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Comments on the Electronic Properties of Cyclopropane, Cyclobutane, and Cyclohexane

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Spectral quantities of cyclopropane, cyclobutane, cyclohexane, and of several derivatives, have been calculated by a semiempirical all-valence electron SCF-CI MO method. In cyclopropane, HOMO is practically localized in the carbon-frame, and LVMO is purely so. In cyclobutane, these two MO's are based on C–H bonds, while cyclohexane holds an intermediate position. Despite the overall similarity – experimental and computed – of the spectra of these molecules, assignments are non-parallel. Like cyclopropane, cyclobutane can extend conjugation, but to a diminished degree; cyclohexane behaves in this respect like an acyclic alkane. An interpretation of this gradation, in terms of the nature of high-lying MO's, is proposed.

Key words: Hybrids, linear combination of ∼ – Saturated organic compounds, MO treatment of ∼ – Spectra, far ultraviolet ∼ – Cyclobutane, auxochromic effect of ∼

1. Introduction

Cyclopropane and cyclobutane have both attracted attention because of their ability to interact with, and to modify – cyclopropane more, cyclobutane less – the electronic spectrum of substituting chromophores [1–3]. In the unsubstituted rings, absorption onsets at lower frequencies than in other alkanes [4]. Cyclohexane does not extend conjugation, but its spectrum is similar to that of cyclopropane [4]. Much effort has been devoted to the recording and interpretation of the cyclopropane spectrum [5], and theoretical analyses, in various degrees of refinement, have been published [6–8]. Less attention has been paid to the spectra of cyclobutane and cyclohexane, but they have been recorded and discussed [4, 9–11].[1]

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[1] We thank Prof. Sandorfy for a large-scale copy of the cyclopropane and cyclobutane absorption curve.

As a step towards a general electronic theory of cyclic alkanes, we present here semiempirical MO results on cyclopropane, cyclobutane, cyclohexane, and some relevant derivatives. The method used was the all-valence-electron LCHO ("Linear Combination of Hybrid Orbitals", see below). A single geometry (D_{3h}, D_{2d}, D_{3d}) was taken for each of the cycloalkanes. The resulting picture is necessarily crude, because Rydberg orbitals were not included in the basis-set, and non-vertical transitions not looked into (cf. [4, 7]). Still, configurational-interaction (CI) was quite extensive for this type of work, so that the omission of non-valence orbitals should not be viewed as implying the loss of essential species of orbital-symmetry and size [12]. Incidentally, attempts to improve semiempirical all-valence electron results, by implementing the basis-set with Rydberg orbitals, have not led to clear-cut conclusions [13]. As for non-verticality, the general resemblance of the computed and observed spectra of cyclobutane and cyclohexane, suggests that it is less decisive in these molecules than it might be in cyclopropane [4]. Anyhow, our understanding of the experimental spectra is not sufficiently advanced to define discrepancies between them and the numbers computed.

2. Method

LCHO is a semiempirical all-valence electron SCF-CI MO method which is based on bonding orbitals and AO's, and is specifically oriented towards the computation of spectral quantities [8, 11]. In a way, it is analogous to Sandorfy's "H-approximation" [14], but application indicates that it is much wider in scope [15]. As used here, the basis-set comprises four hybrid sp^n orbitals at each carbon, with indices n (not necessarily integer) determined from the molecular geometry, and valence orbitals ($1s$ or $2s$, $2p$, respectively) on hydrogen and oxygen. When applied to cyclopropane and cyclobutane, this is seen to be a MO realization of Coulson and Moffitt's bent-bond model [16], except that hydrogens are here included and cyclobutane taken in its realistic non-planar geometry.

Parameters for carbon and hydrogen were taken over from previous work [17]. Hydrogen parameter-values were arrived at by fitting to strong absorptions in the spectra of methane, ethane, and propane [18]. No adjustments were done in dealing with the cyclic alkanes. In the CI process, 53 mono-excited configurations were involved.

The geometries of cyclopropane and cyclobutane were those described [8, 11]. The geometry of other molecules was derived by molecular-mechanical optimization [19].

