methanol solution; each geometric form contributes two peaks to the spectrum. It does not seem unlikely that in a large excess of alcohol the weak hydrogen bonds of the fluorinated diketones should be broken and that the HFACAC enol should be present in more than one geometry. The evidence for the presence of multiple geometries of the HFACAC anion also supports this view.

Upon addition of NaH to the solution of HFACAC in
methanol, the fluorine NMR peaks of the neutral enols are replaced by those of the anion(s) at -78 and -86 ppm. The spectrum is shown in Figure 52. Small peaks at these positions from self-ionization of the HFACAC in pure methanol are observable in the previous spectrum. It is also noteworthy that in the presence of NaH there remains a trace of two of the peaks of the neutral enol at -85.0524 and -90.1465 ppm. Both of these peaks correspond closely to the peaks of one of the forms of enol described in the previous paragraph. In addition, the remaining peaks of the enolic form are those of the enol that was present in the lesser amount in the pure methanol solution. These observations are strong evidence for the presence of two forms of unchelated HFACAC enol in methanol solution which have differing acidities. In the section of this work in which the anions were discussed in detail, the presence of two fluorine peaks for HFACAC\(^-\) was attributed to the presence of two geometric forms of that ion.

The \(^{19}\)F NMR spectrum of the HFACAC anion in methanol with BF\(_3\) etherate is shown in Figure 53. A peak corresponding to unreacted anion is observed at -78 ppm, and new peaks are observed at -79.3770 and -87.8345 ppm. The new peaks have approximately the same ratio of intensities as the peaks of the anions from which they were formed. I believe that the two peaks are due to two
different geometries of BF$_3$ adduct of the type that I have proposed for these compounds. In the case of the HFACAC$^-$ adducts, the fluorine environments seem to be somewhat similar to those present in the anions.

There are three other peaks in the entire spectrum of HFACAC in methanol in the presence of NaH and BF$_3$ at -154, -156 and -159 ppm due to the presence of the BF$_3$ etherate. In an independent experiment I have observed these three peaks in the spectrum of BF$_3$ in methanol in the absence of the diketone. The three peaks are due to the BF$_3$ fluorines in various environments. Certainly some of the BF$_3$ is associated with methanol, some with the diethyl ether, and evidently some is present in some other environment upon which I will not speculate. I believe that the fluorine signals of the BF$_3$ associated with the diketones in the methanol solutions are essentially indistinguishable from these signals. In support of this hypothesis, it is observed that the ratios of the intensities of the three peaks differ in the various spectra. The peaks assigned to BF$_3$ that were recorded in all of the spectra are shown together in Figure 54. In addition to the difference in intensities, the range of chemical shifts of the -154 and -159 ppm peaks is only ~0.1 ppm over three samples, one with HFACAC, one with TFACAC, and the BF$_3$ etherate alone, while the range of values for the -156 ppm peak is
Figure 54

$^{19}$F NMR spectra of peaks assigned to BF$_3$

a. BF$_3$ etherate in MEOH

b. TFACAC in MEOH with NaH and BF$_3$

c. HFACAC in MEOH with NaH and BF$_3$
-0.5 ppm. On close examination, the -156 ppm peak in the TFACAC spectrum can be seen to consist of two unresolved peaks. Perhaps the shift of the central BF$_3$ peak and the slight appearance of a double peak in the case of the TFACAC sample can be attributed to the signal due to the BF$_3$ associated with the diketones. These effects could be merely the result of the differing concentrations of BF$_3$ etherate in the various solutions, however.

The UV spectrum of TFACAC in -20% BF$_3$ etherate/MEOH is shown in Figure 55. The $\lambda_{\text{max}}$ of the BF$_3$ adduct in this case is 275 nm, which is to the blue of the neutral enol $\lambda_{\text{max}}$ at 282 nm. Recall that the enol form of TFACAC has an unusually long wavelength absorption which I have explained on the basis of induced planarity caused by the presence of electron donating and withdrawing substituents on opposite ends of the molecule. For the BF$_3$ adduct of TFACAC, there are two possible structures, 1 and 2 below.

![Structures](image)

The structure in which the BF$_3$ adds to the more electron-rich side (the methyl side) is expected to be predominant. Note that in that structure there are now electron withdrawing substituents on both sides of the molecule, as there are in HFACAC. The $\lambda_{\text{max}}$ of the
Figure 55
Absorption spectra of
a. TFACAC in MEOH with NaH
b. TFACAC in 20% BF$_3$/MEOH
mixture of 1 and 2, which is assumed to be dominated by that of 1, is essentially that of the HFACAC enol; this result supports the proposed structures and the explanation for the long wavelength of the TFACAC enol $\lambda_{\text{max}}$.

The $^{19}$F NMR spectra of TFACAC in methanol and in the presence of NaH and BF$_3$ are shown in Figures 56-58. The spectrum of TFACAC in pure methanol is shown in Figure 56. Figure 57 shows the spectrum obtained after addition of NaH. By comparison with the spectrum in which there is no NaH, it can be seen that in addition to two peaks at -85 and -89 ppm due to leftover neutral enol, there is a new peak for the anion at -79.0121 ppm. A small peak at this position is observed in the previous spectrum due to dissociation. In the presence of NaH, there is also another small peak at -78.5696 ppm which may be due to a small amount of another geometry of TFACAC anion.

Upon addition of BF$_3$ etherate to the solution of TFACAC in methanol with NaH, the anion peak(s) are reduced to the two small peaks at -78.3 and -79.3 ppm. A new stronger peak appears at -79.8 ppm, a small amount of which was present in the enol spectrum. The spectrum is shown in Figure 58. The ratio of the intensities of the remaining neutral molecule peaks is greatly changed from those of the previous spectra. It appears that perhaps the addition of BF$_3$ has caused a change of the anion.
Figure 56

$^{19}\text{F NMR spectrum of TFACAC in MEOH}$
Figure 57

$^{19}$F NMR spectrum of TFACAC in MEOH with NaH
Figure 58

$^{19}\text{F NMR spectrum of TFACAC in MEOH with NaH and BF}_3$
spectrum such that it resembles the enol spectrum, with the exception that the BF$_3$ has a much stronger preference for the more electron-rich oxygen than does the proton.

The spectra of $\alpha$-ME-ACAC in MEOH with NaH, with BF$_3$, and in ~20% BF$_3$/MEOH are shown in Figure 59. The shoulder at approximately 290 nm in the spectrum of the BF$_3$ adduct (at low BF$_3$ concentration) probably corresponds to a chelated BF$_2$ structure and the 260 nm peak probably corresponds to unreacted $\alpha$-ME-ACAC$^-$. The spectrum (normalized) of $\alpha$-ME-ACAC in ~20% BF$_3$/MEOH indicates that these assignments are correct. The $\lambda_{\text{max}}$ of the spectrum is at 292 nm and there is a shoulder on the long-wavelength side of the band, at approximately 315 nm. The appearance of a shoulder indicates that the new species is more rigid than the enol, and supports the hypothesis that it is a chelate. The $\lambda_{\text{max}}$, which corresponds to that of the anion, indicates that the geometry is nearly planar. The assignment of the chelated structure is also strongly supported by the $\lambda_{\text{max}}$ reported in the literature for the BF$_2$ chelate of $\alpha$-ME-ACAC. The sample in that case is a chloroform solution prepared from the solid chelate, and a single peak at 304 nm is reported. The absence of the 260 nm band that was seen in the spectrum of the solution with the lower BF$_3$ concentration confirms the assignment of the short wavelength band to the unreacted anion.
Figure 59

Absorption spectra of

a. $\alpha$-ME-ACAC in MEOH with NaH
b. $\alpha$-ME-ACAC in MEOH with NaH and BF$_3$
c. $\alpha$-ME-ACAC in 20% BF$_3$/MEOH (normalized)
The spectra of the 2-AC-HEX anion and BF$_3$ adduct are shown in Figure 60. The $\lambda_{\text{max}}$ at 292 nm and the presence of a shoulder at approximately 310 nm in the BF$_3$ adduct spectrum indicates that the adduct is chelated and more rigid and planar than the neutral enol.
Figure 60

Absorption spectra of

a. 2-AC-HEX in MEOH with NaH

b. 2-AC-HEX in 1.5% BF$_3$/MEOH
REACTIONS WITH BORON TRIFLUORIDE IN NONPOLAR SOLVENT

The UV spectra of ACAC, BA and DBM in nonpolar solvent with BF₃ are shown in Figure 61. The spectra are very similar to those obtained with the compounds in polar solvent. The only difference is that the vibrational structure in the nonpolar solvent spectra of ACAC, BA and DBM with BF₃ is very slightly enhanced over that observed from the compounds in the polar solvent. The vibrational structure in spectra recorded with a compound dissolved in nonpolar solvents is normally clearer than that in spectra recorded with the same compound dissolved in a polar solvent. The stronger solvent-solute interaction (hydrogen bonding in particular) in polar solvents distorts the vibrations of the solute and causes the vibrational structure of the spectrum to be obscured. Other than the vibrational structure, the general similarity of the λ_max’s and the characteristics of the spectra of the compounds in the two different polarity solvents indicates that the products in both cases are the BF₂ chelates of ACAC, BA and DBM.

