case, the quite different g_v values at 2537 Å compared to the 4358 and 3660 Å g_v values can be interpreted to be reflections of quite different n_v values and hence the fractional partitioning of excess energy into the methylene vibrational modes is significantly different for the excited electronic state of diazomethane produced by 2537 Å photon absorption than for the state produced by 4358 and 3660 Å photon absorption. The possibility of significantly greater collisional relaxation of CH_2 produced in the 2537 Å photolyses compared to the 3660 and 4358 Å photolyses cannot be eliminated and would provide an alternate interpretation. Hopefully, systematic studies with added inert gases, which are known to remove excess energy from $CH_2(^1A_1)$,[21] will aid in establishing the relationship between the g_v values and n_v values for a particular system.

As a note of caution, it is emphasized that if the value of $\Delta H_f[CH_2(^1A_1)]$ turns out to be as high as 112.5 kcal/mol, as discussed earlier, the quantitative aspects of this work will be altered but the qualitative features of broadened $CH_2(^1A_1)$ vibrational energy distributions with increased photon energies will remain unchanged.

References and Notes

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Conformational Analysis. 128. The Woodward–Fieser Rules and α,β-Unsaturated Ketones[1,2]

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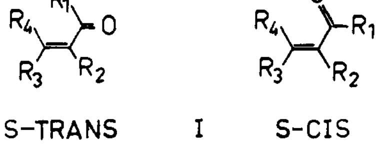
Abstract: The ultraviolet spectra of a series of alkylated α,β-unsaturated ketones have been calculated using the VESCF method. In particular, nonplanar systems have been examined. The applicability of the Woodward–Fieser rules to such systems has also been examined. According to theory, these rules work as well as they do because of some fortuitous cancellations. A reformulation of the rules increases their general applicability for planar systems. For nonplanar systems the situation is complex. There are two transitions at relatively long wavelengths that must be considered. Both of these vary both in wavelength and in oscillator strength as a function of the dihedral angle about the central bond. These variations are highly dependent on the particular pattern of the alkylation. Generalized predictions about the electronic spectra of these compounds are made.

Conformational effects on the longest wavelength $\pi \rightarrow \pi^*$ band[4] in the ultraviolet spectra of α,β-unsaturated ketones are most often discussed in terms of intensity changes.[5] Effects on the position of the absorption maxima are usually assumed to be small. The Woodward–Fieser rules,[6,7] which have been widely used for predicting the position of the longest wavelength $\pi \rightarrow \pi^*$ band of α,β-unsaturated ketones, are well established and have been very successful in correlations between electronic transitions and structures of these compounds. These empirical rules do not take into account any difference in the electronic absorption between s-trans and s-cis forms of the conjugated system. From extensive studies on substituted molecules, the difference in the wavelength of absorption between a cis and a trans diene is well known experimentally and understood theoretically. The main reason for the difference can be traced to the difference in the 1,4 two-electron repulsion integral, which is considerably larger in the cis conformation than in the trans, due simply to the difference in distance between centers in the two cases.[8] It is qualitatively obvious that the same will hold true for an α,β-unsaturated ketone. Thus calculations on different levels of sophistication consistently predict the s-cis conformation to absorb at longer wavelength than the s-trans conformation, the difference in energy being



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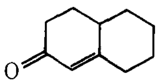
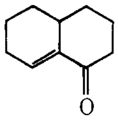
0.3-0.4 eV[9-12] (corresponding to 10-20 nm in the wavelength interval 200-250 nm, where most of these compounds have absorption maxima in ethanol). Comparison with experimental data must be indirect as the barrier between the two forms in acyclic compounds is too low[11] to allow a study of the individual conformers. But how, then, does one explain the following observation from the steroid field?[6,7]



