

Molecular-Orbital Realizations of the Bent-Bond Model: Spiranic Derivatives of Cyclobutanone[★]

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In the frame of our studies on small-ring compounds, we deal here with structures in which a three-membered ring and a carbonylated four-membered ring are fixed in close proximity. The theoretical approach is through an all-valence electron semiempirical method. The experimental background, based on results of other workers, comprises mainly UV and IR spectral data. The main topics to be discussed are: charge-donation and charge-transfer from the 3-ring, hypsochromic and bathochromic shifts of electronic transitions related to the carbonyl, direct substituent effects on the carbonyl stretching frequency, and the across-ring interaction in cyclobutanone.

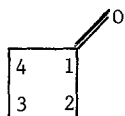
Key words: Hybrids, linear combination of \sim – Saturated organic compounds, MO treatment of \sim – Small rings – Carbonyl stretching frequency

1. Introduction

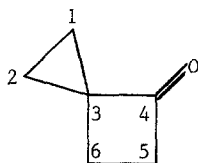
In the present report we discuss electronic properties and the spectra of cyclobutanone (I) and four of its derivatives: spiro[2.3]hexan-4-one (II), spiro[2.3]hexan-5-one (III), dispiro [2.1.2.1]octan-4-one (IV), and dispiro[2.0.2.2]octan-7-one (V). Molecules II–V, in which cyclobutanone is spirannically fused to cyclopropane(s), have been prepared, and their spectra recorded [3].

We have recently called attention to certain peculiarities of cyclopropane and cyclobutane. Both can extend conjugation [2, 4]. Cyclobutane differs from larger rings in manifesting a diagonal (across-ring, C_1 – C_3) interaction [5]. In cyclopropyl-ketones, an absorption of charge transfer, from the ring to the carbonyl, has been predicted and observed [6]. It is our intention now to observe what may

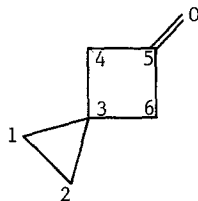
[★]Part XII in series. For previous papers, see Refs. [1, 2].



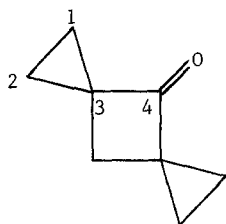
I. Cyclobutanone



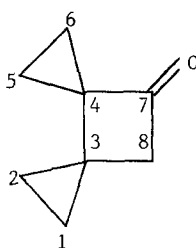
II. Spiro[2.3]hexan-4-one



III. Spiro[2.3]hexan-5-one



IV. Dispiro[2.1.2.1]octan-4-one



V. Dispiro[2.0.2.2]octan-7-one

happen when the three moieties – 3-ring, 4-ring, and carbonyl – are brought into close proximity and the various effects forced to act in cooperation. Our conclusions are drawn in Sect. 5. Details on method and results, and relevant literature data, are given in Sects. 2–4.

The method we use, here as before [1, 2, 5, 6], is LCHO (Linear Combination of Hybrid Orbitals). This is a semiempirical all-valence electron scheme, which was devised specifically for the computation of spectral quantities in organic molecules. It is similar in conception to Sandorfy's "H-approximation" [7], but differs from it in the formulation and parametrization [1], and in making hybridization indices depend heavily on the geometry. The basis set comprises four sp^m hybrids at each carbon, and valence orbitals ($1s$ or $2s$, $2p$, respectively) on hydrogen and oxygen. As applied to molecules I–V, this is seen to be a MO realization of Coulson and Moffitt's bent-bond model [8], extended to include elements other than carbon.

Use of a semiempirical method seems nowadays to warrant an apology [9]. Another apology is required for not using better known semiempirical schemes, such as CNDO/2-CI [10] or CNDO/S [11]. Here we deal with the gradation of spectral properties along a series of small-ring compounds; it seems desirable to employ a method that has withstood test in this particular domain. For example, the first strong absorption of cyclobutanone occurs around 51.6 kK [12]; the computed numbers are 65.0 by CNDO/2-CI, 63.2 by CNDO/S [10], 51.9 kK by LCHO. A non-empirical approach is certainly to be preferred. But the effort required, even in calculating such small molecules as methane [13] or ethane [14], indicates that – for larger molecules – an approximation had better be attempted first.

