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SPECTRAL EFFECTS IN CYCLOBUTANE DERIVATIVES

THE BATHOCHROMIC-HYPOCHROMIC SHIFTS IN COMPOUNDS RELATED TO VERBENONE

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Abstract—The bathochromic-hypochromic spectral shifts, observed in bicyclic enones that contain a 4- or a 3-membered ring, are discussed in molecular-mechanical and molecular-orbital terms. It is proposed that the effect, not only by the cyclopropane but also by the cyclobutane ring, is due to extension of the C=C–C=O chromophore, and not to its mere distortion from "normal" geometry. The high-energy absorption of umbellulone (3), 220 nm in ethanol, is characterized as a second π–π^*. 2-Methylbicyclo[3.2.1]oct-2-en-4-one (7) has been synthesized, and its preparation and spectrum are described.

INTRODUCTION

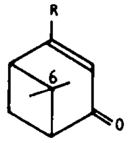
In 1956, Moore and Fisher noted[1] that the UV spectrum of certain unsaturated bicyclo[3.1.1]heptane derivatives, e.g. verbenone (**1a**), was bathochromically shifted with respect to that of the corresponding monocycles, e.g. piperitone (**2**). The phenomenon was also encountered, to an even higher degree, in the bicyclic 3-ring analog umbellulone (**3**). From their own and some previous data,[2,3] Moore and Fisher inferred that, whereas the cyclobutane ring in **3** might be conjugated with the enone system, the cyclobutane ring, in some molecules that are germane to **1a**, and show the effect, is not in a position to extend conjugation. They then suggested that the effect was due to strain *induced in the chromophore* by fusion to the 4-membered ring.

A list of molecules in which a 4-membered ring exerts an auxochromic effect was published in 1956.[4] Other cases, e.g. **4**,[5] have been encountered since; the most extreme seems to be that of tricyclo[3.3.0^{2,6}]octa-3,7-diene (**5**), where absorption is reported to onset at *ca.* 320 nm.[6] In enone-pinene derivatives, e.g. **1b**, the effect is less extreme but, in each of several molecules measured,[7] the absorption was found to occur at a longer wave-length (by *ca.* 20 nm or more) and to have a lower extinction than in the isomeric monocyclic compounds, e.g. **6**.

The distinction between the consequences of chromophore-distortion[8,9] and chromophore-extension transcends obviously the examples above. In particular, it is linked with the recent interest in the electronic properties of cyclobutanes and their similarity (or dissimilarity) to those of cyclopropanes.[6,10,11] In this context, it may be recalled that compounds **1a** and **3** have in common an "anomalous" ^{13}C-NMR signal at C_6.[12]

Here we wish to contribute to the distinction between the consequences of chromophore-distortion and chromophore-extension in enones of types **1**, **3** and **7**.

First, molecular-mechanical estimates of geometry and strain are reported. Next, the spectra are checked against

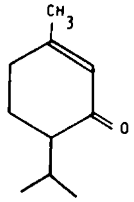


1

a. R = CH_3, λ_{max}(EtOH) 253

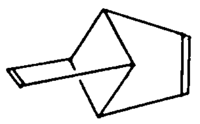
b. R = CH_2OCOCH_3

λ_{max}(EtOH) 247



2

λ_{max}(EtOH) 235.5



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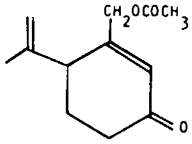
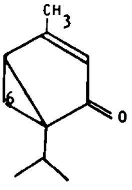


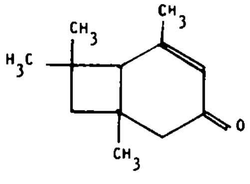
6

λ_{max}(EtOH) 228



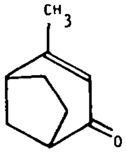
3

λ_{max}(EtOH) 265, 220



4

λ_{max}(MeOH) 245



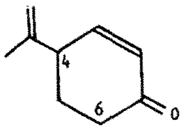
7

various indices of chromophore-distortion. MO calculations, conducted in order to assess the nature and degree of σ-participation in the π-excitations, are discussed last.