The cyclic compounds present an experimental difficulty in that they are very insoluble in the nonpolar solvents that are convenient for UV analysis. The insolubility is likely to be due to the intermolecular hydrogen bonding of these compounds in the
Figure 61

Absorption spectra of
a. ACAC in 3MP with BF$_3$

b. BA in 3MP with BF$_3$

c. DBM in 3MP with BF$_3$
solid state. I have observed that the NMR spectra of several of the cyclic diketones in CCL\textsubscript{4} solution are very complex and have more peaks than the number expected for a monomer. The spectra are interpretable in terms of dimers, trimers, and perhaps larger oligomers in solution. Addition of BF\textsubscript{3} etherate to the solutions causes a simplification of the spectra; the simplification indicates that the hydrogen bonding has been broken by addition of the BF\textsubscript{3}. Unfortunately, the ether resonances largely obscure the remaining peaks. Because the cyclic diketones are unable to chelate BF\textsubscript{2} and because they should be present as neutral molecules in nonpolar solvent, the structures are undoubtedly given by:

Unfortunately, I have been unable to record good UV spectra of the cyclic diketones in nonpolar solvents in the presence of BF\textsubscript{3} because of the solubility and turbidity problems.

The UV spectra of the reaction products of TFACAC and HFACAC with BF\textsubscript{3} in nonpolar solvent are shown in Figures 62 and 63. These spectra sharply differ from those of samples obtained from the same reactions in polar solvents. There is a redshift of the $\lambda_{\text{max}}$'s.
Figure 62

Absorption spectra of

a. TFACAC in 3MP

b. TFACAC in 3MP with BF$_3$
Figure 63

Absorption spectra of

a. HFACAC in cyclohexane

b. HFACAC in cyclohexane with BF$_3$
relative to those of the enols upon addition of BF$_3$; there is also an increase in the absorbance and an increase in the structure of the spectra.

The structures of the reaction products of the fluorinated diketones with BF$_3$ was investigated by $^{19}$F NMR at 100 MHz. The purpose of the experiment was to determine from peak integration whether the reaction produces a chelated BF$_2$ product 1 or a monodentate BF$_3$ product 2.

Recall that the possibility that an open structure may exist was predicted on the basis of the proposed mechanism of formation of chelated BF$_2$ structures by a double attack process and the low electron density on the oxygens of the fluorinated diketones. An open form of a BF$_3$ adduct was hypothesized to exist in the previous section in which the reactions performed in polar solvents were presented.

The spectrum of HFACAC in CCl$_4$ with BF$_3$ etherate is shown in Figure 64. From independent experiments I have determined that the unreacted HFACAC fluorine resonance appears at -80.0 ppm and the unreacted BF$_3$ etherate fluorine resonance appears at -155.7 ppm. New resonances
Figure 64

$^{19}$F NMR spectrum of HFACAC in CCl$_4$ with BF$_3$
are observed at -78.7 and -133.2 ppm. The presence of peaks for the free HFACAC and the BF₃ etherate in the spectrum of the mixture indicates that there is an equilibrium between the reactants and products, i.e. that the reaction does not go to completion with the approximately equal concentrations of reactants in this experiment. The new resonances are clearly due to the CF₃ groups and the BFₓ group of the reaction product, respectively. The integration of the CF₃ peak gives an area of 1.993 for the six fluorines, and that of the BFₓ peak an area of .906. The ratio of the CF₃/BFₓ areas is 2.2 : 1. The ratio of very nearly 2 : 1 indicates conclusively that the reaction product is a monodentate BF₃ adduct that has the structure 2, above, which I will designate as HFACACBF₃.

In an independent experiment a single CF₃ resonance of TFACAC in CCl₄ is observed at -80.1 ppm. Upon addition of BF₃ etherate, new peaks appear at -78.6 and -138.3 ppm for CF₃ and BFₓ, respectively. The spectrum is shown in Figure 65. The peak areas are 1.836 for the three CF₃ fluorines and 1.542 for the BFₓ fluorines. The CF₃/BFₓ ratio is 1.2 : 1. The almost 1 : 1 ratio again indicates a monodentate BF₃ reaction product, which I will designate as TFACACBF₃. There should be two possibilities for a monodentate BF₃ adduct to the
Figure 65

$^{19}\text{F NMR spectrum of TFACAC in CCl}_4$ with BF$_3$
asymmetrical TFACAC molecule, with structures 1 and 2 below.

\[
\begin{align*}
\text{F} & \quad \text{O} & \quad \text{H} \\
\text{1} & \quad \text{CF}_3 \\
\text{F} & \quad \text{O} & \quad \text{BF}_3 \\
\text{2} & \quad \text{CF}_3
\end{align*}
\]

It is expected that the major product would be the one in which the BF$_3$ adds to the more electron-rich oxygen to form product 1. Close examination of the BF$_3$ peak of the TFACAC adduct (see inset) reveals that there is a small side peak which is attributable to the minor product 2. From the graphical integral it is estimated that the minor product constitutes approximately 15% of the total product.

Now that the structures of the reaction products of BF$_3$ with TFACAC and HFACAC in nonpolar solvents have been established, the UV spectra may be interpreted. It should be emphasized that the concentrations of reactants in the NMR experiments were of the same order of magnitude, while the relative concentrations of the diketones in the UV experiments are very much lower. The large excess of BF$_3$ should drive the equilibrium to the products side, and consequently the reaction in the UV experiments may be more nearly complete than those observed in the NMR experiments.

The spectrum of HFACAC in cyclohexane with BF$_3$ was fit by means of the BANDIT computer program to a sum of
four gaussians. The gaussian peaks are at wavelengths of 287, 297, 306 and 317 nm. The 287 nm band is very broad and may be attributable to unreacted HFACAC enol ($\lambda_{\text{max}} = 272$ nm). The appearance of the spectrum and the positions of the other three bands of the fit are extremely reminiscent of the spectrum of HFACAC$^-$. A control experiment was performed in which one drop of diethyl ether was added to a solution of HFACAC in 3MP in the absorption cell. No change in the spectrum was observed. Therefore, the change in the spectrum on addition of BF$_3$ etherate is due to the presence of BF$_3$. The similarity of the spectra of HFACACBF$_3$ and HFACAC$^-$ indicates that the two species have similar degrees of electronic delocalization and suggests that the structure in the spectrum of HFACACBF$_3$ is due to the presence of multiple conformers. The similarity of the electronic structure of HFACACBF$_3$ to that of the anion is probably due to an increase in the symmetry of the electron distribution caused by the presence of the BF$_3$ group. The possibility that there are several conformers of HFACACBF$_3$ seems reasonable because the geometry-constraining hydrogen bond has been eliminated; the anion case is similar. A similarity of the geometries of HFACACBF$_3$ to those of the anion is reasonable because the potential surface of the anion seems to be determined largely by the steric effects of
the trifluoro groups and the charge repulsion of the oxygens, and HFACACBF$_3$ has essentially those same steric factors. The enol proton and the BF$_3$ group do not seem to repel one another strongly enough to prevent formation of a nearly planar geometry. Two possible reasons for this apparent "soft" interaction are that the two groups are not charged in the manner of the protons in the cation and that the BF$_3$ group is less likely than a proton to be freely rotating about the C-O bond due to the steric interaction with the CF$_3$ group. If the BF$_3$ group is in an out-of-plane position for most of the time, free rotation of the enol proton about the C-O bond would not cause a severe steric interaction of the two. By this reasoning, the interaction of the proton and BF$_3$ group is lessened to an extent that it approximates the interaction of the charged oxygens in the anion.

The spectrum of TFACACBF$_3$ has its $\lambda_{\text{max}}$ at the same wavelength (292 nm) as that of TFACAC$^-$ and has an additional weak shoulder at approximately 305 nm that is not present in the anion spectrum. Because of the coincidence of the $\lambda_{\text{max}}$'s of the TFACAC anion and the spectrum of the BF$_3$ adduct(s), it is likely that the TFACACBF$_3$ species are both quite planar. It is unclear from what is known whether the spectrum is dominated by the absorbance of the major product of the reaction or if there is a significant absorption of the minor product as
well. In the first case, obviously the entire spectrum would be attributed to the absorption of the major product. In the second case, however, either of the two bands could correspond to either of the two products.

The spectrum of $\alpha$-ME-ACAC in 3MP and with $BF_3$ is shown in Figure 66. The $\lambda_{\text{max}}$ occurs at 292 nm, and a shoulder appears at approximately 310 nm. The spectrum is consistent with the interpretation that the product is the $BF_2$ chelate of $\alpha$-ME-ACAC. Recall that the same result was observed for the reaction carried out in polar solvent. The product in both instances appears to be quite planar and rigid. In neither case is there evidence for the presence of two geometric forms, as there was for the enols, anions, and cations of $\alpha$-ME-ACAC. The chelating ability of the $BF_2$ group is evidently great enough to overcome the steric repulsions of the methyl groups.

Results similar to those for $\alpha$-ME-ACAC are observed in the case of 2-AC-HEX. The spectra of 2-AC-HEX with and without $BF_3$ are shown in Figure 67. The spectrum of 2-AC-HEX in the presence of $BF_3$ has a $\lambda_{\text{max}}$ at 305 nm and a slight shoulder in the 315 nm region. A small shoulder at approximately 290 nm is probably due to unreacted enol. The redshift to almost the $\lambda_{\text{max}}$ of the ions and the structure indicate that the product is a nearly planar $BF_2$ chelate.
Figure 66

Absorption spectra of
a. \( \alpha\)-ME-ACAC in 3MP
b. \( \alpha\)-ME-ACAC in 3MP with BF3
Figure 67

Absorption spectra of

a. 2-AC-HEX in 3MP

b. 2-AC-HEX in 3MP with BF$_3$
CONCLUSIONS

Previous studies of the enol and anionic forms of \( \beta \)-diketones had correlated the strength of the hydrogen bond of the enol forms with the amount of red shift of the spectrum that occurs upon anion formation. That treatment assumes that the absorption \( \lambda_{\text{max}} \)'s of the enol forms are related to the hydrogen bond strength and that the geometries of the anions that are formed are similar to each other and to the enol form from which they were formed. The UV absorption \( \lambda_{\text{max}} \)'s for the compounds studied do not exhibit a consistent trend that can be related to the strength of the hydrogen bond of the enol form. I conclude that the hydrogen bond strength does not completely determine the geometry of the enol forms. The hydrogen bond strength does appear to have an effect on the extent of the vibrational structure observed in the spectra. The structure in the spectra is more pronounced when the hydrogen bond is stronger. There is no structure in the spectra of the compounds which are incapable of forming intramolecular hydrogen bonds. I present evidence that also indicates that there is in general a geometry change upon ionization and that there are multiple geometric forms in some cases.