2. Method

In applying LCHO to ketones, the basis set comprises:

- a) at each hydrogen, a $1s$ orbital;
- b) at each carbon, four sp^m hybrids (carbonylic carbon: one $2p\pi$ -orbital and three sp^m hybrids), with indices m interdependent with the assumed valence angles through orthogonality relations [15];
- c) at each oxygen (s^2xyz^2) one $2s$ and three $2p$ orbitals, of which one (z) is considered as the site of the nonbonding electron pair (n), cf. [16].

The formulation of integrals, and parameters for carbon and hydrogen, have been reported [1]. Certain of the oxygen parameters come from the “ π -only” work [17]; others were added as required here. No optimization was attempted: in terms of Ref. [1], a_O in

$$(Q; ii) \sim Z_O \exp(-a_Q r_{O1}^2)$$

was taken equal to a_C , $\beta_{O, 2s}$ chosen such that

$$\beta_{O, 2s}/\beta_{O, 2p} = \beta_{C, 2s}/\beta_{C, 2p}$$

and the correction A to off-diagonal monocentrics on oxygen assumed null (see Table 1).

In the first stage of a calculation, the indices m of carbon hybrids and the orientation of directed orbitals are defined. With small rings, this process is often approximate. For example, in cyclobutanone (I), hybrid $C_3 \rightarrow C_2$ is definable in terms of the inter-substituent angle $\theta(\text{HC}_3\text{H}$ in this case):

by symmetry, $m(C_3 \rightarrow C_2) = m(C_3 \rightarrow C_4)$, hence

$$\text{by orthogonality, } m(C_3 \rightarrow C_2) = (1 - 3 \cos \theta) / (1 + \cos \theta)$$

cf. [15]. However, in spirohexanone II the symmetry argument is only a simplifying assumption; in III – where symmetry could be used – bent-bonding renders $\theta(C_1 C_3 C_2)$ undefined.

In the second stage, all necessary integrals are evaluated [1] in internal coordinates [19]. The method is rotation-invariant, because hybrids – and quantities related

W_μ	$I_\mu - (l-1)(\mu\mu, \mu\mu)$
I_{2s}^b	-32.29 eV
$I_{2p}(l=1)$	-17.21 eV
$I_{2p}(l=2, \text{i.e. } n)$	-14.75 eV
Orbital exponent ^c	4.550
Orbital exponent ^d	2.566
β_{2s}^e	-15.929 eV
β_{2p}	-20.000 eV
a^e	0.2456 Å ⁻²

Table 1. Oxygen parameters^a

^a l = occupation number; n = nonbonding pair.

^b Based on data in [18].

^c Slater value, in overlap and dipole length integrals (in [17b], this constant is misprinted).

^d In bielectronic integrals.

^e See text.

to them – are independent of a global coordinate system. It is not, however, invariant to hybridization. This is a sensitivity we wish to conserve, because a change in hybridization implies often, and is implied, by a change in geometry (e.g., reduction of $m(C_3 \rightarrow C_2)$ in I corresponds to closing θ , and *vice versa*). Anyhow, as our main interest lies with a multideterminantal representation of excited states, this insufficiency is probably only of minor consequence [20].

The third stage of the computation is a straightforward SCF-CI process. Input data for molecules I–V were approximate by necessity. Cyclobutanone was taken planar [21], shaped as in [22], with hybrids such that the bending angle $\sim 10^\circ$ (cf. $\sim 10.7^\circ$ in cyclobutane [23]). Spiranonones II–V were constructed by substituting $-\text{CH}_2-\text{CH}_2-$ for appropriate pairs of geminal hydrogens; cyclopropane angle 60° , bending angle 24° ; cf. [24].

3. Electronic Spectra

Consider unsubstituted cyclobutanone, Table 2. Despite probable non-verticality [12, 26], the computed transition energies are in sufficient accord with the experimental to attempt assignments. The HOMO, denoted “ n ” by convention, is actually found to contain only $\sim 32\%$ of O_n , the “nonbonding” AO on oxygen:

$$\begin{aligned} \varphi(n) = & -0.324[C_1(\rightarrow C_2)_\sigma - C_1(\rightarrow C_4)_\sigma] - 0.405[C_2(\rightarrow C_1)_\sigma - C_4(\rightarrow C_1)_\sigma] \\ & + 0.562[O_n] + \dots \end{aligned}$$

