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A THEORETICAL STUDY OF THE ELECTRONIC SPECTRA OF SOME α-DIKETONES AND UNSATURATED KETONES[1,2]

L. W. CHOW

Department of Chemistry, Alabama A and M University, Normal, Alabama 35762

N. L. ALLINGER*

Department of Chemistry, University of Georgia, Athens, Georgia 30601

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Abstract—The electronic spectrum of acetophenone has been calculated by a VESCF modification of the Pariser–Parr–Pople method, and also the spectrum for the molecule when the CO group is twisted 30° from the plane of the aromatic ring. It is suggested that the relationship commonly used to predict the extinction coefficient of the lowest energy $\pi \rightarrow \pi^*$ transition for such a system gives values for the angle of twist which are consistently too large. The electronic spectrum of 2,3-butanedione has been calculated as a function of the dihedral angle between the CO groups by the same method. The effect of including in the configuration interaction treatment only singly-excited configurations, singly-excited plus doubly-excited configurations, and singly-excited plus doubly-excited plus triply-excited configurations was investigated. The electronic spectra of some β, γ-unsaturated carbonyl compounds have also been studied.

INTRODUCTION

IN PREVIOUS papers[3-6] we discussed the development of a Variable Electronegativity Self-Consistent Field (VESCF) Method,[7] and its application to the calculation of the electronic spectra of unsaturated hydrocarbons. The method was also extended to unsaturated ketones.[8]

For $\pi \rightarrow \pi^*$ transitions, the calculated values were ordinarily within about 0·3 eV of the experimentally observed quantities, and the oscillator strengths were usually correct to within a factor of 2.

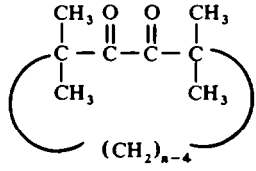
The present work is concerned with extending these calculations to more complicated systems such as acetophenone and 2,3-butanedione, and also to an examination of the usefullness of such calculations for non-planar systems.

The method involves at the outset a separation of the π and σ components of the molecule. The details of the σ part of the molecule are used to assign numerical values to various core integrals, but it is not subsequently explicitly considered. This simplification was quite traditional until the last few years, and it clearly proves to be quite satisfactory for planar systems. For non-planar systems, the adequacy of the method will depend upon the degree of mixing of the σ and π components of the molecule. In principle, such mixing will occur, but whether this mixing will be sufficiently serious as to render invalid the results determined by calculation on the π system alone is not yet clear. There is a fair amount of experimental data available for non-planar systems, and studies on some of these kinds of systems will be described here. Obviously, an approach that would be better in principle would be to use an all-valence

* To whom all inquiries should be addressed.

electron calculation, of which several varieties are now available.[9] Such calculations have so far been applied with a reasonably high degree of success to the calculation of ground state properties of molecules, but spectroscopic calculations utilizing this approach[10] have thus far been quite preliminary compared to what has been done with planar π systems.

A simple chromophore which we first selected for study was the 1,2-dione. Molecules of this type in general tend to be fairly enolic, and the spectrum of the enol is quite intense and interferes with the spectrum of the diketone itself. Leonard and Mader[11] synthesized a series of α-diketones of the type I, and determined their



I

ultraviolet absorption spectra. These compounds cannot enolize, and hence the spectra which they observed are those of the pure diones. By allowing n to assume different values, a series of compounds (I) was generated in which the carbonyl groups were at various angles to one another. The absorption wavelengths of these compounds in the near ultraviolet were found to be severe functions of n, and hence of the dihedral angles between the carbonyls. Leonard and Mader offered the following table to indicate the variation of absorption wavelength with dihedral angle. (The dihedral angles were estimated from models only, there being no direct experimental evidence concerning the actual structures of such compounds.) Their spectra also show the

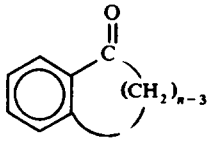
TABLE 1. ELECTRONIC SPECTRA AND ESTIMATED DIHEDRAL ANGLES (θ) BETWEEN CARBONYLS REPORTED FOR COMPOUNDS I

θ	λ_{max} mμ (in ethanol)
0–10°	466[a]
0–60°	380
90–110°	337
100–140°	343
90–180°	365
100–180°	384