The compound \( \alpha \)-ME-ACAC is observed to exist in two neutral and two ionic forms. Previous workers have attributed one form to a U geometry and the other to
either the keto form or the S form. Pascal noted that upon formation of the anion if the second neutral form were indeed the keto tautomer, then it should not be stable. He attributed the second form to the S geometry.

In this work, I have performed potential energy calculations on the enolic and anionic forms of α-ME-ACAC and have concluded that one form has a twisted U shape and the other a twisted W shape. There is strong evidence for the existence of two geometries of those types for many of the various species formed from that compound in this work.

Because previous treatments of the trends in the spectra of the diketones depended primarily upon the hydrogen bond strength and because I have proposed that the hydrogen bond strength does not determine the spectroscopy, an alternative explanation is needed. I have proposed a hypothesis to explain the trend in the $\lambda_{\text{max}}$'s of the β-diketones studied. It appears that if there is an electron withdrawing substituent on one side of the enol ring and an electron donating substituent on the other side of the ring, planarity is favored.

Previously, very little detailed attention has been paid to the less intense bands in the UV spectra of the aromatic diketones, which are attributable to the benzoyl groups. I have shown that the benzoyl transitions in the UV spectra spectra of the aromatic diketones indicate
that the two phenyl rings of DBM in solution are not equivalent. The evidence suggests that the geometry of the DBM in solution is similar to that in the crystal, in which one phenyl ring is nearly coplanar with the enol ring and the other is tilted slightly out of the plane.

The trends in the $\lambda_{\text{max}}$'s and red shifts of the UV absorptions of the anionic forms of the compounds do not correlate with the trend in the hydrogen bond strength of the enol forms. Previously, anomalies in this trend were attributed to the loss of electron delocalization caused by the presence of trifluoro groups. I have shown that the experimental evidence indicates that there is in general a change in geometry upon ionization to the anion. Molecular orbital potential energy calculations performed in this work suggest that multiple geometries of several of the anions of the compounds are likely to exist. I postulate that the anions of ACAC and TFACAC are in a geometry in which the two acetyl groups are twisted away from one another by an equal amount. I postulate that the anion of HFACAC is exists in three geometries; each geometry gives rise to an an absorption band. One geometry corresponds to the type proposed for ACAC and TFACAC, one is a very nearly planar U geometry, and the other is a geometry intermediate between those two in planarity. Previously performed emission work from this group by Cheng gave strong evidence for the
existence of at least two forms of HFACAC anion. As part of this work, I have obtained $^{19}$F NMR data for the anion of HFACAC which also is strong evidence for this assertion.

I have presented strong evidence that the UV absorption spectra of the anions of the aromatic diketones studied indicate that upon formation of the anions the phenyl rings rotate to a more out-of-plane position relative to the plane of the enol ring. I propose that this rotation occurs in order to minimize the negative charge density of the anion by reducing the electron donation capability of the phenyl rings.

The spectra of the cations of many β-diketones were studied long ago and have been largely neglected since that time. However, the previous interpretation did not rationalize the results in terms of changes in the geometry of the molecules. I believe that definitive UV spectra of the cations of the fluorinated diketones may be presented here for the first time. The UV spectra of the cations of the aliphatic diketones are very similar to the spectra of their respective anions. The $\lambda_{\text{max}}$'s of nearly all of the aliphatic cations fall slightly to the blue of the $\lambda_{\text{max}}$'s of the corresponding anions. The slight blue shift indicates that these cations may be slightly more nonplanar than are the anions because of the repulsion of the charge carrying protons on the
The aromatic diketones have been previously observed by NMR spectroscopy to form both monocations and dications. In this work, the UV spectra of the mono- and di-cationic aromatic diketones were studied and I have interpreted the results in terms of the principles developed in this research. The UV $\lambda_{\text{max}}$'s of the monocations of the aromatic diketones fall to the red of the bands of the corresponding anions. The red shift observed for the monocations is the result of the formation of a more nearly planar overall geometry. In contrast to the case of the anionic forms, the phenyl rings are pulled into the plane of the enol rings. The positive charge density is thereby minimized because of the increased electron donating capability of the phenyl rings. It is the electron donation of the phenyl groups which enables the formation of stable dications of these compounds. The published NMR data indicate that the dominant structure of the dications is that of a diprotonated keto form. The keto character of the dications is the cause of a large blue shift of the absorption $\lambda_{\text{max}}$'s relative to the absorptions of the monocations.

It has long been established that the reaction of BF$_3$ with a $\beta$-diketone results in the formation of a chelated BF$_2$ structure. I have shown that the reactions
of the diketones with BF$_3$ are observed to be dependent upon the relative electron-rich or electron-poor character of the diketone in addition to the polarity of the solvent. Reactions of ACAC, BA, and DBM with BF$_3$ in polar or nonpolar solvent result in the formation of a chelated BF$_2$ structure, which has been well documented. However, it is shown that reaction of BF$_3$ with a fluorinated or cyclic diketone in a polar solvent results in the formation of products that have the general structure shown below.

![Chemical structure](image)

It has been suggested that the final product may be a neutral species formed by loss of F$^-$ from the species shown above. The UV spectra observed in this work could be explained at least equally well in terms of such a species. I had predicted that because of the electron-poor character of the fluorinated diketones it would be possible to form monodentate products with BF$_3$. The basis for this prediction was that after BF$_3$ first attached to one of the oxygens (presumably the most electron rich one), then the other oxygen of a fluorinated diketone would be too electron poor to attract a second attack of the BF$_3$ to eliminate HF. Obviously, a cyclic diketone is unable to chelate BF$_3$;
consequently those compounds have served as a basis for comparison. The UV absorption spectra of the structures shown above are very similar to the spectra of the parent neutral enols and suggest that the BF$_3$ group carries the bulk of the negative charge. In some cases, there is also a sharp decrease in the absorptivities of the BF$_3$-anion adducts relative to those of the enolic forms; this observation also indicates the presence of a considerable charge separation or formation of the neutral species mentioned above. The reactions of the $\beta$-diketones with BF$_3$ have also been investigated in this work by means of $^{19}$F NMR spectroscopy. Reaction of the fluorinated or cyclic diketones with BF$_3$ in a nonpolar solvent results in products that have the general structure shown below.

![Structure](image)

The spectra of these forms show a resemblance to the spectra of the corresponding anionic forms. The similarity indicates that the geometry of these products is more nearly planar than the geometry of the enol forms. The structures of the above compounds have been confirmed in this work by means of $^{19}$F NMR spectroscopy.

In this work I have developed several principles or "rules of the game" in the language of the foreword.
Those principles were deduced from the study of many \( \beta \)-diketones in various forms. However, the applicability of the principles is not limited to the diketones, but to conjugated molecules in general. The concepts presented here should aid in the interpretation of spectra of conjugated systems, particularly in the deduction of the geometries of the molecules and the changes in the geometry that accompany ionization or some types of chemical modification.

Future work on the spectroscopy of \( \beta \)-diketones may attempt to answer the major remaining question: what is the spectrum of the \( S \) form of the diketones? Although in this work it is proposed that some of the compounds possess \( S \) distortion, none of the compounds are present in a predominantly \( S \) geometry. Because the \( S \) geometry is obviously not particularly favorable for the \( \beta \)-diketones in general, some ingenuity must be employed to design a molecule for which the \( S \) geometry will be favorable. In order to satisfy the requirements for the UV experiments, the molecule should retain as much as possible the pure \( \beta \)-diketone chromophore. That restriction largely limits the options to designing steric barriers to the \( U \) form. In my opinion, the best starting molecule is 2-acetyl-cyclohexanone, because only \( S \) distortion is possible for that molecule. I believe that a compound of the type illustrated below has the largest probability of
being present to a significant extent in the S form.

\[
\begin{align*}
R_1 &= \text{methyl, ethyl, propyl, etc.} \\
R_2 &= \text{methyl, ethyl, propyl, iso-propyl, t-butyl, etc.}
\end{align*}
\]

A restriction of the steric hindrance approach to force an S geometry is that if the steric factor is too severe, the molecule may be stable only in the perpendicular conformation and would be unable to enolize for the same reason that bicyclo-[2.2.2]-octanetrione is unable to enolize.

Another area of possible future work is in the area of time-resolved studies. Because many of the \(\beta\)-diketones undergo ionization upon excitation, it would be possible to study the proton transfer properties of the excited states and possibly to examine the time evolution of the emissions of the various geometric forms of the anions. In addition it may be possible to study the time-resolved absorption spectra of anions produced by photoionization and to obtain pure absorption spectra for the various geometric forms.