s-trans λ_{max} 241 nm EtOH



s-cis λ_{max} 241 nm EtOH

In cyclic compounds ring-strain effects may complicate the picture. Bienvenüe,[13] in an attempt to correlate observed transition energies with relative concentrations as obtained from IR measurements, arrived at the s-cis/s-trans absorption-energy difference as 2400 cm^{-1} (0.30 eV), in good agreement with calculations. In a recent paper on electronic spectra of β-alkoxy-α,β-unsaturated ketones, Dabrowski and Tencer[14] suggest 8 nm as a correction for the conformational change s-trans → s-cis. These authors also proposed that the apparent conformational independence of the Woodward-Fieser[6,7] rules for the corresponding alkyl-substituted compounds may be accounted for by a compensation of the conformational effect by a solvent effect, the solvation being different for s-cis and s-trans conformations. Available experimental data on 3-buten-2-one and its methyl derivatives, however, do not support this proposal. The bathochromic shifts in 3-buten-2-one (s-trans[11]) and mesityl oxide (twisted s-cis[11]) from vapor phase to ethanol solution are 15 and 15.5 nm,[15] respectively. For the compounds studied by Cottee et al.[16] there is no significant difference in solvation for s-cis and s-trans compounds, comparing spectra in hexane and ethanol solutions.

We have previously calculated the structures and relative energies of the conformations of α,β-unsaturated carbonyl compounds.[11] Using these structures as a starting point, we wish to discuss in this paper the results of conformational effects on the position of longest wavelength $\pi\rightarrow\pi^*$ band in α,β-unsaturated ketones, especially with reference to predictions made by the Fieser-Woodward rules. We particularly want to ask why the rules work as well as they do when they ignore conformational effects, which theory says are important.

Method

All the geometries of compounds studied in this paper were calculated by a molecular mechanics method designed for conjugated systems.[11,17] Electronic transitions were calculated by the VESCF-Cl method,[11,12] including all singly and doubly excited electronic configurations. Corrections for ethanol solution were made by subtracting 0.40 eV from the calculated transition energies.[11]

Results and Discussion

Acyclic α,β-Unsaturated Ketones. In the present work we have carried out the calculations for α,β-unsaturated ketones containing different patterns of substitution as a function of dihedral angle. The predicted absorptions for the first two transitions are shown in Figure 1. Figure 1a is unexceptional, and shows what happens with 3-buten-2-one itself. The first transition shows a greater oscillator strength in the trans conformation than in the cis, which goes to zero at 90 °C. This absorption occurs at a longer wavelength for the cis than for the trans, while nonplanar systems absorb at shorter wavelengths than their planar counterparts. For the second transition a similar curve is seen, but the oscillator strengths are small for the planar conformations and large at 90 °C.

The shape of the curve for the first transition as a function of the substitution is of interest. Beginning with the trans conformation of the parent butenone (Figure 1a), the slope of the curve is not very great. Thus small deviations from planarity do not shift the maximum very much. On the cis side, the slope is greater, and deviations from planarity make correspondingly larger shifts.

When we look at the methylated butenones, we see that the curve for the first transition becomes more shallow with increasing substitution (for example, Figure 1e), and finally the minimum disappears completely (for example, Figure 1d). With compounds such as these, the wavelength of the absorption of the trans conformer is indeed insensitive to torsional angle. The separation between the two transitions in terms of wavelength may be small or large, depending on the torsional angle (in Figure 1d, for example, only 13 nm for the trans conformation, but about 50 nm at 90 °C). Since the extinction coefficients vary with this torsional angle, and the separation between the bands also varies, one may see either a single band which is unresolved, or two separate bands.