3. Results

The computed sequence of molecular orbitals is given in Table 1. For cyclopropane, a comparison is possible with *ab initio* results [7]: our eigenvalues for occupied levels are quite close to the *ab initio* numbers, but the sequence of virtual orbitals differs somewhat. However, a considerable re-ordering takes place at the CI stage.

Table 1. Molecular orbitals

No.	Sym.	%C–C	No.	Sym.	%C–C	No.	Sym.	%C–C
Cyclopropane[a]			Cyclobutane[b]			Cyclohexane[c]		
1, 2	e'	80	1	a_1	0	7	a_{2u}	36
3, 4	e''	0	2	b_2	97	8, 9	e_g	12
5, 6	e'	17	3, 4	e	1	10, 11	e_u	41
7	a_1'	1	5	b_2	3	12	a_{2g}	100
8	a_2''	0	6, 7	e	34	13, 14	e_g	52
9 (LVMO)	a_2'	100	8	a_2	100	15	a_{2u}	12
10, 11 (HOMO)	e'	90	9, 10	e	65	16	a_{1g}	2
12, 13	e''	0	11	a_1	1	17, 18 (LVMO)	e_u	45
14	a_1'	33	12 (LVMO)	b_2	0	19 (HOMO)	a_{1g}	12
15	a_2''	0	13 (HOMO)	a_1	1	20, 21	e_g	51
16, 17	e'	11	14, 15	e	72	22, 23	e_u	3
18	a_1'	66	16, 17	e	3	24, 25	e_u	62
			18	b_1	100	26	a_{1u}	100
			19	b_2	0			

[a] Eigenvalues (eV): 8, 3.40; 9, 3.04; 10, 11, −11.80; 12, 13, −12.50.
[b] Eigenvalues (eV): 11, 3.24; 12, 3.19; 13, −10.90; 14, 15, −11.35.
[c] Eigenvalues (eV): 16, 3.42; 17, 18, 3.24; 19, −11.03; 20, 21, −11.08.

A useful feature of LCHO is that each of the basis orbitals refers to one particular bond, so that MO's are assignable either to skeletal C–C bonding, or to C–H bonds, or as mixed. Data are given in Table 1; they become of importance when substituted rings are discussed.

Table 2 lists the CI transition-energies for cyclopropane. We have no new interpretation for the controversial absorption near 54 kK [4], but obtain the first triplet at 53.1 kK. The computed singlet-triplet separation for this excitation (E', 65% 10, 11 → 9 in V, 93% in T) is 6.63 kK.

Table 2. Cyclopropane transition energies[a]

Energy	f	Symmetry and main contributor	Expt. band[b]	Previous interpretation[b]
59.7	0.1	E' (10, 11 → 9)	60–66 (max. 63)	E' ($e' \rightarrow a_1'$, 3s and $e' \rightarrow 3p$, superposed)
66.7	0.0	E' (10, 11 → 5, 6)	67–72 (max. 69.5) $f \sim 0.04$	$E'(e' \rightarrow e')$ or $A_2''(e'' \rightarrow e')$
69.9	0.3	E' (10, 11 → 7)		
73.0	0.5	E' (12, 13 → 8)	74–85 (max. 80.5) $f \sim 0.7$	$e' \rightarrow 4p$, $e' \rightarrow 5p$ and E' ($e' \rightarrow a_2'$)
75.6	0.1	A_2'' (12, 13 → 5, 6)		
81.6	0.2	E' (10, 11 → 5, 6)		
82.0	0.2	A_2'' (10, 11 → 3, 4)		

[a] Only allowed transitions listed. Energies in kK.
[b] See Ref. [4].