These and other questions remain to be answered, and hopefully they will not be neglected, because of the importance of the \(\beta\)-diketones in their utility as metal chelators and as models for the spectroscopy of other conjugated and hydrogen-bonded systems.
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255
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APPENDIX 1

MNDO Molecular Orbital Calculation Output for Selected Geometries
### α-ME-ACAC 140-W ENOL

**NET ATOMIC CHARGES.**

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**TOTAL ENERGY**  
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**IONIZATION POTENTIAL**  
9.03449 EV

**DIPOLE MOMENT**  
3.60851 DEBYE

---

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**α-ME-ACAC 45-W ANION**

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**TOTAL ENERGY**  
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**IONIZATION POTENTIAL**  
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**α-ME-ACAC 140-W ANION**

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TFACAC 30-W ANION

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HEAT OF FORMATION: -236.26386 KCAL/ MOLE
TOTAL ENERGY: -2779.86948 EV
IONIZATION POTENTIAL: 3.57506 EV

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HFACAC U ANION

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IONIZATION POTENTIAL 4.33593 EV
HFACAC 30-W ANION

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IONIZATION POTENTIAL 4.27867 \text{ EV}\)
HFACAC 40-S ANION

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IONIZATION POTENTIAL: 4.26012 EV
APPENDIX 2

Listings of computer programs
(documentation provided in remark statements)
CURVE DIGITIZER

FOR USE WITH THE GENIUS GT-1212A GRAPHICS TABLET

BY

STEVEN E. ARNOLD

This program was written to digitize UV absorption spectra recorded on a Cary 14 spectrophotometer. The directions below apply to that application. The program as written may be used as general purpose digitizer program.

The program "as is" uses the monochrome screen, so the file qbherc must be run before it will work.

Use yellow puck button (#1) for entering points from 0-1 absorbance units.
Use green puck button (#3) for entering points from 1-2 absorbance units.
Use red puck button (#4) to end data entry.
(The directions above apply to the case of a spectrum recorded with a 0-2 slide wire which has a trip mechanism to fold the spectrum back for absorbances in the 1-2 range.)

The Pascal program SCALER should be run on any file containing points for absorbances from 1-2 in order to rescale those points to reflect the proper values. Those points MUST have been entered using the green puck button in order for this to work.

If baseline correction is desired, digitize the experimental baseline spectrum and run the Pascal program BASELINE. Be sure to digitize a little extra space on each end of the baseline to be sure the baseline covers the entire spectrum. The BASELINE program will prompt for the spectrum and baseline filenames and perform the subtraction.

The program has elementary disk error handling procedures which check for the existence of a file before overwriting with one of the same name.
'It also has a provision for disk full or disk not ready errors to minimize
the possibility of lost data.

CLS
KEY(10) ON
GOSUB cal

MAIN:
' Main Program
DEFINT P
' Dimension data arrays for 2000 points: increase if necessary, and if
' the memory is available
SCREEN 3

WINDOW (0, 12020)-(12000, 0)
' Draw a box on the screen that indicates the limits of the tablet area
LINE (0, 12020)-(12000, 0), 1, B
' Tablet dip switches 2 and 3 ON, all others OFF
' Tablet connected to 1st serial port, 9600 baud, no parity, 8 data bits,
' 1 stop bit, ASCII character communication to tablet, file #1
OPEN "COM1: 9600,N,8,1,ASC" FOR OUTPUT AS #1 LEN = 10
' Delay to allow tablet to get ready to accept commands
' which MUST NOT BE OMITTED!
FOR I = 1 TO 30: NEXT I
' Set tablet to change trail mode
PRINT #1, "A";
' Set tablet to 1000 lines/inch resolution
PRINT #1, "j";
' Set increment distance to 25
PRINT #1, "I";
PRINT #1, CHR$(57);
' Set rate of report to maximum
PRINT #1, "Q";
CLOSE #1
' Switch to recieve communications from tablet, same parameters
OPEN "COM1: 9600,N,8,1,ASC" FOR INPUT AS #1 LEN = 1
P = 0
C = 1
' Beep to signal that program is ready to recieve data
SOUND 880, .8

SPECT:
INPUT #1, X, y, P
'PRESS RED PUCK BUTTON TO END DATA ENTRY
IF P = 4 THEN GOSUB DSKFILE
xcoord(C) = X
YCOORD(C) = y
PVAL(C) = P
PSET (X, y)
C = C + 1
GOTO SPECT

NEWTRACE:
INPUT "Do you want to enter another trace in this data area? (Y/N) "; nt$
LOCATE 1, 1
PRINT " 
LOCATE 1, 1
IF nt$ = "N" OR nt$ = "n" THEN END
IF nt$ = "Y" OR nt$ = "y" THEN CLOSE #1: GOTO MAIN
END

QUIT:
CLOSE #1
END

DSKFILE:
INPUT "Do you want to make a disk file of this data? (Y/N)"; ans$
LOCATE 1, 1
PRINT "
LOCATE 1, 1
IF ans$ = "N" OR ans$ = "n" THEN RETURN NEWTRACE
INPUT "Input path and filename"; pfn$
LOCATE 1, 1
PRINT "
LOCATE 1, 1
'ENABLE DISK ERROR HANDLING
ON ERROR GOTO DISKERROR
NAME pfn$ AS pfn$
OPEN "0", #2, pfn$
FOR I = 1 TO C - 1
'NEXT TWO LINES ARE ONE STATEMENT
PRINT #2, (XLB + (xcoord(I) - XL) * XRESOLUTION), (YLB + (YCOORD(I) - YL) * YRESOLUTION), PVAL(I)
NEXT I
CLOSE #2
'DISABLE DISK ERROR HANDLING
ON ERROR GOTO 0
RETURN NEWTRACE

cal:
' Subroutine to calibrate tablet coordinates
OPEN "COM1: 9600,N,8,1,ASC" FOR OUTPUT AS #1 LEN = 10
FOR I = 1 TO 20: NEXT I
PRINT #1, CHR$(0); FOR I = 1 TO 20: NEXT I
' set tablet to location mode
PRINT #1, "B";
FOR I = 1 TO 20: NEXT I
' set tablet to 1000 lpi resolution
PRINT #1, "j";
FOR I = 1 TO 20: NEXT I
CLOSE #1
OPEN "COM1: 9600,N,8,1,ASC" FOR INPUT AS #1 LEN = 10
FOR I = 1 TO 20: NEXT I
PRINT "Digitize lower left corner of data area"
INPUT #1, XL, YL, P
PRINT "Input values for X and Y of lower left corner"; XLB, YLB
PRINT "Digitize upper right corner of data area"
INPUT #1, XU, YU, P
PRINT "Input values for X and Y of upper right corner"; XUB, YUB
XLINES = XU - XL
XRANGE = XUB - XLB
XRESOLUTION = XRANGE / XLINES
YLINES = YU - YL
YRANGE = YUB - YLB
YRESOLUTION = YRANGE / YLINES
PRINT "AT THE TONE, YOU MAY BEGIN"
FOR I = 1 TO 20: NEXT I
CLOSE #1
RETURN

DISKERROR:
'DISK ERROR HANDLING ROUTINE
DISKERR = ERR
IF DISKERR = 53 THEN RESUME NEXT
IF DISKERR = 58 THEN
      INPUT "FILE ALREADY EXISTS. REPLACE (Y/N)"; R$
      LOCATE 1, 1
      PRINT " ";
      LOCATE 1, 1
      IF R$ = "Y" OR R$ = "y" THEN RESUME NEXT
      IF R$ = "N" OR R$ = "n" THEN
            INPUT "Input path and filename "; pfns$
            " ;
LOCATE 1, 1
PRINT "
LOCATE 1, 1
RESUME
END IF
END IF
IF DISKERR = 61 OR DISKERR = 71 THEN
   INPUT "DISK IS NOT READY OR DISK IS FULL: CORRECT AND HIT RETURN", DUM$ 
   GOSUB DSKFILE
END IF
RESUME
(* SCALER --- A PROGRAM TO BE RUN ON FILES CREATED BY CURVE DIGITIZER*)
(* TO CONVERT VALUES OF ABSORBANCES FROM 1-2 TO THE PROPER*)
(* BY STEVEN E. ARNOLD *)

PROGRAM SCALER;

VAR
    INFIL,OUTFIL : STRING[80];
    WAVELENGTH : REAL;
    J : INTEGER;
    P : INTEGER;
    ABSORBANCE : REAL;
    COUNTER : INTEGER;
    INFILE : TEXT;
    OUTFILE : TEXT;
    WAVE : ARRAY[1..5000] OF REAL;
    ABS : ARRAY[1..5000] OF REAL;

BEGIN
    COUNTER := 1;
    WRITELN ('Input path and filename of the input file ');
    READLN(INFIL);
    ASSIGN (INFILE, INFIL);
    WRITELN ('Input path and filename of the output file ');
    READLN (OUTFIL);
    ASSIGN (OUTFILE, OUTFIL);
    RESET (INFILE);
    WHILE NOT EOF(INFILE) DO
        BEGIN
            READ (INFILE,WAVELENGTH);
            READ (INFILE,ABSORBANCE);
            READ (INFILE,P);
            IF (P=3) THEN
                BEGIN
                    ABSORBANCE := ABSORBANCE +1;
END;
WAVE[COUNTER] := WAVELENGTH;
ABS[COUNTER] := ABSORBANCE;
COUNTER := COUNTER +1;
END;
CLOSE (INFILE);
REWRITE (OUTFILE);
FOR J := 1 TO COUNTER-1 DO
BEGIN
WRITE (OUTFILE,WAVE[J]:8:5);
WRITE (OUTFILE,' ');
WRITE (OUTFILE,ABS[J]:8:5);
WRITE (OUTFILE,' ');
WRITELN (OUTFILE,P);
END;
CLOSE (OUTFILE);
END.
Baseline is a program designed to do baseline correction on UV spectra which have been digitized by the CURVE DIGITIZER program. If there are points in the spectrum which have absorbance values in the range from 1-2, the SCALER program should be run on the file before application of this program.