Experimental data and predictions using Fieser's rules for the longest wavelength $\pi\rightarrow\pi^*$ band in 3-buten-2-one and its methyl derivatives are given in Table I. Table I also includes the dihedral angle (ω) of the calculated lowest energy conformation of each compound. (ω = 0° and 180° for a planar s-cis and s-trans conformation, respectively). Comparing experimental values and empirical predictions for the calculated conformations, a significant difference in the ability of Fieser's rules to predict the absorption maxima of s-trans and (twisted) s-cis compounds is clearly seen (calcd I, Table I). The difference between calculation and experiment was 6-9 nm in the former case and 1-5 nm in the latter. We interpret this result as a consequence of the neglect of conformational effects in the rules suggested by Fieser. It is, however, of interest to note that the error introduced by this neglect is significantly smaller than the 10-20 nm that might have been expected from theoretical studies. In Figure 1a is shown the calculated (VESCF-Cl) dependence of the longest wavelength $\pi\rightarrow\pi^*$ transition on the dihedral angle ω for 3-buten-2-one, Fieser's "parent" compound. Our calculated difference in absorption maximum between s-cis and s-trans forms is 15 nm (0.39 eV), in accord with earlier theoretical calculations. The "parent" value used by Fieser, 215 nm, is seen to correspond to a twisted ($\omega \approx 20°$) s-cis conformation and not to the lowest energy planar s-trans conformation, for which the experimental number is 208.5-209[15,18] as calculated. It is thus not surprising that the empirical rules give a better prediction for compounds having a s-cis than for those having a s-trans conformation. It is, however, important to note that the difference in the calculated λ_{max} between a 20° twisted s-cis conformation and a planar s-trans conformation is only about half of the difference between *planar* s-cis and s-trans conformations. All s-cis compounds included in Table I have twisted chromophores (ω = 12.9-48.9°). It then follows that the empirical predictions would work, on the average, reasonably well for these compounds as well as for the s-trans compounds which are all planar or close to planar, provided that the "parent" value is adjusted to the experimental number for 3-buten-2-one, 209 nm. The conformational effect would then be averaged out, the difference between experiment and calculations now being within 5 nm for all compounds. A still better agreement (average deviation from experiment ±1.8 nm) may be obtained if different parent values for s-cis and s-trans, 215 and 209 nm, respectively, are used. (For α,β-unsaturated aldehydes the experimental λ_{max} for acrolein, 207 nm, is used as the parent value.[19] In this case there is no problem with the conforma-