[a]This value is that for camphor quinone. The wavelength might be anomalous (unusually high) because of the severe steric constraints on the system.

second transition at about 290 mμ, regardless of the value of the dihedral angle. Similar studies have also been carried out by Alder *et al.*[12]

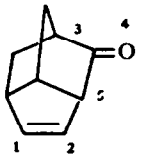
Analogous experimental studies have been carried out with compounds related to acetophenone.[13] The acetophenone molecule itself is planar. However, if the ketone moiety is built into a ring, such as in compounds of structure II, it is possible to force the carbonyl group out of the plane of the aromatic ring. Again, experimental data



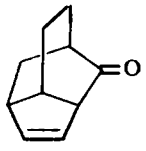
II

on the dihedral angles between the carbonyl and the ring as a function of the size of n are not directly available, but these angles have been estimated in various ways. For the series of benzocyclanones, two transitions have been studied, which occur in acetophenone itself at 279 mμ (ε 1,100); and 241 mμ (ε 12,300). These are both $\pi \rightarrow \pi^*$ transitions. The $n \rightarrow \pi^*$ transitions are of low oscillator strength, and they are not observed experimentally.

Finally, we studied tricyclo[4.2.1.$0^{3,7}$]nonan-4-en-2-one (III), and its homolog tricyclo[4.3.1.$0^{3,7}$]decan-4-en-2-one. These compounds were reported[14] to have UV spectra which were quite different from one another, which seemed unexpected for compounds having what appear to be very similar chromophores. As a model compound for these studies, we also examined 3-methylenecyclobutanone.



III



IV

METHOD OF CALCULATION

The basic method has been described previously,[3–6,8] and is summarized as follows:

Effective nuclear charge. To evaluate $Z_{original}$, the sp^2-sp^2 C—C and C—O bonds are taken as nonpolar. For carbon, having one alkyl substituent, the value of 3·073 was used, this value having been determined from experimental ionization potentials of various radicals. For oxygen *pi*- and *n*-orbitals in planar cases, the values were used such that after the VESCF treatment, the charge for oxygen *n*-orbital is greater by 0·083 than the charge on the oxygen *p*-orbital. In the non-planar cases, the average value of the *trans* and *cis* planar Z_π was used. Since there is no reason to require orbitals centered on the same atom to have the same nuclear charge, and they usually do not, we empirically chose this difference of 0·083 so as to fit the experimental acetone spectrum.

Ionization potentials. Due to the inductive effect of the σ-system in the VESCF treatment, the electron densities about different atoms in a molecule in general differ markedly from one another and from those in the free atoms. Consequently, in constructing the Hamiltonian one should use ionization potentials for the atoms with the effective nuclear charges which they have in the molecule, rather than using the

ionization potentials of the free atoms. The following equations relating the ionization potentials and effective nuclear charges were used:

$$I_C(Z) = 0{\cdot}8409\,Z^2 + 5{\cdot}4861\,Z - 15{\cdot}1718 \quad (1)$$

$$I_{O\text{-}pi}(Z) = -0{\cdot}575\,Z^2 + 18{\cdot}7475\,Z - 56{\cdot}1872 \quad (2)$$

$$I_{O\text{-}n}(Z) = -0{\cdot}511\,Z^2 + 17{\cdot}587\,Z - 55{\cdot}925 \quad (3)$$

Resonance integrals. The resonance integrals were evaluated between all orbitals of the *pi*-system. When the overlap integrals (S) has a value equal to or greater than 0·14, Mulliken's formula was used:

$$\beta_{ij} = \beta_0 \frac{(I_i + I_j)\,S_{ij}/(1 + S_{ij})}{2I_0S_0/(1 + S_0)} \quad (4)$$

where $\beta_0 = -2{\cdot}5$ ev, $I_0 = 8{\cdot}52893$ ev and $S_0 = 0{\cdot}32818$. When S was smaller than 0·14, $S_{ij}/(1 + S_{ij})$ is replaced by a polynomial,[3] and β_{ij} becomes:

$$\frac{\beta_0(I_i + I_j)\,(1 + S_0)}{2\,S_0I_0}(44{,}095\,S^5 + 15{,}084\,S^4 + 1{,}785\,S^3 - 80{\cdot}4\,S^2 + 1{\cdot}6\,S) \quad (5)$$

since the β *vs* distance function is empirical anyway, the polynomial was used so that the value of β was not as high as distances between 1·8–2·8A as it would have been if the Mulliken relation were used.