Included in this analysis is the spectrum of 2-methylbicyclo[3.2.1]oct-2-en-4-one (**7**), a bicyclic enone that contains a 5-membered ring. The idea behind this inclusion was that in **7** the cyclopetane ring may introduce some chromophore-distortion, without chromophore extension. Compound **7** was synthesized from bicyclo[3.2.1]octan-2-one through a Grignard reaction with methylmagnesium iodide, followed by dehydration to 2-methyl-bicyclo[3.2.1]oct-2-ene[13] and oxidation with sodium chromate.

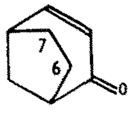
Geometry and strain

The molecular geometry of four model structures, **8–11**, has been calculated by the force-field method.[14] As applied to the structures at hand, the method is heavily parametrized and, admittedly, not expected to provide very accurate numbers. In what follows, therefore, we report the values obtained, but base the discussion on general trends alone.



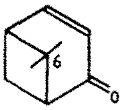
8

monocyclic



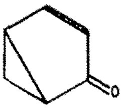
9

[3.2.1] system



10

[3.1.1] system



11

[3.1.0] system

Calculations were conducted under Allinger's 1973 force field,[15] implemented by appropriate ketone parameters.[16,17] In the enone moiety (C=C–C=O), the "natural" values of the =C–C= and –C=O interatomic distances were assumed equal to the electron-diffraction values in acrolein,[18] namely, 1.482 and 1.210 Å, and the stretching force constant k_s(=C–C=) was taken as 7.0 mdyn Å^{-1}, which is an average of the C–C and C=C values (4.4 and 9.6, respectively). For the [3.1.0] system, cyclopropane constants were also required. Many of these have established values[19] and others were assigned by analogies. We consider the calculations for this ring-system as less reliable than for the other structures.

Some pertinent results are given in Table 1, together with acrolein values[18] for comparison. The C=C–C=O grouping deviates from "ideal" geometry in all the cases investigated, but the nature of the deviation varies from one case to another.

In the monocyclic enone **8**, bond-lengths and angles are not unusual, but C=C–C=O is non-coplanar. Insertion of a 1-bridge to produce **10**, imposes coplanarity on C=C–C=O, but this at the expense of severe bond-angle bending. A compromise is provided in the 2-bridge derivative **9**: here, bond angles and the dihedral angle C=C–C=O are like in the monocycle **8**, but the other dihedral angles resemble those in **10**; this molecule has also the feature of a long C=O bond. As our numbers for **11** show, the worst distortions occur when C=C–C=O is fused to a 3-membered ring.

It might be useful now to arrange the four model structures by orders of increasing non-coplanarity, and of increasing bond-angle bending. The first sequence is: [3.1.1] < [3.2.1] < monocyclic < [3.1.0]; the second: monocyclic < [3.2.1] < [3.1.0] < [3.1.1].

It is also helpful to obtain at this point an estimate of relative strains in the series of enones. In most contexts, the term "strain energy" refers to the difference between the observed heat of formation and a hypothetical value, calculated from group-increments.[20] Here, however, this approach is not practicable, for we shall also need localized (fractional) contributions to the overall strain energy. Such an eventuality is provided for by the particular force field which we use: strain energy is taken as the difference in computed heat of formation between a realistic structure of the molecule, including distortions and non-bonded interactions, and a hypothetical counterpart, constructed by "welding together" strain-free

Table 1. Computed geometry of model systems

Parameter		8 (monocyclic)	9 ([3.2.1])	10 ([3.1.1])	11 ([3.1.0])	Acrolein[a]
Dihedral	C-C=C-C(=O)	2	1	3	11	-
angles	C=C-C(=O)-C	17	2	1	10	0[b]
(deg.)	C=C-C=O	167	171	180	160	180[b]
Bond	C-C=C	122	119	104	114	-
angles	C=C-C(=O)	122	123	133	106	121
(deg.)	=C-C(=O)-C	115	113	106	109	114[c]
Bond-	C=C	1.339	1.341	1.346	1.347	1.335
lengths	=C-C(=O)	1.488	1.482	1.484	1.489	1.478
(Å)	C=O	1.214	1.248	1.209	1.238	1.208

[a] Ref. 18 [b] Assumed [c] CCH-angle

fragments.[21] The required parameters are available, except for molecules containing 3-membered rings. Therefore, structure **11** was not calculated. One may safely assume that it is more strained than **8–10**.