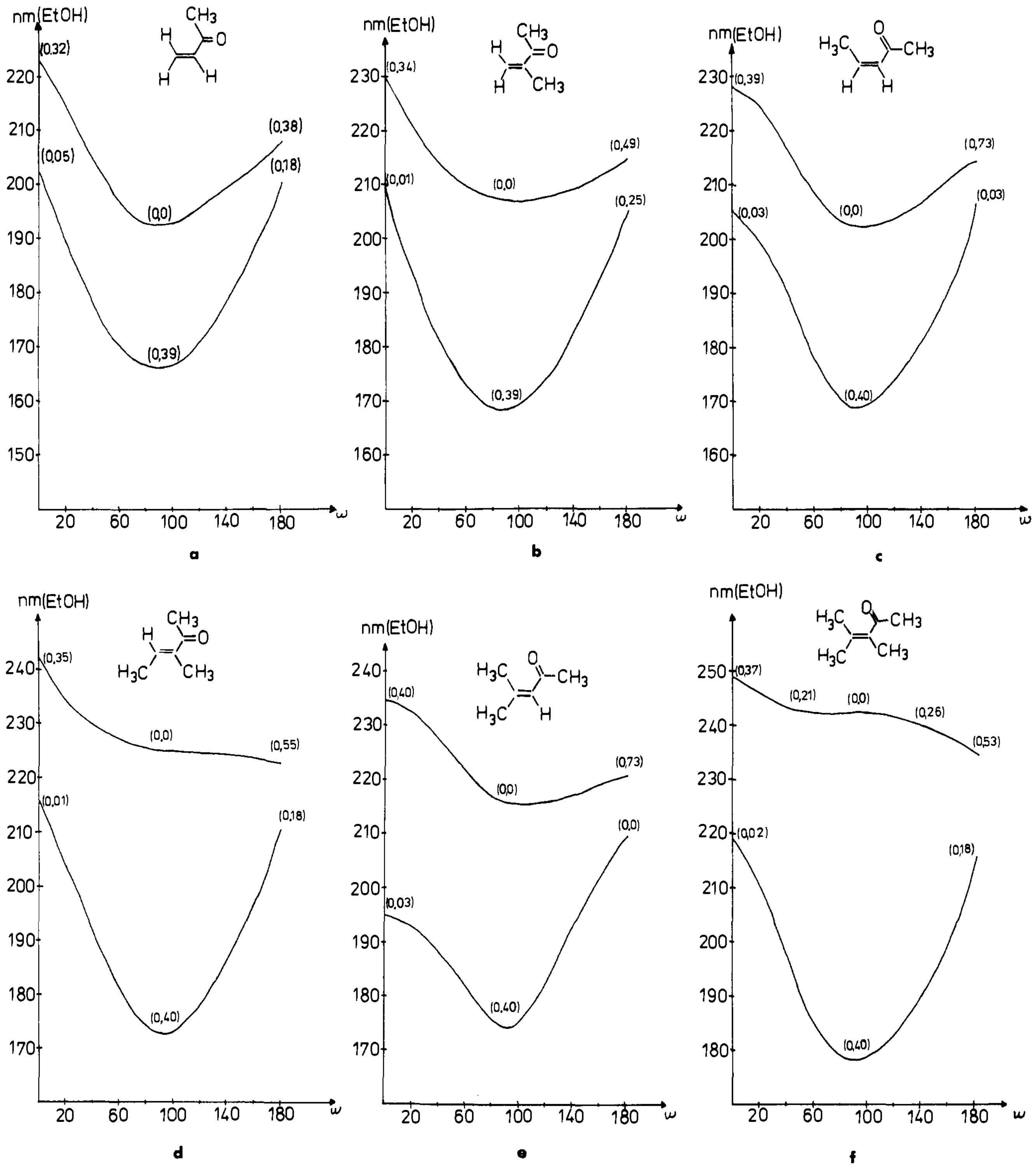


Figure 1. The two $\pi \rightarrow \pi^*$ transitions of lowest energy calculated for various substitution patterns of α,β-unsaturated ketones as indicated on the individual figures.

tional effect, acrolein and all its methyl-substituted derivatives being *planar* s-trans.[11])

Cyclic Compounds. The most important application of Fieser's rules has been in correlations between the structures and spectra of steroids. Since the success of the rules depends on averaging out conformational effects between *twisted* s-cis conformers and *planar* s-trans conformers, we have calculated the geometries of various bi- and tricyclics being "parent" structures of steroid systems (Chart I).

These compounds show the same conformational behavior as the derivatives of 3-buten-2-one. The s-trans compounds are all close to planar, while the s-cis compounds are significantly twisted. In the former case this is also shown in x-ray structures of the corresponding steroids.[20] To our knowledge there are no experimental structures on compounds similar to the s-cis compounds shown in Chart I.

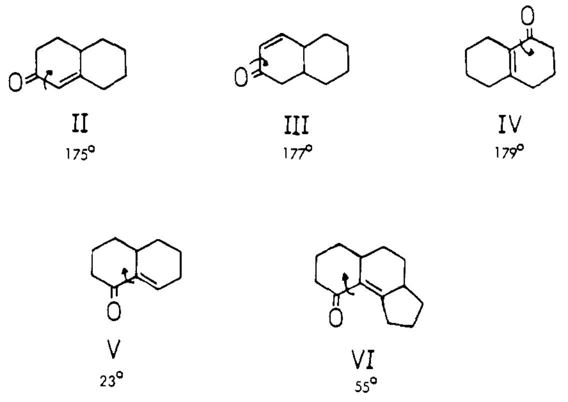
It is interesting to note that of the five structures shown in Chart I, all have different values for ω than those of their corresponding acyclic α,β-unsaturated ketones (Chart II). Also, comparing the longest wavelength $\pi \rightarrow \pi^*$ UV band for acyclic and cyclic compounds, it is clear there is no significant difference in the first three cases shown in Chart I. This means that the effect of the conformational change, twisted s-cis → planar s-trans, which we have shown above to be about 6 nm,