One-center repulsion integrals. The one-center repulsion integrals (Γ_{ii}) in ordinary SCF treatments are obtained from atomic spectral data[15] as the difference between the valence-state ionization potential and the electron affinity. Since the theoretical one-center repulsion integrals are proportional to the effective charge Z_i, and since the atomic spectral value G corresponds to a Slater Charge Z_s, the one-center repulsion integral is corrected by a factor of Z_i/Z_s:

$$\Gamma_{ii} = G(Z_i/Z_s) \quad (6)$$

The starting values for Γ_{ii} are tabulated in Table 2.

TABLE 2. ONE-CENTER REPULSION INTEGRALS FOR VARIOUS CHARGES

Orbital	Z	Γ_{ii}
C_{pi}	3·073	10·47657
C_{pi}	3·183	10·85185
C_{pi}	3·25	11·08000
O_{pi}	4·55	14·52000
O_n	4·55	14·52000

Atomic exchange repulsion integrals. These are usually small and consequently they are neglected (Zero Differential Overlap Approximation). However, for orbitals on the same center, such as oxygen *n*- and *p*-orbitals in a ketone, this type of integral

is large and no longer can be safely neglected. In such cases they are evaluated in the same manner as for the one-center repulsion integrals:

$$\chi = \chi_0 \frac{(1/2)(Z_{pi} + Z_n)}{Z_s} \tag{7}$$

where

$$\chi_0 = (\pi_0\bar{\pi}_0/\pi_0\bar{\pi}_0) \tag{8}$$

This integral has an empirical value[8] of 0·8476 for a center with the Slater charge of an O atom.

Configuration interaction. Both singly- and doubly-excited configurations were included.[3–5] In the case of α-diketones, the triply-excited configurations were included in a subsequent calculation. However, as was found earlier with polyenes, they did not improve the $\pi \rightarrow \pi^*$ transitions very much, although the $n \rightarrow \pi^*$ transitions became a little better. The inclusion of doubly-excited configurations is important, however, as usual.

Oscillator strength. The average oscillator strength is calculated by:

$$f = 8\pi^2 mcE\lambda^2/3h \tag{9}$$

where E is the energy of the transition, λ^2 is the electronic transition moment. (The expansion of the transition moment in terms of the wave functions and position vectors is described in Ref. 16.)

RESULTS AND DISCUSSION

For acetophenone, the agreement between the calculated electronic transition energies and the experimental spectrum is good when the configuration interaction is limited to singly-excited configurations, and excellent when both the singly- and doubly-excited configurations are included (Table 3). These results indicate the importance of the extent to which the configuration interaction calculations are carried.

TABLE 3. THE CALCULATED AND THE EXPERIMENTAL SPECTRA OF ACETOPHENONE

Experimental				Calculated[b]			
Solution[c]		Vapor Phase[d]		Singly E.S.		Singly + Doubly	
λ_{max} mμ	(ε)	λ_{max} mμ	(ε)	λ_{max} mμ	(f)	λ_{max} mμ	(f)
320	(45)	(320[a])		305	(0)	314	(0)
278	(1,000)	275	(950)	254	(0·0356)	273	(0·0156)
243	(12,600)	230	(13,000)	245	(0·1296)	231	(0·1899)
199	(20,000)	196	(48,000)	192	(0·8179)	191	(0·3885)
		191	(46,000)	177	(1·0032)	184	(0·0951)
		179	(24,000)	158	(0·5520)	182	(0·7093)
		167	(21,000)	154	(0·1601)	169	(0·3008)

[a] Wave length estimated, as transition too weak to observe in gas phase

[b] The maxima below 200 mμ observed experimentally are probably vibrational fine structure, and no direct correspondence with the calculated values is implied

[c] Ref. 21

[d] K. Kimura and S. Nakakura, *Theor. Chim. Acta Berl.* 3, 164 (1965)

If the CO group in acetophenone is rotated by 30° with respect to the benzene ring, the calculations indicate that the first transition ($n \rightarrow \pi^*$) is shifted slightly toward lower wavelength and becomes slightly allowed. The second transition shows little change, and the third transition energy stays approximately constant, but the oscillator strength decreases. Comparison of the calculated spectra for acetophenone and 30°-rotated acetophenone is given in Table 4. These changes are expected. The *n*-orbital