(O_n antibonding with C_1-C_2 and C_1-C_4). The next MO has π symmetry, but is based mainly on C–H bonds:

$$\varphi(\pi) = 0.272[C_\pi] + 0.543[O_\pi] + \dots$$

There are two deeper orbitals that contain O_n , and two that contain π , but these do not contribute to the spectrum in the range of interest. LVMO is essentially π^* ,

$$\varphi(\pi^*) = 0.691[C_\pi] - 0.570[O_\pi] + \dots$$

In these terms, the first transition is $n \rightarrow \pi^*$. The second band is interpreted as made up of $n \rightarrow \sigma^*$ transitions (not $n' \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ [10]). The cluster that follows

Table 2. Electronic spectrum of cyclobutanone

Energy ^a (expt. ^b)	Current assignment	This calculation Energy ^a	Assignment
30.58–38.00 (~ 330 nm) ^c	$n-\pi^*$	32.1 (0)	$A_2, n-\pi^*$
48.53–54.95 (~ 190 nm)	$B_1, n-\sigma^*$ (CO)	51.3 (0.000)	$A_1, n-\sigma^*$ (CH, CC)
	or $n'-\pi^*$	51.9 (0.004)	$B_1, n-\sigma^*$ (CO, CH)
	or $\sigma-\pi^*$	53.4 (0.001)	$B_1, n-\sigma^*$ (CO)
55.5–59.5 (0.007) (~ 170 nm)	$B_2, n-\sigma^*$ (CO)	57.3 (0.003)	B_2, σ (CH, CO)– π^*
		57.9 (0.017)	$A_1, n-\sigma^*$ (CC)
		58.8 (0.003)	$B_1, n-\sigma^*$ (CH, CO)
		61.5 (0.041)	$A_1, n-\sigma^*$
		62.0 (0.014)	$B_2, n-\sigma^*$ (CH)
59.96	Rydberg, $n-4s$	65.5 (0.000)	$B_1, n-\sigma^*$
62.45 (0.2)	$A_1, \pi-\pi^*$	65.5 (0.000)	$A_1, \sigma-\sigma^*$
		66.9 (0.205)	$A_1, \pi-\pi^*$

^a In kK. Oscillator strengths in parentheses.

^b Data compiled from Refs. [10, 12, 25, 26].

^c In isoctane [27]: 265^s ($\epsilon=13$), 272 (17), 280 (20), 289 (19), 301^s (14), 313^s (7), where *s* denotes a shoulder.

is essentially $n \rightarrow \sigma^*$. At cutoff (~ 62 kK) one observes the $\pi-\pi^*$ absorption; by computation, this is only 44% in $\pi-\pi^*$, the rest being made up of $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$. Although Rydberg orbitals were not included in the calculation, CI was extensive, and we believe that – qualitatively at least – the analysis in Table 2 is representative (cf. [1]).

Spiranic fusion, as in molecules II–V, is expected to produce three effects: a hypsochromic shift of $n-\pi^*$, a bathochromic shift of $\pi-\pi^*$ [28–30] and the appearance of a charge-transfer band $\Delta \rightarrow \pi^*$ (where Δ denotes the three-membered ring) [6]. As yet, only the near ultraviolet range has been scanned, in isoctane solution [3]. It contains two broad massifs: one at around 280 (finely structured), the other at around 200 nm.

Our results for spirohexan-4-one (II), Table 3, illustrate all three of the expected effects. First, the charge-transfer band $\Delta \rightarrow \pi^*$ is predicted at around 180 nm; such a band had been observed and assigned in several *alpha*-cyclopropyl ketones [6]. Second, interaction with the carbon skeleton of cyclopropane splits the $\pi-\pi^*$ state, and one of its components *invades* the near UV (calc. 194, obs. λ_{\max} 205 nm). In this molecule,

$$\varphi(\pi) = 0.158[C_\pi] + 0.429[O_\pi] + 0.741[C-C \text{ in } \Delta] + \dots$$

$$\varphi[\pi^*] = 0.641[C_\pi] - 0.542[O_\pi] + 0.458[C-C \text{ in } \Delta] + \dots$$

The states denoted in Table 3 as $\pi-\pi^*$ and $n-\sigma^*$ (CH, CO) contain, respectively, 44 and 18% of $\pi-\pi^*$. Third, $n-\pi^*$ is computed at a somewhat higher energy than in cyclobutanone.

Table 3. Electronic spectrum of spiro[2.3]hexan-4-one (II)

E (kK)	λ (nm)	Oscillator strength	Assignment ^a	Experimental ^b
32.3	309	0	A' , $n-\pi^*$	270 ^s (22), 278.5 (27), 286 (29), 291 ^s (27), 296 ^s (22)
51.6	194	0.023	A' , $\pi-\pi^*$	190–235, max. 205 (990)
53.2	188	0.018	A' , $n-\sigma^*$ (CH, CO)	
53.8	186	0.005	A' , $\Delta-\pi^*$	
55.2	181	0.005	A' , $n-\sigma^*$	

^a Δ denotes the three-membered ring.