Table I. Calculated (by the Fieser-Woodward Rules) and Experimental Longest Wavelength $\pi \rightarrow \pi^*$ UV Bands and Lowest Energy Conformations for α,β-Unsaturated Ketones

Compd	R_1	R_2	R_3	R_4	ω^0 [a]	Exptl, nm (EtOH)	Ref	Calcd I,[b] nm	Calcd II,[c] nm	Calcd III,[d] nm
Ia	Me	H	H	H	180.0	209	15, 18	215	209	208
Ib	Me	Me	H	H	180.0	217.8	16	225	219	214
Ic	Me	H	Me	H	180.0	220	18, 26	227	221	215
Id	Me	H	H	Me	12.9	226	11, 13	227	227	227
Ie	Me	Me	Me	H	177.6	228	16	237	231	222
If	Me	Me	H	Me	34.8	235.5	27	237	237	233[e]
Ig	Me	H	Me	Me	18.8	237	16	239	239	233
Ih	Me	Me	Me	Me	48.9	244.5	16	249	249	243[f]
					Average deviation from experiment			±4.8	±1.8	±3.4

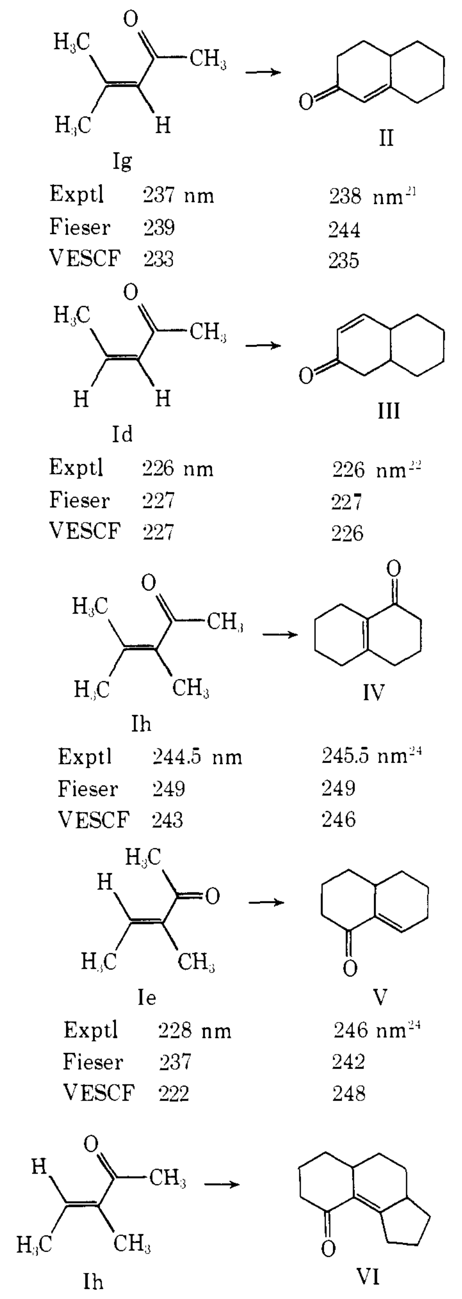
[a] Reference 11. [b] According to Fieser's rules, using 215 nm as "parent" value. [c] Using Fieser's rules, but allowing for the conformational effect by using 215 and 209 nm as the parent values for s-cis and s-trans, respectively. [d] VESCF calculation (ref 11). [e] A second transition is also predicted: λ_{max} 200 nm, ε 800. [f] A second transition is also predicted: λ_{max} 191 nm, ε 1800.

Chart I[a]



[a]The angles shown are the C=C–C=O dihedral angles.