TABLE 4. COMPARISON OF THE CALCULATED SPECTRA OF ACETOPHENONE AND 30°-ROTATED ACETOPHENONE

Acetophenone		30°-Rotated acetophenone	
Singly + Doubly E. S.		Singly + Doubly E.S.	
λ_{max} mμ	(f)	λ_{max} mμ	(f)
314	(0)	292	(0·0077)
273	(0·0156)	270·5	(0·0173)
231	(0·1899)	228	(0·1097)

is orthogonal to the *pi*-system in the planar case and thus the $n \rightarrow \pi^*$ transition is forbidden; when the molecule is twisted, the *n*-orbital is no longer perpendicular to, and now overlaps the *pi*-system, and the transition becomes weakly allowed. For the $\pi \rightarrow \pi^*$ transitions, on the other hand, rotation from coplanarity causes the overlap between the *p*-orbitals of the two chromophores to decrease. The appearance of these transitions consequently tends toward those of the isolated chromophores with increased twisting.

Comparison of the experimental 1-tetralone spectrum with that of acetophenone shows that the presence of the alkyl group on the ring causes a shift of λ_{max} to longer wavelength. Within the benzocyclanone series, however, as the aliphatic ring gets larger, the λ_{max} stays roughly at the same position with a decrease in absorption intensity. The calculated spectrum of 30°-rotated acetophenone with inclusion of double-excited states is in good agreement with the available data on the benzocyclanones. In Table 5 are given the experimental absorption maxima of the benzocyclanones, which vary with the size of the aliphatic ring. In the past it has often been assumed that the extinction coefficients for these compounds were proportional to the $\cos^2$ of the angle of twist.* We pointed out earlier that the accuracy of this approximation was in doubt. This approximation suggests dihedral angles of 20° for benzosuberone (II, $n = 7$) and 46° for benzocyclooctanone (II, $n = 8$), assuming a value of 0° for 1-tetralone (II, $n = 6$). The present calculation of 30°-rotated acetophenone suggests that the previously estimated rotational angles are too severe, as the calculated oscillator strengths appear to fall off with dihedral angle even more rapidly than the $\cos^2$ relationship would predict. The angles of twist for benzosuberone and benzocyclooctanone are now estimated to be near 15° and 30° respectively.

The 2,3-butanediones were next studied. The UV spectra were calculated as a function of the torsional angle about the 2,3-bond. Values for these quantities can be estimated from the experimental data obtained by Leonard and Mader (See Table 1).[11]

The calculated electronic spectra are for the gas phase, whereas the experimental

* See Ref. 13 for a thorough discussion of this point, together with leading references.

TABLE 5. THE EXPERIMENTAL $\pi \rightarrow \pi^*$ TRANSITIONS OF BENZOCYCLANONES

Compound	1st λ_{max} mμ	(ε)	2nd λ_{max} mμ	(ε)
Acetophenone	279	(1,100)	241	(12,300)
1-Tetralone (II, $n = 6$)	293	(1,600)	247	(11,300)
Benzosuberone (II, $n = 7$)	286	(1,500)	246	(9,300)
Benzocyclooctanone (II, $n = 8$)	289	(800)	248	(5,800)

spectra are usually run in some solvent. In general, the long-wavelength, low-intensity absorption bands ($n \rightarrow \pi^*$) of carbonyl compounds shift to shorter wavelength in polar solvents, but exceptions have been found. There are different explanations for the solvent shifts.[17] The direction and the magnitude of the solvent shifts of the $n \rightarrow \pi^*$ transitions are complicated, and not really very well understood. Consequently, the calculated transitions are not corrected for the effect of solvent when they are compared with the experimental results, but it should be borne in mind that the experimental values for the $n \rightarrow \pi^*$ absorption bands may be lower than the gas phase values by 10–20 mμ if they were determined in polar, especially hydroxylic, solvents. Because of the solvation problem, as well as the fact that the molecular geometries are not known with high precision, the relative transition energies calculated are expected to be more significant than their absolute values.

In Table 6 are given the calculated results for the electronic spectrum of butanedione as a function of the torsional angle between the carbonyls, truncating the configuration interaction after inclusion of all of the single-excited configurations.