^b Given: λ (nm) and ϵ in isoctane solution [3]; s denotes a shoulder.

In dispirane IV there are two cyclopropyls vicinal to the carbonyl. As Table 4 shows, calculation foretells a bathochromic-hyperchromic shift of $\pi-\pi^*$ with respect to that in monospirane II. So does one observe: in II, $\lambda_{\max} = 205$ ($\epsilon = 990$); in IV, $\lambda_{\max} = 213.5$ nm ($\epsilon = 1200$). For comparison, the corresponding absorption in the cyclopentanone analog of II (i.e., spiro[2.4]heptan-4-one) has, in a non-polar solvent, $\lambda_{\max} = 194.5$ ($\epsilon = 3020$) [30]¹. In fact, it is not only λ_{\max} that shifts to an unusual position: the entire band, in II and IV, is observed *above* 190 nm. We do not know of other saturated ketones in which the 200-band can be recorded, in its entirety, by a near-UV spectrometer.

Spirohexan-5-one (III), unlike II and IV, carries the spiro-junction at position *beta* to the carbonyl. Its near-UV spectrum, Table 5, reveals how short-ranged the cyclopropane effect apparently is: the recorded absorptions are essentially those of cyclobutanone. Yet, calculation suggests a certain hypsochromic shift of $n-\pi^*$, in III with respect to I, and this seems to be substantiated by experiment. If the shift is real, then it must be due to the particular electronic structure in cyclobutanone: in the cyclopentanone analog of III (i.e., spiro[2.4]heptan-5-one) it is nonexistent [29].

Now, in III, one expects to detect consequences of the cyclobutanic *diagonal*

Table 4. Electronic spectrum of dispiro[2.1.2.1]octan-4-one^a (IV)

E (kK)	λ (nm)	Oscillator strength	Assignment	Experimental
31.4	318	0	A_2 , $n-\pi^*$	283 (42), 288 ^s (39), 296 ^s (29)
50.2	199	0.045	A_1 , $\pi-\pi^*$	195–255, max. 213.5 (1200)
51.8	193	0.004	B_2 , σ (CO) $-\pi^*$	
54.0	185	0.052	B_1 , $n-\sigma^*$ (CH, CO)	
54.2	184	0.020	B_1 , $n-\sigma^*$, $\Delta-\pi^*$	

^a See footnotes to Table 3.

¹ In this paper, ketone I is spiro [2.4] heptan-4-one.

Table 5. Electronic spectrum of spiro[2.3]hexan-5-one^a (III)

E (kK)	λ (nm)	Oscillator strength	Assignment	Experimental
32.5	308	0	$A_2, n-\pi^*$	251 (21), 256 (21), 263 (21), 272 (18), 281 (19), 291 (18), 305 (23), 316 (6)
52.0	192	0.011	$A_1, n-\sigma^*$ (CH)	tail
54.1	185	0.002	$B_1, n-\sigma^*$ (CO)	
56.6	176	0.001	$B_1, n-\sigma^*$ (CO)	
58.9	170	0.001	$A_1, \pi-\pi^*$	
59.3	169	0.450	$A_1, \pi-\pi^*$	

^a See footnotes to Table 3.

interaction, i.e., the weak through-space interaction between carbons 3 and 5 [5]. By calculation, this is small, but noticeable:

$$\varphi(n) = 0.551[\text{O}_\pi] + 0.283[\text{C-C in } \Delta] + 0.091[\text{C-H in } \Delta] + \dots$$

$$\varphi(\pi^*) = 0.678[\text{C}_\pi] - 0.565[\text{O}_\pi] + 0.163[\text{C-C in } \Delta] + 0.012[\text{C-H in } \Delta] + \dots$$

$$\varphi(\pi) = 0.094[\text{C}_\pi] + 0.259[\text{O}_\pi] + 0.806[\text{C-C in } \Delta] + 0.149[\text{C-H in } \Delta] + \dots$$

(in $\varphi(\pi)$ and $\varphi(\pi^*)$, $[\text{C}_\pi]$ is bonding with $[\text{C}_3 \rightarrow \text{C}_1]$ and $[\text{C}_3 \rightarrow \text{C}_2]$). The outcome of this mixing is that, with respect to cyclobutanone, $\pi-\pi^*$ should shift to the red, $n-\pi^*$ to the blue.