PROGRAM BASELINE;

VAR LASTINDEX : INTEGER;
    WAVE : ARRAY[1..2000] OF REAL;
    ABS : ARRAY[1..2000] OF REAL;
    BASWAV : ARRAY[1..2000] OF REAL;
    BASABS : ARRAY[1..2000] OF REAL;
    I, MAXSPEC, MAXBAS, COUNTER : INTEGER;
    INDEXMINDIFFLEFT, INDEXMINDIFFRIGHT : INTEGER;
    INFILE1, INFILE2, OUTFILE : TEXT;
    SPECFIL, BASFIL, OUTFIL : STRING[80];
    WAVELENGTH, ABSORBANCE, MINDIFFLEFT : REAL;
    DIFFLEFT : REAL;
    DELTAWAV, FRACWAV, DELTAABS, ABSCORR : REAL;

BEGIN
    CLRSCR;
    WRITELN ('Input path and filename of the SPECTRUM input file ');
    READLN (SPECFIL);
    ASSIGN (INFILE1, SPECFIL);
    WRITELN;
    WRITELN ('Input path and filename of the BASELINE input file ');
    READLN (BASFIL);
ASSIGN (INFILE2,BASFIL);
WRITELN;
WRITELN ('Input path and filename of the output file ');
READLN (OUTFIL);
ASSIGN (OUTFILE,OUTFIL);
REWRITE (OUTFILE);
(* READ SPECTRUM INPUT FILE *)
RESET (INFILE1);
COUNTER := 1;
WHILE NOT EOF(INFILE1) DO
  BEGIN
    READ (INFILE1,WAVELENGTH);
    READLN (INFILE1,ABSORBANCE);
    WAVE [COUNTER] := WAVELENGTH;
    ABS [COUNTER] := ABSORBANCE;
    COUNTER := COUNTER + 1;
  END;
CLOSE (INFILE1);
(* READ BASELINE INPUT FILE *)
RESET (INFILE2);
MAXSPEC := COUNTER - 1;
COUNTER := 1;
WHILE NOT EOF(INFILE2) DO
  BEGIN
    READ (INFILE2,WAVELENGTH);
    READLN (INFILE2,ABSORBANCE);
    BASWAV [COUNTER] := WAVELENGTH;
    BASABS [COUNTER] := ABSORBANCE;
    COUNTER := COUNTER + 1;
  END;
CLOSE (INFILE2);
MAXBAS := COUNTER - 1;
COUNTER := 1;
MINDIFFLEFT := 10000;
WRITELN;
WRITELN ('WORKING ---- THIS WILL TAKE A FEW MOMENTS ---- PLEASE WAIT');
(* FOR EACH POINT, FIND NEAREST NEIGHBORS IN BASELINE *)
LASTINDEX := 1;
FOR COUNTER := 1 TO MAXSPEC DO
BEGIN
FOR I := LASTINDEX TO MAXBAS DO
BEGIN
  IF BASWAV[I] <= WAVE[COUNTER] THEN
  BEGIN
    DIFFLEFT := WAVE[COUNTER] - BASWAV[I];
    IF DIFFLEFT < MINDIFFLEFT THEN
    BEGIN
      MINDIFFLEFT := DIFFLEFT;
      INDEXMINDIFFLEFT := I;
      INDEXMINDIFFRIGHT := I + 1;
    END;
  END;
  IF BASWAV[I] > WAVE[COUNTER] THEN
  BEGIN
    I := MAXBAS;
  END;
(* INTERPOLATE BETWEEN BASELINE POINTS *)
DELTAWAV := BASWAV[INDEXMINDIFFRIGHT] - BASWAV[INDEXMINDIFFLEFT];
FRACWAV := (WAVE[COUNTER] - BASWAV[INDEXMINDIFFLEFT]) / DELTAWAV;
DELTAABS := BASABS[INDEXMINDIFFRIGHT] - BASABS[INDEXMINDIFFLEFT];
ABSCORR := BASABS[INDEXMINDIFFLEFT] + (FRACWAV * DELTAABS);
MINDIFFLEFT := 10000;
LASTINDEX := INDEXMINDIFFLEFT;
END;
(* OUTPUT ROUTINE *)
FOR COUNTER := 1 TO MAXSPEC DO
BEGIN
WRITE (OUTFILE,WAVE[COUNTER]:8:5);
WRITE (OUTFILE,'    ');  
WRITELN (OUTFILE,ABS[COUNTER]:8:5);
END;
CLOSE (OUTFILE);
WRITELN;
WRITELN ('DONE. ---- OUTPUT FILE HAS BEEN WRITTEN.');
END.
Spectrum plotter is a program written in Microsoft Quickbasic to plot data from ASCII disk file(s) consisting of wavelength and absorbance values. Output is to a Hewlett-Packard 7470A plotter. The bottom axis is a wavelength scale (nanometers), the top axis is a wavenumber scale (inverse centimeters), and the y axis is an absorbance scale.

Star Trek fans will note that the program as it is works like the Guardian of Forever. That is, "it is programmed to present the data in this manner."

The plotter should be set to 2400 baud, no parity, 8 data bits, 1 stop bit and US paper size.

'Dip switch settings:

CLS
GOSUB LOGO
CLS
PRINT INPUT "HOW MANY SPECTRA ARE TO BE IN THIS PLOT "; NS
DIM WAVE(NS, 2000), ABSORPT(NS, 2000), COUNT(NS), LTYP(NS)
MINWAVE = 1000: MAXWAVE = 0
MINABS = 0: MAXABS = 0
FOR FIL = 1 TO NS
PRINT
PRINT "PATH AND FILENAME OF DATA FILE "; FIL;
INPUT DF$
PRINT "READING DATA FILE "; FIL
OPEN "I", #1, DF$
I = 1
WHILE NOT EOF(1)
  INPUT #1, WAVE(FIL, I), ABSORPT(FIL, I)
  'MULTIPLY ABSORBANCES BY 10 TO ACCOMODATE INTEGER SCALING FOR PLOTTER
  ABSORPT(FIL, I) = ABSORPT(FIL, I) * 10
  IF WAVE(FIL, I) < MINWAVE THEN MINWAVE = WAVE(FIL, I)
  IF WAVE(FIL, I) > MAXWAVE THEN MAXWAVE = WAVE(FIL, I)
  IF ABSORPT(FIL, I) < MINABS THEN MINABS = ABSORPT(FIL, I)
  IF ABSORPT(FIL, I) > MAXABS THEN MAXABS = ABSORPT(FIL, I)
  I = I + 1
WEND
COUNT(FIL) = I - 1
CLOSE #1
NEXT FIL
PRINT
PRINT "THE WAVELENGTH RANGE OF THE DATA IS "; MINWAVE; " TO "; MAXWAVE; "NM."
PRINT
INPUT "WHAT RANGE DO YOU WISH TO PLOT (MIN,MAX) ", MINXPLOT, MAXXPLOT
'SCALE Y AXIS SUCH THAT THE MAXIMUM WILL BE AN INTEGER MULTIPLE OF 2
'(2 ABSORBANCE UNITS) BUT NOT LESS THAN THE MAXIMUM OF ANY SPECTRUM
Y = MAXABS \ 2 'INTEGER DIVISION
Y = Y + 1
MAXYPLOT = Y * 2
MINYPLOT = 0
PRINT
INPUT "PRIME THE PLOTTER PEN AND HIT RETURN TO START PLOTTING ", DUM$
PLOT:
' SET PLOTTER TO 2400 BAUD, NO PARITY, 8 DATA BITS, 1 STOP BIT, ASCII MODE
OPEN "COM1: 2400,N,8,1,ASC" FOR RANDOM AS #1 LEN = 1
' DELAY TO ALLOW PLOTTER TO GET READY TO ACCEPT COMMANDS
FOR D = 1 TO 1000: NEXT D

' INITIALIZE PLOTTER, SELECT PEN 1 AND SET P1 AND P2
PRINT #1, "IN;"
' DELAY TO ALLOW PLOTTER TO INITIALIZE
FOR D = 1 TO 1000: NEXT D
PRINT #1, "SP1;IP1600,1500,9250,5200;"

'SET ENQUIRE/ACKNOWLEDGE HANDSHAKE
'DATA BLOCK SIZE 128 BYTES, ENQUIRY CHARACTER DEC 18, ACKNOWLEDGEMENT STRING
'DEC 49
PRINT #1, CHR$(27); ".H128;18;49;"
'500 ms TURNAROUND DELAY, OUTPUT TRIGGER CHARACTER = "?" (DEC 63),
'NO ECHO TERMINATE CHARACTER, OUTPUT TERMINATOR CARRIAGE RETURN (DEC 13),
'INTERCHARACTER DELAY 5 ms
PRINT #1, CHR$(27); ".M500;63;0;13:"; CHR$(27); ".N5;"

'SET PEN VELOCITY TO 5.7 cm/s
PRINT #1, "VS5.7;"

'SET CHARACTER DIRECTION TO PLOT HORIZONTALLY RELATIVE TO P1 AND P2
GOSUB ENQ
PRINT #1, "DR1,0;"

'SET AXIS SCALES TO GRAPH UNITS WITH DECREASING VALUES ALONG X AXIS
GOSUB ENQ
PRINT #1, "SC"; MAXXPLOT; MINXPLOT; MINYPLOT; MAXYPLOT; ";"
' DRAW BOX FOR DATA AREA
GOSUB ENQ