A comparison of the data in Tables 1 and 6 shows that the calculated wavelengths for the first transiton ($n \rightarrow \pi^*$, $V_0 \rightarrow V_{45}$ in planar cases) are too short by about 50–100 mμ, compared with the experimental values.

TABLE 6. CALCULATED ULTRAVIOLET SPECTRA VS. INTERCARBONYL ANGLE FOR BUTANEDIONE (SINGLY-EXCITED CONFIGURATIONS ONLY)

$V_0 \rightarrow$	V_{45}		V_{35}		V_{25}		V_{15}	
θ	mμ	(f)	mμ	(f)	mμ	(f)	mμ	(f)
trans-180°	314	(0·0000)	314	(0·0000)	180	(0·9131)	154	(0·0000)
165°	311	(0·0000)	311	(0·0010)	179	(0·8857)	154	(0·0100)
150°	305	(0·0000)	304	(0·0030)	177	(0·8231)	156	(0·0365)
135°	296	(0·0000)	295	(0·0030)	173	(0·7378)	158	(0·0710)
120°	284	(0·0000)	284	(0·0018)	164	(0·6353)	162	(0·0965)
105°	279	(0·0000)	279	(0·0000)	156	(0·6330)	165	(0·1210)
90°	281	(0·0000)	280	(0·0000)	156	(0·5418)	165	(0·1435)
75°	284	(0·0000)	282	(0·0000)	159	(0·4790)	165	(0·1568)
60°	296	(0·0002)	288	(0·0015)	168	(0·3979)	162	(0·1829)
45°	320	(0·0003)	301	(0·0032)	180	(0·3782)	156	(0·2635)
30°	339	(0·0002)	310	(0·0028)	188	(0·3603)	152	(0·3514)
15°	353	(0·0001)	317	(0·0013)	193	(0·3495)	149	(0·4675)
cis-0°	359	(0·0000)	320	(0·0000)	194	(0·3471)	147	(0·5460)

The calculated values for the second transitions ($n \rightarrow \pi^*$, $V_0 \rightarrow V_{35}$) are degenerate with the first ones until doubly-excited configurations are included. The third transition ($\pi \rightarrow \pi^*$, $V_0 \rightarrow V_{25}$) is calculated to occur at 180–194 mμ with substantial intensity ($f = 0{\cdot}3$–$0{\cdot}9$) in the planar molecules, and the wavelength decreases to a minimum value of 156 mμ at 90°. The experimental spectrum shows absorption of low intensity at about 290 mμ for all planar and non-planar diketones, so the agreement is very poor.

The inclusion of doubly-excited configurations improves considerably the correspondence between the calculated spectra and the experimental ones. (Table 7). The first and second transitions are still at too short a wavelength, now by about 40–80 mμ. The wavelengths for the ($V_0 \rightarrow V_{25}$) transitions are increased by about 20 mμ as compared with the corresponding values in Table 6, and the intensities are much reduced (to $f = 0{\cdot}02$ or less). In addition, another forbidden transition ($V_0 \rightarrow V_{3355}$) is now calculated at about 190 mμ for the planar cases. The transition acquires considerable oscillator strength and shifts to lower wavelength with increasing nonplanarity.

Inclusion of triply-excited configurations (Table 8) causes the $V_0 \rightarrow V_{45}$ and $V_0 \rightarrow V_{35}$ transitions to shift about 10 mμ further towards the red, a small improvement.

The behavior of the long wavelength absorption which we calculate follows that observed by Leonard and Mader very well in certain respects. The *cis* planar conformation absorbs at longer wavelength than does the *trans*, and the latter is at longer wavelength than the perpendicular conformation by 52 mμ (calculated) compared with 47 mμ (experimental). The systematic errors in wavelength (of some 40 mμ) amount to about 0·4 ev. Since many of Leonard's compounds are rather strained, and solvation cannot be allowed for, perhaps the conclusion to be drawn is that the shift of wavelength with dihedral angle which is calculated is in good agreement with experiment, and the absolute calculated values are fair.