Chart II



	Ig	II
Exptl	237 nm	238 nm^{21}
Fieser	239	244
VESCF	233	235

	Id	III
Exptl	226 nm	226 nm^{22}
Fieser	227	227
VESCF	227	226

	Ih	IV
Exptl	244.5 nm	245.5 nm^{24}
Fieser	249	249
VESCF	243	246

	Ie	V
Exptl	228 nm	246 nm^{24}
Fieser	237	242
VESCF	222	248

	Ih	VI
Exptl	244.5 nm	260–263 nm in steroids^{25}
Fieser	249	259
VESCF	243	256

is approximately compensated by the effect of ring closure. This "ring closure effect" does not come from the theory of the spectra as calculated from the π system alone. The geometric effect of distorting bond angles and bond lengths by ring closures seems too small to account for it. We can only speculate that this is a result of changes which occur in the σ system upon ring closure, which of course are not evident in a π system calculation. Whatever the nature of this "ring closure effect", it appears to result from cyclization of unsaturated ketone. It does not seem to be related to the exocyclic nature of the double band, as in the Fieser-Woodward rules. The necessary choice of 215 nm as "parent" value for cyclic compounds by Fieser was thus a consequence of a twisted s-cis conformation in the acyclic ketone and close compensation of the conformational effect by a ring closure effect. The acyclic ketone Ih, corresponding to the s-cis compound VI, is also s-cis. This means that the ring closure effect cannot be compensated for. Compounds Ih and VI consequently do not have similar λ_{max} (Chart II). Instead Fieser used "increments for exocyclic double bonds" (in VI equal to 10 nm) to account for the ring closure effect not averaged out by a conformational effect. Compound II also has an exocyclic double bond, but it is clear that increment is not necessary in this case (it is included, according to Fieser's rules, in the number given in Chart II). The predicted λ_{max} would be 239 nm without any exocyclic increment, in better agreement with experiment. We believe that the exocyclic increment given by Fieser should be interpreted as a ring closure effect not compensated by a conformational change.

The sequence Ie → V involves an s-trans → twisted s-cis change. Since s-cis absorbs at longer wavelengths than s-trans and the ring closure gives a bathochromic shift, the difference in λ_{max} between Ie and V, 18 nm, should be equal to $\Delta\lambda$(twisted s-cis → s-trans) + the ring closure effect. The first term here is 6 nm (Table I), so the ring closure effect is evidently about

+12 nm in this example. Since Fieser uses the twisted s-cis conformation as "parent" conformation the first term is taken care of (the λ_{max} of the acyclic s-trans ketone Ie is overestimated by 9 nm (Table I)). The remaining difference between experiment and prediction is then (partly) accounted for by Fieser with a +5 nm "increment for exocyclic double" which, according to the discussion above, approximately equals the effect of ring closure.

Also shown in Table I and in Chart II are the values for λ_{max} as determined by the VESCF calculation method. The molecular mechanics geometries were obtained, and the spectra calculated as usual. If the double bond was in a ring, a "ring closure increment" of +12 nm was also added. These results are calcd III in Table I.

Conclusions

The apparent conformational independence of the longest wavelength UV band of α,β-unsaturated ketones has been analyzed. For acyclic compounds the conformational effect is clearly seen when the original "parent" value of Fieser, 215 nm, is used. Since this value actually corresponds to a twisted s-cis conformation and since the lowest energy conformation of s-cis compounds is invariably significantly twisted, the conformational effect is reduced to about half the expected. This remaining conformational effect was largely averaged out for acyclic compounds by adjustment of the "parent" value. For cyclic compounds the conformational effect was partly compensated for by a ring closure effect in those cases where an acyclic twisted s-cis compound corresponds to a cyclic s-trans compound. If this was not the case, the empirical scheme constructed by Fieser separately accounted for the ring closure effect by additional increments.

There is no doubt that the empirical Fieser-Woodward rules have been highly useful for the prediction of the ultraviolet spectra of α,β-unsaturated ketones. They are empirical rules, which is to say, they give good predictions. The application of theory as is now available indicates that these rules can be put on a theoretically sounder basis by small changes in the calculations of the increments. The original rules were quite accurate in the steroid field. The new rules should be about equally accurate there, and will be much more broadly applicable to compounds where the original rules gave relatively poor predictions.