The calculated strain energies are:

monocyclic (**8**, isopropenyl replaced by H), 9.58
[3.2.1] (**9**), 16.66
[3.1.1] (**10**), 48.99 kcal mol^{-1}.

For comparison, the numbers derived[21] for some hydrocarbons are: cyclohexane, 1.75; bicyclo[3.2.1]octane, 8.50; bicyclo[2.2.1]hexane, 44.32 kcal mol^{-1}.

Another pertinent analysis provides the strain energy at the cyclohexenone moiety of the three structures. To obtain these indices, we first replaced by hydrogens the bridges in **9** (C_6 and C_7) and **10** (C_6), and performed the calculation for the ensuing structures. Next, in order to eliminate artifact interactions and to bring all numbers to the same origin, we subtracted from the values obtained all non-bonded interactions due to the added hydrogens (for consistency, interactions due to one hydrogen at C_4 and one at C_6 were subtracted in **8**). This provides:

monocyclic, 8.72
[3.2.1], 9.41
[3.1.1], 19.42 kcal mol^{-1}.

In other words, if the cyclohexenone strain energy in **8** is taken as 0.0, it is 0.7 in **9**, and 10.7 kcal mol^{-1} in **10**.

Spectra and their relation to structural indices

π–π^*-Transitions of pertinent enones, in non-polar and polar media, are listed in Table 2. The well-documented[22] solvent shift is manifested throughout. Theoretical values (last column of Table) should be compared with absorption wave-lengths in non-polar solvents.

The hitherto undescribed spectrum of 2-methylbicyclo[3.2.1]oct-2-en-4-one (**7**) is extremely similar to that[25] of the acyclic mesityl oxide. It differs from those of monocyclic enones by its solvent shift and the lower extinction, and has but a superficial resemblance to the spectrum of the [3.1.1] and [3.1.0] enones. The n–π^* portion of the spectrum appears (in cyclohexane) as a

Table 2. Enone $\pi \rightarrow \pi^*$ transitions

Type	Molecule	Solvent	expt. λ_{max} (ε mol)	Ref.	calcd. λ (f)
Acyclic	$Me_2CH{=}CHCOMe$	Hex	231 (11,500)	22	
		EtOH	236 (10,600)	22	
Monocyclic	3-Me-cyclohexenone	i-Oct	226 (17,800)	23	226 (0.746)
		EtOH	235 (12,600)	22	
	Piperitone 2	i-Oct	225 (14,200)	24	
		EtOH	235.5 (17,780)	1	
	6	CH	223	a	
		EtOH	228 (10,700)	12	
[3.2.1]	Me-bicyclo=	CH	228 (11,600)	a	231 (0.734)
	octenone 7	EtOH	241 (7,200)		
[3.1.1]	Verbenone 1a	CH	241 (6,400)	a	237 (0.624)
		EtOH	253 (6,840)	1	
	4-Oxomyrtenylacetate 1b	CH	238 (5,300)	a	
		EtOH	247 (7,453)	12	
			[220 (5,900)]		
[3.1.0]	Umbellulone 3	EtOH	261 (3,290);		242 (0.427)
			220 (5,900)	2	

[a] This work.

Solvents: Hex - hexane, CH - cyclohexane, i-Oct - isooctane, EtOH - ethanol. Calculated spectra are for the model structures 8 (Isopropenyl replaced by H) and 9–11. The computed λ- values were incremented by 12 nm to account for the effect of methyl on C=C-C=O.[22] f-Oscillator strength. λ in nm.

fine-structured massif at 300–360 nm; the two peaks that flank the innermost absorption, 337 nm ($\epsilon = 48$), are spaced at 1190 cm^{-1} (*cf.*[26]).