There is one apparent serious difference between the calculated and the experimental spectra. In our calculations, all transitions show dependence on the intercarbonyl angle, but Leonard and Mader found the longest wavelength transition was dependent on θ, while the second was not. Further, the experimental absorption is at about 290 mμ, whereas we calculate transitions at around 350 and 220 in the planar systems, neither of which is in agreement with experiment. The lack of agreement between the calculated and experimental transition energies is sufficiently serious that the 290 mμ transition is almost certainly due to the neglect of the σ-system. The extra transition observed experimentally is probably of the $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ type,[18] analogous to the "mystery bands" in ethylene derivatives, or it may involve the *n*-orbitals, which must in reality be mixed in with the σ-system, and hence it does not appear from our calculations.

The strongly allowed $\pi \rightarrow \pi^*$ transition is predicted to occur at 185 mμ ($f = 0{\cdot}69$) for the *trans* conformation. The wavelength decreases to 167 mμ with rotation to 90°, and the oscillator strength reaches a very small value. The transitions mix together so much with the nearly perpendicular systems that no simple comparisons are possible. The oscillator strength and wavelength increase from 45° to the *cis*-planar conformation. The calculations give λ_{max} 196 mμ ($f = 0{\cdot}28$) for the latter; thus, the absorption is at longer wavelength than is that of the *trans* isomer, and with a lower

TABLE 7. CALCULATED ULTRAVIOLET SPECTRA VS. INTERCARBONYL ANGLE (SINGLY- + DOUBLY-EXCITED CONFIGURATIONS) FOR BUTANEDIONE

V_0 → / θ	V_{45} mμ	(f)	V_{35} mμ	(f)	V_{25} mμ	(f)	V_{15} mμ	(f)	V_{3355} mμ	(f)
trans-180°	342	(0·0000)	342	(0·0000)	201	(0·0000)	186	(0·6800)	186	(0·0000)
165°	338	(0·0000)	337	(0·0001)	198	(0·0000)	188	(0·4100)	186	(0·0010)
150°	328	(0·0000)	325	(0·0011)	191	(0·0000)	188	(0·2890)	183	(0·0018)
135°	314	(0·0000)	312	(0·0015)	186	(0·0001)	184	(0·1900)	172	(0·3900)
120°	296	(0·0000)	295	(0·0010)	184	(0·0050)	175	(0·0340)	166	(0·5000)
105°	289	(0·0000)	289	(0·0000)	183	(0·0136)	169	(0·0320)	160	(0·4660)
90°	291	(0·0000)	290	(0·0000)	183	(0·0190)	168	(0·0700)	158	(0·4000)
cis-75°	294	(0·0000)	293	(0·0000)	184	(0·0208)	171	(0·0510)	161	(0·3254)
60°	308	(0·0000)	299	(0·0010)	178	(0·0010)	185	(0·0130)	171	(0·3200)
45°	338	(0·0000)	316	(0·0020)	185	(0·0010)	188	(0·1000)	180	(0·1900)
30°	361	(0·0000)	329	(0·0020)	190	(0·0000)	194	(0·1700)	184	(0·1000)
15°	379	(0·0000)	339	(0·0030)	197	(0·0000)	198	(0·2100)	187	(0·0400)
cis-planar	386	(0·0000)	344	(0·0000)	200	(0·0000)	199	(0·2800)	189	(0·0000)

TABLE 8. CALCULATED UV SPECTRA VS. INTERCARBONYL ANGLE (SINGLY-, DOUBLY-, AND TRIPLY-EXCITED CONFIGURATIONS) FOR BUTANEDIONE

V_0 → / θ	V_{45} mμ	(f)	V_{35} mμ	(f)	V_{25} mμ	(f)	V_{15} mμ	(f)	V_{3355} mμ	(f)
trans-180°	351	(0·0000)	351	(0·0000)	219	(0·0000)	185	(0·6900)	182	(0·0000)
165°	347	(0·0000)	346	(0·0000)	214	(0·0000)	187	(0·3700)	183	(0·0000)
150°	336	(0·0000)	334	(0·0008)	205	(0·0000)	187	(0·2600)	183	(0·0002)
135°	322	(0·0000)	320	(0·0010)	194	(0·0000)	184	(0·1800)	180	(0·0001)
120°	304	(0·0000)	303	(0·0007)	186	(0·0040)	175	(0·0400)	166	(0·5120)
105°	298	(0·0000)	298	(0·0001)	185	(0·0110)	167	(0·0310)	160	(0·4800)
90°	299	(0·0000)	298	(0·0000)	185	(0·0150)	167	(0·0830)	158	(0·5770)
cis-75°	302	(0·0000)	300	(0·0000)	186	(0·0170)	170	(0·0550)	161	(0·3300)
60°	316	(0·0000)	307	(0·0006)	187	(0·0110)	178	(0·0010)	171	(0·3230)
45°	346	(0·0000)	323	(0·0017)	195	(0·0004)	188	(0·0810)	181	(0·0014)
30°	370	(0·0000)	336	(0·0016)	208	(0·0000)	193	(0·1410)	184	(0·1340)
15°	388	(0·0000)	347	(0·0005)	218	(0·0000)	196	(0·1960)	187	(0·0650)
cis-0°	395	(0·0000)	352	(0·0000)	223	(0·0000)	196	(0·2790)	189	(0·0000)