As for dispirooctan-7-one (V), we have reasons to suspect that the geometry assumed was of a lower quality than in the other cases (see below). The data are assembled in Table 6. Note that the $n-\pi^*$ band is here observed in the very low wavelength range of 240–260 nm.

A note, in concluding, on the fine structure manifested by $n-\pi^*$ in a non-polar solvent. This is usual in unsaturated ketones [31] and, among the saturated, characterizes cyclobutanone [27] and cyclopentanone [32], but not cyclohexanone [33]. The separation between successive vibrational subbands, 1000–1200 cm^{-1} , has been attributed to the carbonyl stretch in the excited state [31]. In unsaturated ketones, the $n-\pi^*$ band lies usually to the red of 290 nm; in the saturated – whether structured or not – it lies to the blue [34]. What makes spiranes III and V exceptional is that a *structured* band is observable at such a low wavelength. This must have to do with the nature of cyclopropane: 3,3-dimethylcyclobutanone, for example, absorbs above 270 nm [35].

4. Carbonyl Stretching Frequency

Factors that may affect the carbonyl stretching frequency ($\bar{\nu}$) have been discussed extensively. An early proposition related trends in $\bar{\nu}$ to the hybridization at the

Table 6. Electronic spectrum of dispiro[2.2.0.2]octan-7-one^a (V)

E (kK)	λ (nm)	Oscillator strength	Assignment	Experimental
32.3	310	0	A'' , $n-\pi^*$	240 ^s (204), 252 (266), 257 (216), 262 ^s (204)
50.7	197	0.057	A' , $n-\sigma^*$	max. 212 (1620)
54.1	185	0.027	A'' , $\Delta-\pi^*$	
54.3	184	0.008	A' , $n-\sigma^*$ (CH, CO)	
55.3	181	0.002	A' , $n-\sigma^*$ (CO)	

^a See footnotes to Table 3.

carbonyl group and, hence, to the strength of the C–C linkage [36]. More recent theoretical analyses of cycloalkanones stress the mechanical consequences of modifying the angle C–CO–C [37]. While this differentiation of effects is hard to substantiate [38], especially as hybridization is intricately linked with molecular geometry and ring size, a more pragmatic approach – recast in quite different terms – has now been proposed [39]. According to this, the carbonyl stretching frequency is taken to reflect essentially the corresponding force constant, and this is analyzed in terms of two factors. One, “indirect”, is the local geometry at –CO– (this should encompass somehow the hybridization effect); the other, “direct”, refers to the effect of substituents on C=O. One may note that the “indirect–direct” terminology provides the investigator with a *modus operandi*: if calculations for a series of compounds are based on standard geometries, one is in position to detect direct effects; when, however, accurate geometries are used (e.g., experimental), the more subtle indirect influences may be revealed. Previously detected relations, between $\bar{\nu}$ and theoretical indices of the C=O bond (Hückel [40, 41] and SCF [42] π -bond orders, π -charge density on oxygen [41], σ and π ionic character in C–O [39]), are probably manifestations of the direct environmental effect.

As our calculations were performed for non-optimized geometries, with the cyclobutanone moiety transferred unmodified from one molecule to another, a search for “direct” indices was undertaken. In Table 7, we compare the experimental

Table 7. Overlap populations and carbonyl stretching frequencies^a

Molecule	P	P'	$\bar{\nu}$ from P	$\bar{\nu}$ from P'	$\bar{\nu}$ (expt.)
IV	1.0332	0.0889	1773	1772	1772
V	1.0354	0.0975	1781	1782	1774
II	1.0350	0.0964	1780	1781	1782
I	1.0374	0.1043	1789	1790	1788
III	1.0377	0.1052	1790	1791	1791

^a Frequencies ($\bar{\nu}$) in cm^{-1} . Experimental values (in CCl_4 solution) from [3]. The expt. error is probably $\pm 2 \text{ cm}^{-1}$.

frequencies (in CCl_4 [3]; $\bar{\nu}$ is rather solvent sensitive [35]) with two measures of overlap population in the carbonyl. The first,

$$P = p[\text{C}(\rightarrow\text{O})_{\sigma}; \text{O}(\rightarrow\text{C})_{\sigma}] + p[\text{C}_{\pi}; \text{O}_{\pi}],$$

is the sum of populations in the σ and π contributions to $\text{C}=\text{O}$ bonding. The other, P' , is the sum of *all* populations in $\text{C}=\text{O}$ (so-called “reduced” overlap population). The use of P' draws on the observation that, within the carbonyl group, there are non-zero overlap populations other than those in P , of which $p[\text{C}(\rightarrow\text{O})_{\sigma}; \text{O}_{2s}]$ is negative.