As compared with the monocyclic, the π–π^* absorption of enones that contain a 4- or a 3-membered ring is shifted bathochromically and hypochromically. Is this in line with geometrical indices? It has been suggested, on the body of accumulated data, that twisting C=C–C=O around =C–C= would be slightly hypsochromic and highly hypochromic.[9] This is not observed; rather, on passing from the practically coplanar enone ([3.1.1] system) to the distorted form (monocyclic enones), the shift is highly hypsochromic and highly hyperchromic. In the complete series of structures the effect does not even evolve parallel to the order of increasing non-planarity. Also, it is not in line with the order of bond-angle bending in C=C–C=O.

Therefore, and contrary to previous suggestions,[1] the shift cannot be localized at the C=C–C=O portion of the molecule. It is clear that the presence of the small ring (in [3.1.0], [3.1.1] and perhaps also in [3.2.1]) has a role in determining the spectral properties of C=C–C=O.

Is it strain, total molecular or localized at the cyclohexenone moiety, that is decisive? If so, the bathochromic-hypochromic shift in [3.1.1] systems seems to be too small. Yet, the correspondence with computed strains is in the correct sense, which suggests a long-range interaction. It turns out that the nature of this interaction stands out in the molecular orbital analysis.

Molecular orbital analysis

The MO calculations which we report are all semiempirical SCF-CI, and fall into two types. The first is our usual π-electron procedure.[27] This was used to calculate the isolated C=C–C=O pi-chromophore in the various model structures (**8**–**11**), taken in the computed geometry but *without* the σ-skeleton and the rest of the molecule. The second technique is the LCHO (Linear Combination of Hybrid Orbitals) extension of the former,[10,28] which allows for a simultaneous consideration of π-orbitals and σ-network. Here, molecular orbitals are based on a set of pure AO's (for oxygen and hydrogen) and (for carbon) on hybrid atomic orbitals which are derived from the molecular geometry. Calculations of the latter type were performed on the entire molecular skeleton (that is, **8** less isopropenyl, **9**, **10** less the methyls on C_6, **11**) excluding—because of computer memory and time limitations—the C–H bonds.† For the cyclobutane-enone (**10**), the structure in Fig. 1 (hydrogens included) was also computed. To facilitate comparison between the experimental data, which are for β-methyl-$\alpha\beta$-unsaturated ketones, and the computed, the theoretical λ-values (below and in Table 2) have been incremented by 12 nm.[22]

Consider first the location and oscillator strengths predicted for the *non-interacting* C=C–C=O π-chromophore:

monocyclic (**8**), 213 nm (f = 0.76)
[corresponding en-enone, 217 (0.58)]
[3.2.1] (**9**), 217 (0.80)
[3.1.1] (**10**), 216 (0.84)
[3.1.0] (**11**), 217 (0.70).

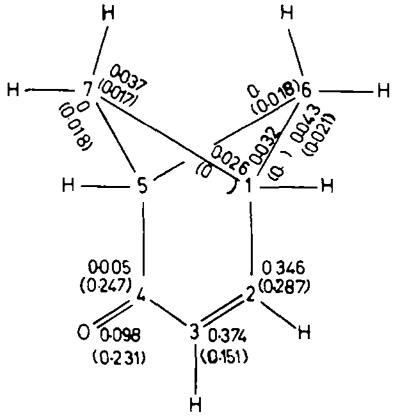


Fig. 1. Bicyclo[3.1.1]hept-2-en-4-one. Squared AO coefficients in the π(and π^*) molecular orbital. The input geometry was that of the 6,6-dimethyl derivative.

Clearly, neither the bathochromic shift, nor the correct sequence in absorbance, are reproduced. We take this negative result as a further confirmation that the effect is not localized in C=C–C=O.

Everything, however, falls in line when one considers LCHO results for the *complete* skeletons: realistic wave-length shifts and extinction-decreases are obtained (Table 2). This being so, we turn to the molecular orbitals themselves.