Table 3. Cyclobutane transition energies[a]

Energy	f	Symmetry and main contributor	Expt. band[b]
58.0	0.00	$B_2\,(14, 15 \rightarrow 9, 10)$	56.8 (1,000)
62.4	0.00	$E\,(13 \rightarrow 9, 10)$	58.7 (1,300)
63.5	0.01	E	60.8 (1,700)
65.5	0.01	$E\,(14, 15 \rightarrow 12$, and $14, 15 \rightarrow 11)$	62.6 (2,000)
65.8	0.01	$B_2\,(13 \rightarrow 12$, and $14, 15 \rightarrow 9, 10)$	
66.0	0.00	E	
68.2	0.06	E	
70.2	0.29	$E\,(14, 15 \rightarrow 8$, and $13 \rightarrow 3, 4)$	71.2 (6,800) max.
70.3	0.01	$B_2\,(14, 15 \rightarrow 6, 7)$	
71.4	0.03	$B_2\,(13 \rightarrow 2)$	72.6 (7,100)
73.2	0.02	$E\,(14, 15 \rightarrow 5)$	
73.3	0.03	$B_2\,(13 \rightarrow 5$, and $14, 15 \rightarrow 3, 4)$	75.3 (7,900)
77.2	0.31	$B_2\,(14, 15 \rightarrow 3, 4)$	77.0 (9,500)
79.8	0.27	$E\,(14, 15 \rightarrow 2)$	79.2 (11,500) max.
81.7	0.02	$E\,(14, 15 \rightarrow 1)$	83.5 (11,200)

[a] Only allowed transitions listed. Energies in kK.

[b] Ref. [4]. Expt. molar extinctions (in parentheses) estimated from published curve [10].

In cyclobutane, ring-angle strain is milder than in cyclopropane, and one expects excitation processes to be simpler. The similarity of the computed spectrum (Table 3) to the experimental [10] suggests that our results are significant, at least as concerns symmetry and the regional character (CH → CH*, etc.) of transitions.

The main features in the spectrum of cyclohexane [9] are a structured absorption near 63 kK, a broad peak – most probably a valence-shell transition [4] – around 69 kK, a vibrational series starting at ca. 72 kK, and a high-energy transition, ca. 84 kK, also considered as valence-shell. These four features have their counterpart in the calculation (Table 4).

4. Discussion

We comment first on the changes predicted, in the regional character of molecular orbitals, as one passes from the three- to the four- and six-membered rings.

In cyclopropane, the highest occupied molecular orbital (HOMO) is essentially localized in the carbon frame, and the lowest vacant (LVMO) is purely so. The former is preceded, the other followed, by MO's that are based on C–H bonds. In cyclobutane, on the other hand, HOMO, LVMO, and LVMO + 1 are obtained as C–H; the next deepest and next highest orbitals are mixed but of appreciable C–C content. In cyclohexane, the regional character is blurred. If anything, the computed sequence of occupied levels resembles more that of cyclobutane: HOMO is predominantly C–H, and is followed by an orbital that contains an appreciable C–C percentage, then by C–H, and C–C again. In this respect, cyclopropane differs from the other two, which are more similar to *acyclic* alkanes [12, 18].

Table 4. Cyclohexane transition energies[a]

Energy	f	Symmetry and main contributor	Expt. band[b]
63.1	0.09	$E_u\,(19 \rightarrow 17, 18)$	63
64.9	0.01	$A_{2u}\,(20, 21 \rightarrow 17, 18)$	
68.6	0.13	$E_u\,(20, 21 \rightarrow 17, 18)$	
70.6	0.48	$A_{2u}\,(19 \rightarrow 15)$	69
71.4	0.11	$E_u\,(20, 21 \rightarrow 15)$	72
74.6	0.47	E_u	
76.8	0.03	A_{2u}	
78.1	0.01	$E_u\,(20, 21 \rightarrow 10, 11)$	
78.6	0.00	A_{2u}	
79.5	0.00	$E_u\,(20, 21 \rightarrow 7)$	
81.8	0.11	$E_u\,(20, 21 \rightarrow 7)$	
84.5[c]	0.11	E_u	84

[a] Only allowed transitions listed. Energies in kK.
[b] Refs. [4, 9].
[c] Close to CI limit.