New Rules for the Prediction of Ultraviolet Spectra for α,β-Unsaturated Carbonyl Compounds. For an alkylated α,β-unsaturated ketone which is planar or moderately twisted, be it cyclic, acyclic, s-cis, or s-trans, the absorption wavelength can be estimated using the following rules.

Simplified Scheme. A parent value of 209 nm is used for s-trans, and 215 nm is used for s-cis. Shifts for alkyl substitutions are counted as usual; for an α substitution add 10 nm, for a β substitution 12 nm.

If the double bond is endocyclic in a six-membered ring, a ring closure correction of +7 nm is added.

The above values are appropriate for ethanol solution. For the gas phase, one needs to add 0.40 eV to the transition energy in ethanol. Corrections to other solvents can be made according to Fieser. We have not examined dienones, and are uncertain what modifications might be desirable with those. Note that the "exocyclic" double bond increment of Fieser is not included in the above.

This new scheme works very nicely. The average deviation from experiment for acyclic compounds (Ia-h) is ±1.8 nm (calcd II, Table I) and for cyclic compounds (II-VI) ±3 nm.

While the above rules will be useful for the laboratory worker, a more thorough exposition of the calculation of the ultraviolet spectrum for such compounds is outlined below. This more complicated procedure will also permit one to make estimations regarding the second transition which is often seen in CD and ORD spectra. It is in addition applicable to most acyclic nonplanar systems. For cyclic systems, or perhaps a few peculiarly strained acyclic ones, it may be necessary to carry out the full scale calculations. Such systems as are not simply twisted about the formally single bond will generally be too deformed for the scheme below to apply. Ordinary nonplanar acyclic systems can be treated in more detail as discussed below.

Looking only at the two longest wavelength $\pi \rightarrow \pi^*$ transitions, the longer wavelength one is strongly allowed for near-planar systems, and the second one forbidden. These allowedness relationships are interchanged as the dihedral angle between the chromophores goes to 90°. For systems between planar and 90°, one needs to examine both the transitions.

For systems which are seriously nonplanar, one cannot really use additive alkyl "increments" to predict spectra. The difficulty here can best be seen in this way. If the unsaturated ketone has a dihedral angle of 90° about the central bond, then substitution of an alkyl group on the double bond affects only the two atomic orbitals of the double bond, which are orthogonal to the π orbital of the ketone. But as the torsional angle changes from 90° to some other value, interaction between the two π systems occurs, and hence the effect of the alkyl group is spread around in the molecular orbitals. The effect of the alkyl group is to donate electrons into the p orbital of the atom to which it is attached, which raises the ground state energy of that orbital, and hence of the ground state π energy of the molecule. The presence of the alkyl group causes a red shift of transitions originating from that orbital (particularly the longest wavelength transition). The amount of this red shift is thus a function of the dihedral angle. Hence one cannot have really simple rules with additive increments for alkyl groups for nonplanar systems. The increments would also have to be functions of the dihedral angle.

We have sought an alternative way to express this information. In Figures 1b-f are shown the calculated wavelengths for the two longest wavelength transitions for a series of α,β-unsaturated ketones as a function of the torsional angle about the central bond. For each different pattern of alkylation (α; β; α,β; β,β; α,β,β) a separate graph is shown. The oscillator strength of each of these transitions is shown at 0, 90, and 180°.

Detailed Scheme. To predict the ultraviolet spectrum of an alkylated α,β-unsaturated ketone in general, one proceeds as follows:

(1) The dihedral angle about the central bond must be determined. This can generally be done by molecular mechanics, or with reasonable accuracy in many cases by examination of models or comparison of analogous compounds of known structure.