The first Π^* state of the monocyclic enone (**6**) contains about 92% of the $\pi - \pi^*$ configuration. The two states that follow correspond both to forbidden transitions, and are characterizable as $\pi - \pi^*$ and $\pi - \sigma^*$. The spectrum computed for the structure with the 5-membered ring (**9**) is very similar: the Π^* state contains about 96% of $\pi - \pi^*$. In the [3.1.0] system **11**, the first Π^* state is only 85% $\pi - \pi^*$, the balance being n – π^*, an internal $\pi - \pi^*$ and $\sigma - \pi$ contributions. Calculations predict that the band is accompanied, at about 50 nm on its blue side, by a stronger band (f = 0.44), also characterizable as $\pi - \pi^*$. Such a band has in fact geen observed,[2] and is listed on Table 2.

In the case of the controversial cyclobutane derivative **10**, we have results for a complete skeleton (Fig. 1, all hydrogens included in the calculation). The main contributions to the π and π^* MO's are:

$$\pi = 0.178C^1(\rightarrow C^6) - 0.161C^1(\rightarrow C^7) + 0.208C^6(\rightarrow C^1) - 0.192C^7(\rightarrow C^1) + 0.588\pi_2 + 0.612\pi_3 - 0.069\pi_4 - 0.313\pi_0$$

$$\pi^* = 0.144C^6(\rightarrow C^1) - 0.132C^6(\rightarrow C^5) - 0.130C^7(\rightarrow C^1) + 0.135C^7(\rightarrow C^5) + 0.537\pi_2 - 0.389\pi_3 - 0.497\pi_4 + 0.480\pi_0.$$

In these expressions, π_i are π-type AO's in the C=C–C=O moiety, $C^i(\rightarrow C^j)$ are σ-hybrids, directed from carbon C_i to carbon C_j. The squares of the coefficients are marked in Fig. 1. These may be taken as an approximation to the charge-distribution due to an electron in the π or π^* MO.

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† That is, the C hybrid-orbital that points at H, and the 1s–AO on the corresponding hydrogen. The discrepancy (of perhaps 10 nm, Table 2) in the case of umbellulone is attributable, at least in part, to the lower quality of the input geometry (see above, main text). The n – π^* transitions are reproduced well at the pi-electron level (cf. [28,29]) but blue-shifted at an incomplete σ-input; they revert to their correct location when C–H bonds are included.

In the molecules studied here, trends in computed oscillator strengths can be assumed to parallel trends in the extinction coefficient, because the general form of the bands, and their width, do not change much on going from one compound to another.

Further technical and other details will be given elsewhere.

By these data, the effect of the 4-membered ring on the $\pi - \pi^*$ excitation can be analyzed as 3-fold.

(a) The 4-membered ring contributes to both the π and π^* MO's, and thus extends the system that undergoes $\pi - \pi^*$ excitation.

(b) The computed total electronic charges (not listed here) indicate that, in the ground state, there is a transfer of charge from the enone to the 4-membered ring. It is attended by an elevation of the π-MO (with respect to that of, say, acrolein; this might be likened to the elevation of the highest-occupied π-MO on passing from butadiene to hexatriene). On $\pi - \pi^*$ excitation, some of the extra charge in the 4-membered ring drifts back, with a small lowering of π^*. The presence of cyclobutane induces therefore a narrowing of the $\pi - \pi^*$ gap.

(c) Figure 1 shows that excitation is accompanied by a re-distribution of charge *within* the 4-membered ring. In the source orbital (π), the distribution is unsymmetrical, with charge concentrating in those bonds that are close to C=C, namely, C_1–C_6 and C_1–C_7. In the destiny orbital (π^*), some of the charge on C_1 is lost to the enone, and that on C_6 and C_7 shifts away from the proximity of the double bond, to distribute itself almost evenly among all C→C links that emanate from these vertices ($C_6 \rightarrow C_1$, $C_6 \rightarrow C_5$; $C_7 \rightarrow C_1$, $C_7 \rightarrow C_5$). In more pictorial terms: on $\pi - \pi^*$ excitation, the charge-cloud within the 4-membered ring "mimics" the flow of charge, from C=C towards C=O, at the C=C–C=O portion of the molecule.