' NEXT TWO LINES ARE ONE STATEMENT
PRINT #1, "PU"; MAXXPLOT; MINYPLOT; "PD"; MINXPLOT; MINYPLOT; MINXPLOT;
   MAXYPLOT; MAXXPLOT; MAXYPLOT; MAXXPLOT; MINYPLOT; "PU;"

' SET CHARACTER SIZE AND TICK LENGTH FOR MAJOR TICKS
GOSUB ENQ
PRINT #1, "SI.2,.3;TL0,2;"

'TICK AND LABEL X AXIS
FOR X = MAXXPLOT TO MINXPLOT STEP -20
GOSUB ENQ
PRINT #1, "PA"; X; MINYPLOT; "XT;"
GOSUB ENQ

PRINT #1, "CP-2.5,-1;LB"; X; CHR$(3)
NEXT X

XCENTER = MAXXPLOT - ((MAXXPLOT - MINXPLOT) / 2)
GOSUB ENQ

' NEXT TWO LINES ARE ONE STATEMENT
PRINT #1, "PA"; XCENTER; MINYPLOT; ";"; "CP-7.5,-2.5; LBWAVELENGTH (nm)";
   CHR$(3)

'SET TICK LENGTH FOR MINOR TICKS AND ADD THEM
GOSUB ENQ
PRINT #1, "TL0,1;"
FOR X = MAXXPLOT - 10 TO MINXPLOT STEP -20
GOSUB ENQ
PRINT #1, "PA"; X; MINYPLOT; "XT;"
NEXT X

'RESET TICK LENGTH FOR MAJOR TICKS
GOSUB ENQ
PRINT #1, "TL0,2;"
'TICK AND LABEL WAVE NUMBER AXIS
'SET TICK LENGTH FOR TOP AXIS
GOSUB ENQ
PRINT #1, "TL2,0;"
FOR X = MAXXPLOT TO MINXPLT STEP -20
GOSUB ENQ
PRINT #1, "PA"; X; MAXYPLOT; "XT;"
WAVENUM = 1E+07 / X
GOSUB ENQ
PRINT #1, "CP-2.5,1; LB";
PRINT #1, USING "####"; WAVENUM;
GOSUB ENQ
PRINT #1, CHR$(3);
NEXT X
GOSUB ENQ
PRINT #1, "PA"; XCENTER; MAXYPLOT; ";"; "CP-7,2.5; LB WAVE NUMBER (cm"; CHR$(3)
GOSUB ENQ
PRINT #1, "CP0,.5;LB-1"; CHR$(3)
GOSUB ENQ
PRINT #1, "CP0,-.5;LB")"; CHR$(3)
'RESET TICK LENGTH TO POSITIVE
GOSUB ENQ
PRINT #1, "TL0,2;"

'TICK AND LABEL Y AXIS
FOR Y = 0 TO MAXYPLOT STEP 2
GOSUB ENQ
PRINT #1, "PA"; MAXXPLOT; Y; "YT;"
GOSUB ENQ
PRINT #1, "CP-5.0,0;LB";
PRINT #1, USING ".#"; Y / 10;
PRINT #1, CHR$(3);
NEXT Y
YCENTER = MINYPLOT + ((MAXYPLOT - MINYPLOT) / 2)
'SET CHARACTER DIRECTION TO PLOT VERTICALLY ALONG Y AXIS
GOSUB ENQ
PRINT #1, "DR0,1;"
GOSUB ENQ
PRINT #1, "PA"; MAXXPLOT; YCENTER; ";"; "CP-5,3.5; LBABSORBANCE"; CHR$(3)
'RESET CHARACTER DIRECTION TO PLOT HORIZONTALLY
GOSUB ENQ
PRINT #1, "DR1,0;"

FOR FIL = 1 TO NS
'PLOT GRAPH OF SPECTRUM
'SET LINE TYPE
CLS
PRINT
PRINT "  0 = DOTS ONLY AT PLOTTED POINTS 4 = --"  "
PRINT "  1 = .  .  5 = ------ -"  "
PRINT "  2 = ------ 6 = ---- -"  "
PRINT "  3 = ------ 7 = -------"  "
PRINT
PRINT "NUMBER OF THE LINE TYPE FOR SPECTRUM "; FIL;
SOUND 500, 3
SOUND 25000, 5
INPUT LTYP(FIL)
GOSUB ENQ
IF LTYP(FIL) <> 7 THEN
PRINT #1, "LT"; LTYP(FIL); ";"
ELSE
PRINT #1, "LT;"
END IF
PRINT #1, "VS38.1;"
'PLACE PEN AT BEGINNING OF SPECTRUM
GOSUB ENQ
PRINT #1, "PU;PA"; WAVE(FIL, 1); ABSORPT(FIL, 1); "PD"
FOR J = 1 TO COUNT(FIL)
GOSUB ENQS
PRINT #1, USING "####.####"; WAVE(FIL, J); ABSORPT(FIL, J);
NEXT J
GOSUB ENQS
PRINT #1, "PU;"
NEXT FIL
PRINT
INPUT "DO YOU WANT TO ADD A LEGEND (Y/N)"; ANS$
IF ANS = "Y" OR ANS = "y" THEN GOSUB LEGEND
INPUT "DO YOU WANT TO ADD A TITLE (Y/N)"; ANS$
IF ANS = "Y" OR ANS = "y" THEN GOSUB TITLE
CLOSE #1
SOUND 500, 3
SOUND 25000, 5
END

ENQ:
'SEND ENQUIRE CHARACTER AND WAIT FOR ACKNOWLEDGE
FOR T = 1 TO 4000: NEXT T
PRINT #1, CHR$(18);
PRINT #1, "?": INPUT #1, Z
RETURN

ENQS:
PRINT #1, CHR$(18);
PRINT #1, "?": INPUT #1, Z
RETURN

LEGEND:
'SET PEN VELOCITY TO 5.7
GOSUB ENQ
PRINT #1, "VS5.7;"
CLS
PRINT
'SEND PAPER TO FRONT OF PLOTTER TO ALLOW USER TO SEE ENTIRE PLOT

GOSUB ENQ
PRINT #1, "PA"; MAXXPLOT; MINYPLOT; ";";

'PLOT LEGEND ON SPECTRUM

INPUT "COORDINATES nm,abs FOR APPROX. TOP LEFT CORNER OF LEGEND"; X, Y
Y = Y * 10
GOSUB ENQ
PRINT #1, "PA"; X, Y; ";" 
FOR FIL = 1 TO NS
PRINT
PRINT " > = TURN ON SUPERSCRIPTING"
PRINT "< = TURN ON SUBSCRIPTING"
PRINT "! = TURN OFF SUPER/SUB SCRIPTING"
PRINT
PRINT "LEGEND FOR SPECTRUM NUMBER "; FIL
LINE INPUT LG$ 
LENGTH = LEN(LG$)
DIM LEGEND$(LENGTH)
FOR I = 1 TO LENGTH
LEGEND$(I) = MID$(LG$, I, 1)
NEXT I

'SET LINE TYPE FOR LEGEND LINE
IF LTYP(FIL) <> 7 THEN
PRINT #1, "LT"; LTYP(FIL); ";"
ELSE
PRINT #1, "LT";
END IF

'PLOT LEGEND LINE
GOSUB ENQ

'STORE PEN
PRINT #1, "SP";
INPUT "PRIME PEN AND HIT RETURN TO START ", DUM$ 

'PICK UP PEN
GOSUB ENQ
PRINT #1, "SP1;";
GOSUB ENQ
PRINT #1, "PD;PR"; -10, 0; "PU";
'POSITION PEN FOR LEGEND TEXT
PRINT #1, "CP1,-.25;"
FOR I = 1 TO LENGTH
IF LEGEND$(I) = ">" THEN
  GOSUB ENQ
  PRINT #1, "CP0,.25;"
  INDEX = 1
END IF
IF LEGEND$(I) = "<" THEN
  GOSUB ENQ
  PRINT #1, "CP0,-.25;"
  INDEX = -1
END IF
IF LEGEND$(I) = "!" THEN
  IF INDEX = 1 THEN
    GOSUB ENQ
    PRINT #1, "CP0,-.25;"
  ELSE
    GOSUB ENQ
    PRINT #1, "CP0,.25;"
    INDEX = 0
  END IF
END IF
IF LEGEND$(I) <> "<" AND LEGEND$(I) <> ">" AND LEGEND$(I) <> "!" THEN
GOSUB ENQ
PRINT #1, "LB"; LEGEND$(I); CHR$(3);
END IF
NEXT I
'SEND CARRIAGE RETURN/LINE FEED
GOSUB ENQ
PRINT #1, "CP;"
' MOVE HALF SPACE UP FOR NEXT LEGEND LINE
GOSUB ENQ
PRINT #1, "CP0,.25;"
' MOVE PEN BACK FOR LEGEND LINE
GOSUB ENQ
PRINT #1, "PR10,0;"
ERASE LEGEND$
NEXT FIL
RETURN

TITLE:
LINE INPUT ; "INPUT TITLE FOR PLOT "; TIT$
LENGTH = LEN(TIT$)
' NEXT TWO LINES ARE ONE STATEMENT
PRINT #1, "PA"; XCENTER; MAXYPLOT; ";; "CP"; -LENGTH / 2; ";,5;LB"; TIT$;
CHR$(3);
RETURN

' PROGRAM LOGO
LOGO:
CLS
PRINT
PRINT
PRINT "; CHR$(201);
FOR Z = 1 TO 45
PRINT CHR$(205);
NEXT Z
PRINT CHR$(187)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
PRINT SPC(13); CHR$(186); " SpecPlot "; SPC(16); CHR$(186)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
'NEXT TWO LINES ARE ONE STATEMENT
PRINT SPC(13); CHR$(186); "    SPECTRUM PLOTTER "; SPC(13);
CHR$(186)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
PRINT SPC(13); CHR$(186); "    BY "; SPC(16); CHR$(186)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
'NEXT TWO LINES ARE ONE STATEMENT
PRINT SPC(13); CHR$(186); "    STEVEN E. ARNOLD "; SPC(13);
CHR$(186)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
PRINT SPC(13); CHR$(186); "    FEBRUARY 1990 "; SPC(13); CHR$(186)
PRINT SPC(13); CHR$(186); SPC(45); CHR$(186)
PRINT SPC(13); CHR$(200);
FOR Z = 1 TO 45
PRINT CHR$(205);
NEXT Z
PRINT CHR$(188)
LOCATE 24, 1
INPUT "    TURN ON THE PLOTTER AND HIT RETURN TO CONTINUE ", DUM$
RETURN
MOLECULE VIEWER

By

STEVEN E. ARNOLD

Molecule Viewer is a program designed to produce 3-D screen plots of molecules which may be rotated in all planes on the screen. As written, the program uses Hercules monochrome graphics.