(2) Having the dihedral angle, the substitution pattern of the alkylation is determined, and the appropriate figure (1b-f) is located. The dihedral angle is read off the chart, and this will correspond to two wavelengths for the first two transitions. The relative intensities of these transitions can be estimated from the oscillator strengths given at the 90° point and at the nearest planar dihedral angle. This gives us, then, the two wavelengths and two oscillator strengths expected for transitions of the compound in question. The oscillator strengths can be converted to approximate extinction coefficients by multiplying by 10 000.

(3) If the molecule is cyclic with the double bond in a ring, an increment of 12 nm should be added for a "ring closure effect". (If the system deviates considerably from planarity, the accuracy of the value is uncertain.)

References and Notes

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(2) This work was supported by Grant AM14042 from the National Institutes of Health.
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Must a Molecule Have a Shape?

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Abstract: The idea of molecular structure is discussed from the point of view of the quantum theory: we show that the modern picture of a molecule as a bound collection of electrons and nuclei is not invariably equivalent to the classical molecular model of atoms joined by bonds, and hence molecular structure is not an intrinsic property. High-resolution gas-phase experiments on "small" molecules in dilute gases and molecular beams are characterized as being concerned with a *novel state of matter distinct from the classical gas* since they probe the *molecular stationary states* which cannot be understood in terms of molecular structures: these experiments thus need to be distinguished from investigations of dense gases and condensed matter (or "large" molecules generally) for which the notion of structure is the key concept that essentially "solves" the macroscopic many-body problem. These ideas can be applied to a wide area of physical chemistry; for example, the kinetic theory of gases, optical activity, "polar" and "nonpolar" gases, high-resolution spectroscopy, and much else.

Introduction

In recent years there has been a growing awareness of the limitations of the conventional Born–Oppenheimer approximation in the analysis of chemical experiments: the inclusion of vibronic interactions is essential for a proper understanding of molecular properties deriving from the excited states of "large" molecules, as may be seen in the modern theory of radiationless transitions.[1] At the same time similar difficulties have been identified in discussions of the reactions and spectroscopy of "small" molecules: according to Faist and Levine,[2] "If a system existed which contained a multitude of curve-crossings, the flow of electronic energy could be essentially unrestricted: in such a situation, one may expect a nearly statistical electronic state product distribution". They cite the alkali dimer–halogen atom reactions

$$M_2 + X \rightarrow MX + X^* \qquad (1)$$

as a class of reactions of this type. Another example is to be found in the analysis of the visible spectrum of NO_2 under high resolution.[3] Several writers have given theoretical discussions of the adiabatic hypothesis and the general features of potential energy surfaces, and have concluded that there must necessarily be regions of nuclear configuration space where the adiabatic hypothesis fails completely.[4-6] The existence of branch-cut singularities in the potential energy surfaces of systems containing more than two atoms, and the related discontinuities in the electronic wave function, known since the work of Teller,[7] have recently been discussed again by Davidson.[6]

The adiabatic separation of electronic and nuclear motion has always been regarded as a sine qua non of (quantum) chemistry, it being understood that due consideration of vibronic perturbations may be needed in order to obtain the correct physical or chemical interpretation of experiments. Textbooks of molecular quantum theory usually suggest that without the Born–Oppenheimer separation of electronic and nuclear motion it would not be possible to perform calculations of the quantum states of molecules, or understand their properties; actually, however, it seems much more likely that the real motivation for the conventional methods of quantum chemistry arises from a powerful "felt need" to make contact with the classical idea of *molecular structure*. This feeling appears to be the main barrier hindering the development of "nonadiabatic" calculational procedures since it seems likely that nonadiabatic computations on small molecules, for example, the hydrides of the first-row elements, in which electrons and nuclei are treated on the *same* footing, are perfectly feasible.[8] Although the accuracy obtainable now is not of spectroscopic quality, we can expect improvements as experience is gained with such calculations.

The quantum theory of molecular structure and the role of the Born–Oppenheimer approximation has been discussed in some detail in the recent literature:[9-15] this paper is a continuation of this discussion in a chemical context, and argues that it will be essential in the future to try to understand an im-

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