extinction, analogous to what is found for the related chromophore *butadiene*. The *cis*- and *trans*-diones are predicted to show $\pi \rightarrow \pi^*$ absorption as given in Table 9. Such absorption should be observable in many cases with modern instrumentation, but the measurements reported by Leonard did not go down to sufficiently short wavelengths to detect it.

TABLE 9. PREDICTED $\pi \rightarrow \pi^*$ ABSORPTION OF 2,3-DIONES (HEXANE SOLVENT)

	λ_{max} mμ	(f)	ε
cis-2,3-Dione	196	0·28	6,000
trans-2,3-Dione	185	0·69	12,000
perpendicular-	158	0·58	10,000
2,3-Dione	167	0·08	2,000

Since we have had reasonable success in calculating the electronic spectra of α,β-unsaturated ketones (at least for planar systems),[8] and since the rigid system tricyclo-[4.2.1.$0^{3,7}$]nonan-4-en-2-one (III) and tricyclo[4.3.1.$0^{3,7}$]decan-4-en-2-one (IV) are of some current interest,[14] we wished to extend the VESCF-CI method to calculation of the ultraviolet spectra of β,γ-unsaturated ketones. A few calculations on such systems have been reported previously, but they have not been very detailed.[19] It was considered desirable to carry out the calculation of a β,γ-unsaturated ketone in which the chromophores are known experimentally to interact in order to see whether the present method might be reliably applied to the above mentioned compounds, and 3-methylenecyclobutanone was chosen for this purpose, even though its geometry is not accurately known. The reason for the choice was the unusual absorption spectrum which has been reported for the molecule.[20] The agreement between the experimental and the calculated $\pi \rightarrow \pi^*$ transitions (Table 10) is fair considering the

TABLE 10. UV SPECTRA OF 3-METHYLENECYCLOBUTANONE

Experimental[a]		Calculated[b]	
λ_{max} mμ	(ε)	λ_{max} mμ	(f)
293	(22)	299	(0)
215	(1,550)	196	(0·3460)

[a] Corrected to gas phase

[b] Including singly- and doubly-excited configurations.

uncertainty in molecular geometry. Our calculational method can then apparently be extended to the predictions of electronic spectra of other β,γ-unsaturated ketones.

The spectra reported for the tricyclic compounds III and IV are given in Tables 11 and 12. For III, the band reported at 237 mμ with an extinction coefficient of 2,200 is most unusual, since for β,γ-unsaturated ketones, the $n \rightarrow \pi^*$ transitions and $\pi \rightarrow \pi^*$ transitions are typically observed around 290 mμ and 180 mμ, respectively. The experimental spectrum of the other compound IV, on the other hand, is quite ordinary.

TABLE 11. UV SPECTRA OF TRICYCLO[4.2.1.0$^{3\ 7}$]NONAN-4-EN-2-ONE (III)

Experimental[a]		Calculated[b]	
λ_{max} mμ	(ε)	λ_{max} mμ	(f)
308	(14)	275	(0·0000)
237	(2,200)	171	(0·0492)

TABLE 12. UV SPECTRA OF TRICYCLO[4.3.1.0$^{3\ 7}$]DECAN-4-EN-2-ONE (IV)

Experimental[a]		Calculated[b]	
λ_{max} mμ	(ε)	λ_{max} mμ	(f)
297	(234)	274	(0·0004)
[c]		171	(0·0337)
		171	(0·0247)

[a] In ethanol solution

[b] Including singly- and doubly-excited configurations

[c] Maximum not observed. The value of ε was 2,000 at 200 mμ and increasing.