Excluding molecule V, both P and P' are found to verify a linear regression (corr. coeff. > 0.98),

$$\bar{\nu}(\text{CCl}_4)/\text{cm}^{-1} = 3875P - 2231$$

$$\bar{\nu}(\text{CCl}_4)/\text{cm}^{-1} = 1122P' + 1673.$$

Inspection of other indices suggests that the trend has to do with a short-range charge donation, from a three-membered ring to vicinal positions, and vicinal only, on cyclobutanone. Thus, III resembles I, but II, IV (and V) are different. For V, we compute $P = 1.0354$, $P' = 0.0975$, whereas incidence with the experimental requires 1.0335 and 0.0900. Qualitatively, the deviation is insignificant; quantitatively, it cannot be passed by. A possible explanation is that the eclipsed α, β -disubstitution imposes in this molecule such changes of structure (e.g., at angles $\text{C}-\text{CO}-\text{C}$ and $\text{C}-\text{C}=\text{O}$) which render the assumed geometry less representative than in I–IV. In other words, an “indirect” effect is being overlooked.

Charge donation, from cyclopropane to the four-membered ring, should be reflected in the dipole moment, which is an observable. In cyclobutanone, charge separation resides virtually within the carbonyl and $\text{C}-\text{H}$ bonds; in spirohexan-5-one (III), on the other hand, there is a net positive charge on the three-membered ring, and net negative at methylenes 4 and 6. As a consequence, the centers of positive and negative charge shift from the carbonyl inwards, and their distance diminishes. A rough calculation, excluding overlap and polarization contributions, yields dipole moments of 2.53 D in I, 2.43 D in III.

Experimentally, the dipole moment of cyclobutanone is 2.89 in the gas phase [43] and 2.76 D in solution (benzene, 25° [44]). For spirohexan-5-one (III) one reports 2.58 D (benzene, 20° [3]). We are not aware of another saturated ketone with such a low dipole moment.

To come back to the stretching frequencies, regularities as in Table 7 are expected to hold only for certain cyclobutanones. In a wider range of molecules, it is the “indirect” effect (carbonyl local geometry) that predominates [39]. Yet – and this has still to be checked – the findings above suggest that overlap populations provide a key, *within* classes of similar compounds, to delicate modifications in $\bar{\nu}$.

5. Conclusion

In this section, we resume and interpret briefly the various phenomena encountered.

5.1.

A cyclopropane ring, vicinal to the carbonyl, brings about a hypsochromic shift of the $n-\pi^*$ band. This is a general phenomenon which has been commented upon in other contexts [28, 29]. Computationally, $n-\pi^*$ is obtained as an extensive mixture of configurations, and the interpretation is not straightforward.

5.2.

A cyclopropane ring (Δ), vicinal to the carbonyl, brings about a bathochromic shift of the $\pi-\pi^*$ band. There are grounds to anticipate this from other evidence [30], but the shift in cyclobutanones is extreme. The effect is due to a raising of $\varphi(\pi)$ through interaction with Δ .

5.3.

In ketones where cyclopropane is vicinal to the carbonyl, a charge-transfer transition ($\Delta\rightarrow\pi^*$) occurs at around 180 nm. This band was not sought experimentally in molecules II, IV, and V, but has been observed by us in other instances [6].

5.4.

A cyclopropane ring, *beta* to the carbonyl, exerts no noticeable influence on the near-UV spectrum [29]. If, however, the carbonyl is embedded in cyclobutane, $n-\pi^*$ shifts to the blue and $\pi-\pi^*$ is predicted to shift to the red. This is a manifestation of a general property of cyclobutanes, the diagonal C_1-C_3 interaction [5].

5.5.

Junction of cyclopropane to cyclobutanone (and, possibly, to other electron attracting residues) brings about a short-range charge donation from the three-membered ring. This is reflected in the very low dipole moment of spirohexan-5-one (III).

5.6.

A cyclopropane ring, vicinal to the carbonyl in cyclobutanone, acts to reduce overlap populations in $C=O$; the reverse, but smaller by an order of magnitude, is true for the *beta*-junction. The ensuing populations correlate linearly with the measured stretching frequencies. This is a manifestation of the "direct" effect that substituents may have on the carbonyl [39].

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