This program is handy for checking input coordinates for molecular orbital calculations. It requires the following input format to be placed in an ASCII disk file for each molecule.

A title line, up to 80 characters
# of atoms in structure, # of bonds in structure
X, Y, Z coordinates of atoms (separated by space(s))
There is one XYZ coordinate line for each atom
# of atom 1 of bond 1, # of atom 2 of bond 1 (separated by a comma)
There is one line of the above type for each bond
Atom numbers for bonds refer to the input order of the coordinates.

Control keys for use while viewing a structure are described below.
The right and left cursor keys control rotation about the Y-axis
The up and down cursor keys control rotation about the X-axis
Function keys 1 and 2 control rotation about the Z-axis
Function key 3 sets the zoom factor; the larger the number, the larger the molecule will be shown. The zoom factor is always relative to the initial size that appears when the program starts.
Function key 4 "centers" the molecule in the screen by rescaling the screen to reveal parts of the molecule that may have been cut off during rotation.
Function key 5 resets the rotation angle increment. The initial value is .1 radian.
Function key 6 creates a new disk file in MOLVIEW format with the current coordinates as seen on the screen.
Function key 7 displays a directory of the disk path specified in response.
'to a prompt.
'Function key 9 displays the assignment of the control keys as described here.
'Function key 10 exits the program.
'NOTE: The statement below sets the stack space to 10000. Due to the
'limits of stack space, there is a limited number of moves allowed in a
'particular run when in the Quickbasic environment.

'SET STACK SPACE
CLEAR , , 10000
CLS
MAXX = -100000: MAXY = -100000: MAXZ = -100000
MINX = 100000: MINY = 100000: MINZ = 100000
FOR I = 1 TO 14: KEY(I) ON: NEXT I
INPUT "INPUT PATH AND FILENAME FOR DATA FILE "; PFN$
OPEN "I", #1, PFN$
LINE INPUT #1, TITLE$
INPUT #1, NATOM, NBONDS
DIM X(NATOM), Y(NATOM), Z(NATOM), BONDS(NBONDS, NBONDS)
DIM XP(NATOM), YP(NATOM), ZP(NATOM)
'ROTATION ANGLE INCREMENT (RADIANS)
THETAINC = .1
FOR I = 1 TO NATOM
INPUT #1, X(I), Y(I), Z(I)
IF X(I) > MAXX THEN MAXX = X(I)
IF X(I) < MINX THEN MINX = X(I)
IF Y(I) > MAXY THEN MAXY = Y(I)
IF Y(I) < MINY THEN MINY = Y(I)
IF Z(I) > MAXZ THEN MAXZ = Y(I)
IF Z(I) < MINZ THEN MINZ = Y(I)
NEXT I
FOR I = 1 TO NBONDS
INPUT #1, BONDS(I, 1), BONDS(I, 2)
NEXT I
CLOSE #1
SCREEN 3
'THE .707 AND 1.293 MULTIPLICATION FACTORS SET THE
'PROPER ASPECT RATIO FOR THE HERCULES MONOCHROME SCREEN.
XRANGE = MAXX - MINX
YRANGE = MAXY - MINS
IF XRANGE > YRANGE THEN
    LEFT = MINX - 10
    RIGHT = MAXX + 10
    BOTTOM = (MINY - 10)
    TOP = .707 * (MINY + 20 + XRANGE)
ELSE
    BOTTOM = (MINY - 10)
    TOP = (MAXY + 10)
    LEFT = MINX - 10
    RIGHT = 1.293 * (MINX + 20 + YRANGE)
END IF
ZOOMFAC = 1
WINDOW (ZOOMFAC * LEFT, ZOOMFAC * TOP)-(ZOOMFAC * RIGHT, ZOOMFAC * BOTTOM)
MAIN:
IF TITCMT = 0 THEN PRINT TITLE
FOR C = 1 TO NATOM
    CIRCLE (X(C), Y(C)), .1
    PAINT (X(C), Y(C))
NEXT C
FOR C = 1 TO NBONDS
    LINE (X(BONDS(C, 1)), Y(BONDS(C, 1)))-(X(BONDS(C, 2)), Y(BONDS(C, 2)))
NEXT C
'KEY TRAPS
ON KEY(11) GOSUB YZB
ON KEY(14) GOSUB YZF
ON KEY(12) GOSUB XZCO
ON KEY(13) GOSUB XZCL
ON KEY(1) GOSUB XYCO
ON KEY(2) GOSUB XYCL
ON KEY(10) GOSUB QUIT
ON KEY(3) GOSUB ZOOM
ON KEY(4) GOSUB CENTER
ON KEY(5) GOSUB ANGLEINC
ON KEY(9) GOSUB HELP
ON KEY(6) GOSUB OUTFILE
ON KEY(7) GOSUB DIRECTORY
ON KEY(8) GOSUB FUTURE
GOTO MAIN
END

FUTURE:
'THIS IS A DUMMY SUBROUTINE TO TAKE THE PLACE OF ROUTINES TO BE ADDED.
'IT IS NECESSARY IN ORDER TO PREVENT COMPUTER LOCK-UP DUE TO PRESSING
'UNASSIGNED KEYS
KEY(8) ON
RETURN MAIN

XZCO:
'ROTATION IN THE XZ PLANE COUNTERCLOCKWISE
THETA = -THETAINC
FOR B = 1 TO NATOM
XP(B) = X(B) * COS(THETA) - Z(B) * SIN(THETA)
ZP(B) = Z(B) * COS(THETA) + X(B) * SIN(THETA)
YP(B) = Y(B)
NEXT B
FOR J = 1 TO NATOM
X(J) = XP(J); Y(J) = YP(J); Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(12) ON
RETURN MAIN

XZCL:
'ROTATION IN THE XZ PLANE CLOCKWISE
THETA = THETAINC
FOR B = 1 TO NATOM
    XP(B) = X(B) * COS(THETA) - Z(B) * SIN(THETA)
    ZP(B) = Z(B) * COS(THETA) + X(B) * SIN(THETA)
    YP(B) = Y(B)
NEXT B
FOR J = 1 TO NATOM
    X(J) = XP(J): Y(J) = YP(J): Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(13) ON
RETURN MAIN

YZF:
'ROTATION IN THE YZ PLANE (FORWARD)
THETA = THETAINC
FOR B = 1 TO NATOM
YP(B) = Y(B) * COS(THETA) - Z(B) * SIN(THETA)
ZP(B) = Z(B) * COS(THETA) + Y(B) * SIN(THETA)
XP(B) = X(B)
NEXT B
FOR J = 1 TO NATOM
X(J) = XP(J): Y(J) = YP(J): Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(14) ON
RETURN MAIN

YZB:
'ROTATION IN THE YZ PLANE (BACKWARDS)
THETA = -THETAINC
FOR B = 1 TO NATOM
YP(B) = Y(B) * COS(THETA) - Z(B) * SIN(THETA)
ZP(B) = Z(B) * COS(THETA) + Y(B) * SIN(THETA)
XP(B) = X(B)
NEXT B
FOR J = 1 TO NATOM
X(J) = XP(J): Y(J) = YP(J): Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(11) ON
RETURN MAIN
XYCO:
'ROTATION IN XY PLANE (COUNTERCLOCKWISE)
THETA = THETAINC
FOR B = 1 TO NATOM
XP(B) = X(B) * COS(THETA) - Y(B) * SIN(THETA)
YP(B) = Y(B) * COS(THETA) + X(B) * SIN(THETA)
ZP(B) = Z(B)
NEXT B
FOR J = 1 TO NATOM
X(J) = XP(J): Y(J) = YP(J): Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(1) ON
RETURN MAIN

XYCL:
'ROTATION IN XY PLANE (CLOCKWISE)
THETA = -THETAINC
FOR B = 1 TO NATOM
XP(B) = X(B) * COS(THETA) - Y(B) * SIN(THETA)
YP(B) = Y(B) * COS(THETA) + X(B) * SIN(THETA)
ZP(B) = Z(B)
NEXT B
FOR J = 1 TO NATOM
X(J) = XP(J): Y(J) = YP(J): Z(J) = ZP(J)
NEXT J
THETA = 0
CLS
TITCNT = 0
KEY(2) ON
RETURN MAIN

ZOOM:
CLS
INPUT "NEW ZOOM FACTOR "; ZOOMFAC
ZOOMFAC = 1 / ZOOMFAC
WINDOW (ZOOMFAC * LEFT, ZOOMFAC * TOP)-(ZOOMFAC * RIGHT, ZOOMFAC * BOTTOM)
CLS
TITCNT = 0
KEY(3) ON
RETURN MAIN