A comparison of the calculated and experimental spectra of the two compounds is given in Tables 11 and 12.

The $n \rightarrow \pi^*$ transition of cyclopentanone is observed at 299 mμ in hydrocarbon solvent, which is about 20 mμ higher than the acetone $n \rightarrow \pi^*$ transition.[21] Our VESCF-CI method is based on acetone, and therefore may be presumed to predict the $n \rightarrow \pi^*$ absorption bands of five-membered ring ketones too low by about 20 mμ. The error probably results from a mixing of the *n*-orbital with the sigma system of the molecule, something which the present calculations cannot take into account. For calculations on these two tricyclic compounds then, we would expect to obtain a transition which is about 20 mμ lower than the experimental value.

The calculated $n \rightarrow \pi^*$ transition for IV is too low by about 23 mμ, which as explained in the previous paragraph, is expected. The calculated spectrum corresponds rather closely to a mixture of separate acetone and 2-butene molecules. The $n \rightarrow \pi^*$ transition is calculated to be very weakly allowed, $f = 0{\cdot}0004$. The experimental spectrum shows the usual enhancement in extinction coefficient typical of β,γ-unsaturated ketones. The experimental enhancement is rather large relative to the very small calculated oscillator strength; however, this trend is what might be expected for a vibrating versus a non-vibrating system. It is known from other work[22] that the fall off of overlap with distance is too rapid with Slater orbitals at distances such as those under consideration here, and the use of SCF atomic basis functions would increase the interactions in question.

The calculated spectra of these two tricyclic compounds are very similar, which is not unreasonable if one examines the models. The calculation does not predict any

transition between 230 to 240 mμ, which was observed in the solution spectra of compound III. It is likely that the experimental spectrum corresponds to some compound other than this rigid tricyclic system.*

APPENDIX

The bond lengths and bond angles for the *trans*-coplanar α-diketone used in this calculation are within the experimental error of those reported by LuValle and Schomaker[23] as follows: C = O 1·216 Å, C—C 1·450 Å, O—C—C angle 120°.

For the acetophenone, the ring C—C bond lengths are taken to have the same value as the experimental bond length in benzene (1·397 Å), and the other values are the same as those used for the α-diketones.

The geometries of the two tricyclic compounds III and IV were calculated by a modified Westheimer–Hendrickson–Wiberg method,[24] which minimizes the total energy of a molecule by systematically varying all of the bond lengths and bond angles. Atom 5 in either case is used for determining the direction cosines of the orbitals in question although it is not a part of the *pi*-system. The atomic coordinates of the pertinent portions of these two compounds are listed in Tables 13 and 14.

TABLE 13. ATOMIC COORDINATES OF TRICYCLO[4.2.1.0$^{3\ 7}$]NONAN-4-ENE-2-ONE

		x	*y*	*z*
	1	− 1·74271	− 0·96341	− 0·43513
	2	− 0·81342	− 1·69094	0·17966
	3	1·24521	− 0·30870	0·00548
	4	2·16109	− 1·00133	− 0·41167
r_{12} = 1·331 Å				
r_{34} = 1·222 Å	5	− 0·40816	0·98673	− 1·28474

TABLE 14. ATOMIC COORDINATES OF TRICYCLO[4.3.1.0$^{3\ 7}$]DECAN-4-ENE-2-ONE

		x	*y*	*z*
	1	− 2·06053	− 0·63392	− 0·39290
	2	− 1·97481	0·41304	0·42579
	3	0·31425	1·25927	0·06140
	4	0·25846	2·47714	− 0·02470
r_{12} = 1·332 Å				
r_{34} = 1·222 Å	5	− 0·57780	− 0·46827	0·97520

For 3-methylenecyclobutanone, the C=C and C=O bond lengths were assumed to have bond lengths of 1·331 Å and 1·222 Å, respectively. The $C_{sp}2$—$C_{sp}3$ bond length was assumed to be 1·504 Å. It is assumed that all the carbon and oxygen atoms lie in a plane, and the internal bond angles of the ring were taken such that the angle strain was minimized, 85·5° at the saturated carbons and 95·5° at the unsaturated carbons.

* Some time after this conclusion was reached and communicated to Dr. N. A. LeBel, he informed us that a more exhaustive purification of the compound eliminated this absorption, which was in fact due to an impurity that had previously resisted separation by any of several and repeated techniques.

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