It is interesting to note that the three effects relate to carbons 1, 6 and 7, but not to carbon 5. The cyclobutane ring affects therefore the spectrum through its linkage to the C=C end of C=C–C=O, less so by its proximity to C=O. Indeed, the bathochromic-hypochromic shift is observed even in molecules where C=O is not in a position to carry cross-conjugation to C=C: two cases in point, namely myrtenal (**12**) and pinocarvone (**13**), are just those that served Moore and Fisher as the starting point in their discussion.[1]

Summing up. When compared with derivatives of the moocyclic enone **2**, the UV spectrum of [3.1.1] enones **1**, as well as of the [3.1.0] structure **3**, shows a bathochromic-hypochromic shift. The shift in the [3.2.1] molecule **7** is much smaller.

Two possible interpretations of the phenomenon may be offered.

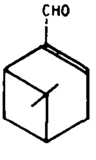
(a) The presence of small rings in **1** and **3** induces strain which distorts C=C–C=O from its geometry in **2**, and this brings forth spectral shifts.

(b) The small ring forms part of that region of the molecule that undergoes excitation, and by extending the chromophore affects the spectrum.

We have estimated, by molecular-mechanical techniques, molecular geometries and strain energies, and carried out MO calculations on both the isolated C=C–C=O in the various molecules, and on their overall skeletons.

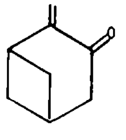
By calculation, C=C–C=O distortion cannot account for the shifts; however, a model with chromophore-extension can. Details have been given for the [3.1.1] structure in Fig. 1. The 4-membered ring participates in absorption both by donating charge and by simultaneously mimicking the electronic events within C=C–C=O. The participation depends mainly on its linkage to C=C, less so on proximity to C=O.

Two further remarks are here in line. First, the effect depends on the detailed structure, so that our conclusions for **1** cannot be carried over unmodified to other cyclobutane derivatives. Second, the quantitative aspect of the theoretical analysis should not be disregarded: qualitatively, our discussion of the [3.1.1] system is extensible to systems [3.1.0] and [3.2.1]; quantitatively, structural details are such that the computed spectra in the three cases are unlike, as are the observed ones.



12

λ_{max}(EtOH) 247



13

λ_{max}(EtOH) 242

EXPERIMENTAL

2-*Methylbicyclo*[3.2.1]*oct*-2-*ene*. Bicyclo[3.2.1]octan-2-one was treated with MeMgI according to the procedure of Petit *et al.*[13] The resulting epimeric mixture of alcohols was most conveniently dehydrated by slow heating to 150° under N_2, in the presence of an excess of anhyd oxalic acid.[30] Washing with $NaHCO_3$aq, followed by distillation, afforded 2-methylbicyclo[3.2.1]oct-2-ene, b. 155° (lit.[13] 155°).

2-*Methylbicyclo*[3.2.1]*oct*-2-*en*-4-*one* (7). To a soln of the former compd (742 mg) in AcOH (14 ml) and Ac_2O (7 ml), was added, under flowing N_2, sodium chromate (1.62 g) in small portions. The mixture was stirred overnight under N_2, then diluted with water, extracted with ether, and the combined extracts washed with $NaHCO_3$, dried and distilled, b. *ca.* 120°/20 min.

2-Methylbicyclo[3.2.1]oct-2-en-4-one (300 mg) was isolated by preparative TLC (30% ether in petroleum ether, silica gel, R_f 0.3), and the analytical sample further purified by preparative GLPC (5% C20-M on Chrom G, 180°). IR (CCl_4) 1685, 1625 cm^{-1}; NMR (CCl_4, downfield from TMS) δ 5.5, 1.97 (d, J = 1 Hz); *m/e* 130 (m$^+$, 32), 108 (4), 94 (100), 67 (38); m$^+$ 136.0876 ($C_9H_{12}O$ requires: 136.0888).

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