CENTER:
CLS
TITCNT = 0
FOR I = 1 TO NATOM
   IF X(I) > MAXX THEN MAXX = X(I)
   IF X(I) < MINX THEN MINX = X(I)
   IF Y(I) > MAXY THEN MAXY = Y(I)
   IF Y(I) < MINY THEN MINY = Y(I)
   IF Z(I) > MAXZ THEN MAXZ = Y(I)
   IF Z(I) < MINZ THEN MINZ = Y(I)
NEXT I
XRANGE = MAXX - MINX
YRANGE = MAXY - MINY
IF XRANGE > YRANGE THEN
    LEFT = MINX - 10
    RIGHT = MAXX + 10
    BOTTOM = (MINY - 10)
    TOP = .707 * (MINY + 20 + XRANGE)
ELSE
    BOTTOM = (MINY - 10)
    TOP = (MAXY + 10)
    LEFT = MINX - 10
    RIGHT = 1.293 * (MINX + 20 + YRANGE)
END IF
WINDOW (ZOOMFAC * LEFT, ZOOMFAC * TOP)-(ZOOMFAC * RIGHT, ZOOMFAC * BOTTOM)
KEY(4) ON
RETURN MAIN

ANGLEINC:
CLS
INPUT "INPUT NEW ANGLE INCREMENT "; THETAINC
CLS
THETACNT = 0
KEY(5) ON
RETURN MAIN

HELP:
CLS
PRINT "
PRINT CHR$(201);
FOR K = 1 TO 39
PRINT CHR$(205);
NEXT K
PRINT CHR$(187)
PRINT SPC(16); CHR$(186); " FUNCTION KEYS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F1 ROTATE C.C.W. ABOUT Z AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F2 ROTATE CLOCKWISE ABOUT Z AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F3 RESET ZOOM FACTOR " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F4 CENTER MOLECULE IN SCREEN " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F5 RESET ANGLE ROTATION INCREMENT " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F6 MAKE DISK FILE WITH CURRENT COORDS. " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F7 VIEW DISK DIRECTORY " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F8 " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F9 HELP " ; CHR$(186)
PRINT SPC(16); CHR$(186); " F10 EXIT MOLVIEW " ; CHR$(186)
PRINT SPC(16); CHR$(186); " " ; CHR$(186)
PRINT SPC(16); CHR$(186); " CURSOR KEYS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " RIGHT ARROW ROTATE ABOUT Y AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " LEFT ARROW ROTATE ABOUT Y AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " UP ARROW ROTATE ABOUT X AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(186); " DOWN ARROW ROTATE ABOUT X AXIS " ; CHR$(186)
PRINT SPC(16); CHR$(200);
FOR K = 1 TO 39
PRINT CHR$(205);
NEXT K
PRINT CHR$(188)
TITCNT = 0
KEY(9) ON
INPUT " HIT RETURN TO CONTINUE ", ES$
OUTFILE:
'THIS WILL CREATE A DISK FILE WITH THE CURRENT COORDINATES
CLS
INPUT "PATH AND NAME OF OUTPUT FILE "; FIL$
OPEN "0", #2, FIL$
PRINT #2, TITLE$
PRINT #2, NATOM, NBONDS
FOR J = 1 TO NATOM
PRINT #2, USING "###.#####"; X(J), Y(J), Z(J)
NEXT J
FOR I = 1 TO NBONDS
PRINT #2, BONDS(I, 1), BONDS(I, 2)
NEXT I
CLOSE #2
TITCNT = 0
KEY(6) ON
CLS : RETURN MAIN

DIRECTORY:
CLS
PRINT
INPUT "PATH FOR DIRECTORY "; PATH$
FILES PATH$
PRINT
INPUT "HIT RETURN TO CONTINUE ", DUMMY$
TITCNT = 0
KEY(7) ON
CLS : RETURN MAIN

QUIT:
PRINT " GOODBYE"

END
MOLECULE PLOTTER
A PROGRAM TO PLOT MOLECULE VIEWER FILES ON THE HP PLOTTER
BY STEVEN E. ARNOLD

CLS
MAXX = -100000: MAXY = -100000: MAXZ = -100000
MINX = 100000: MINY = 100000: MINZ = 100000
INPUT "INPUT PATH AND FILENAME FOR DATA FILE "; PFN$
OPEN "I", #1, PFN$
LINE INPUT #1, TITLE$
INPUT #1, NATOM, NBONDS
DIM X(NATOM), Y(NATOM), Z(NATOM), BONDS(NBONDS, NBONDS)
FOR I = 1 TO NATOM
  INPUT #1, X(I), Y(I), Z(I)
  X(I) = X(I) * 1000
  Y(I) = Y(I) * 1000
  Z(I) = Z(I) * 1000
  IF X(I) > MAXX THEN MAXX = X(I)
  IF X(I) < MINX THEN MINX = X(I)
  IF Y(I) > MAXY THEN MAXY = Y(I)
  IF Y(I) < MINY THEN MINY = Y(I)
  IF Z(I) > MAXZ THEN MAXZ = Z(I)
  IF Z(I) < MINZ THEN MINZ = Z(I)
XRANGE = MAXX - MINX
YRANGE = MAXY - MINY
IF XRANGE > YRANGE THEN
'MAKE MINIMUM BOUNDARY AROUND MOLECULE 7% OF WINDOW LENGTH
BOUND = .07 * XRANGE
'MAKE RADIUS OF ATOM CIRCLES .9% OF WINDOW LENGTH
RADIUS = .009 * XRANGE
MAXX PLOT = MAXX + BOUND
MINX PLOT = MINX - BOUND
MINY PLOT = MINY - BOUND
MAXY PLOT = MINY PLOT + XRANGE + 2 * BOUND
ELSE
BOUND = .07 * YRANGE
RADIUS = .009 * YRANGE
MAXX PLOT = MAXY + BOUND
MINX PLOT = MINY - BOUND
MINY PLOT = MINX - BOUND
MAXY PLOT = MINX PLOT + YRANGE + 2 * BOUND
ENDIF
MINX PLOT = INT(MINX PLOT)
MAXX PLOT = INT(MAXX PLOT)
MINY PLOT = INT(MINY PLOT)
MAXY PLOT = INT(MAXY PLOT)
NEXT I
FOR I = 1 TO NBONDS
INPUT #1, BONDS(I, 1), BONDS(I, 2)
NEXT I
CLOSE #1
INPUT "PRIME PEN AND HIT RETURN TO PLOT ", DUM$
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FOR D = 1 TO 1000: NEXT D
'INITIALIZE PLOTTER, SELECT PEN AND SET PI AND P2 TO A SQUARE AREA
PRINT #1, "IN;"
'DELAY TO ALLOW PLOTTER TO INITIALIZE
FOR D = 1 TO 1000: NEXT D
PRINT tl, "SPl;IP500,500,4200,4200"
'SET ENQUIRE/ACKNOWLEDGE HANDSHAKE
PRINT #1, CHR$(27); ".H128;18;49:"
PRINT #1, CHR$(27); " .M500;63 ;0; 13 :" ; CHR$(27); ".N5:"

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'SET PEN VELOCITY TO 10 cm/S
GOSUB ENQ
PRINT #1, "VSIO;"
GOSUB ENQ
PRINT /I, "SC";

MINXPLOT; MAXXPLOT; MINYPLOT; MAXYPLOT;

'DRAW BOX FOR DATA AREA
GOSUB ENQ
'NEXT TWO LINES ARE ONE STATEMENT
PRINT /I, "PU"; MINXPLOT; MINYPLOT; "PD"; MAXXPLOT; MINYPLOT; MAXXPLOT;
MAXYPLOT; MINXPLOT; MAXYPLOT;MINXPLOT; MINYPLOT; "PU;"
'CIRCLE ATOMS
FOR I = 1 TO NATOM
GOSUB ENQCIRC
'PRINT #1, "PA"; X(I); Y(I); ";"; "CI100,10;"
PRINT #1, "PA"; X(I); Y(I); ";"; "Cl"; RADIUS; ",10;"
NEXT I
w
o
ÜI


'DRAW BONDS
FOR I = 1 TO NBONDS
GOSUB ENQ
'NEXT TWO LINES ARE ONE STATEMENT
PRINT #1, "PA"; X(BONDS(I, 1)); Y(BONDS(I, 1)); "PD"; "PA"; X(BONDS(I, 2)); 
Y(BONDS(I, 2)); ";"; "PU";
NEXT I

END

ENQCIRC:
'SEND ENQUIRE CHARACTER AND WAIT FOR ACKNOWLEDGE DURING CIRCLE DRAWING
FOR D = 1 TO 20000: NEXT D
PRINT #1, CHR$(18);
PRINT #1, "?": INPUT #1, Z
RETURN

ENQ:
'SEND ENQUIRE CHARACTER AND WAIT FOR ACKNOWLEDGE
FOR D = 1 TO 8000: NEXT D
PRINT #1, CHR$(18);
PRINT #1, "?": INPUT #1, Z
RETURN
VITA

Steven Eugene Arnold was born on October 4, 1962 on Torrejón Air Base, Torrejón de Ardoz, Spain. He attended Newellton High School, Newellton, Louisiana, and graduated in 1980.

He entered Louisiana State University in 1980 and received his B.S. in chemistry in 1985. He then entered the graduate school of Louisiana State University.

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Title of Dissertation: The Effect of Structure and Geometry on the Spectroscopy of Beta-Diketones

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