Yet, the analysis above has also its quantitative aspect: unlike in cyclopropane, the two high-lying occupied levels, in cyclobutane and cyclohexane, are so close by eigenvalue that a reversal of their order may occur, e.g., under the influence of an interacting substituent. Moreover, the gap in cyclohexane is computed so small (0.05 eV) that the alternative sequence might be obtained for a slightly different input geometry, or when using another computational technique.[2] We come back to this point later.

In the spectrum of cyclopropane (Table 2), the first absorption (around 63 kK) is interpreted as CC → CC* (E'), the second (70) – as CC → CH* (E'), and the third (80) – as mixed (E' and A_2'') but predominantly CH → CH*.

In cyclobutane, HOMO is C–H, and the first virtual C–C orbitals (9, 10 and 8 in Table 1) are not low-lying. Assignments are therefore different. The CI analysis (Table 3) indicates a first cluster of weak absorptions (around 65 kK) as a group of overlapping CC, CH → CH* transitions (E and B_2). The second band (70) may be interpreted as analogous to CC → CC* in cyclopropane; it contains, however, an appreciable amount of CH → CC, CH* (E and B_2). The last band (80) is characterized as constituted mainly by two close absorptions, one CC(CH) → CH(CC)* (B_2), the other CC(CH) → CC* (E).

Cyclohexane is still different, despite the overall similarity of its spectrum to that of cyclopropane [4]. It is generally impossible to distinguish here the role of C–H bonds from that of the carbon-frame. The first absorption (63 kK, Table 4) is

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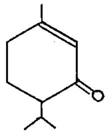
[2] This has indeed been reported for CNDO [9], but the input geometry was not specified. Users of CNDO/2 may recall that, just by inputting somewhat long C–C bonds in benzene, a degenerate sigma-pair is indicated as HOMO.

characterized as CH → CH, CC*, but is followed closely by transitions that are based on the complete molecular network. The next maximum (observed around 69 kK, computed at 70.6, A_{2u}) is assignable as CH → CH*. Absorptions at higher frequencies are again interpreted as mixed.

To conclude, the spectral onset is CC → CC* in cyclopropane, CC, CH → CH* in cyclobutane, CH → CH, CC* in cyclohexane. Cyclopropane holds a unique position among all alkanes; as the ring gets larger, excitation processes in the cycloalkanes resemble more and more those of the acyclic.

5. Effect on Chromophores

Cyclopropane is known as capable of extending conjugation [1–3], and this is ascribable to interaction of its highest-lying C–C orbital-pair (HOMO, *e′*, computed eigenvalue −11.80 eV, 90% C–C) with pi-orbitals of a suitably-oriented chromophore. A corresponding effect is expected in derivatives of cyclobutane: here also, a high-lying C–C orbital-pair is available (HOMO-1, *e*, computed eigenvalue −11.35 eV, 72% C–C). This is not indicated as the highest-occupied, but its eigenvalue does not differ greatly from the corresponding number in cyclopropane, and the (HOMO, HOMO-1)-gap is small anyhow, so that rearrangement may take place. What does make cyclobutane different from cyclopropane is that the high *e*-orbitals contain only about 70% of C–C bonding, which makes interactions less efficient: the substituent is linked to a carbon, and its interaction with distant C–H bonds is necessarily small. The minimum effect documented [20] is for chromophores linked to an acyclic alkyl radical, or to a ring larger than C_4. For example [20a], the pi → pi* transition of the enone grouping (C=C–C=O) shifts bathochromically by 12 nm for each alkyl added at position beta (–C=C–C=O → R–C=C–C=O).



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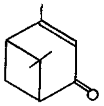

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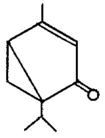

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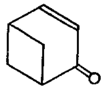

IV

Perhaps the best illustration of the gradual effect is provided by the series of piperitone (I), verbenone (II) and umbellulone (III). In ethanol, the pi-pi* absorptions (and molar extinctions) of these compounds have been given as [21]:

I, 235.5 nm (17,780)
II, 253 (6,840)
III, 261 (3,290).

Note that the shifts in compounds II and III come *on top* of the usual alkyl effect, which already operates in I. The "bare" chromophore, that is, *trans*-$CH_3CH{=}CHCOCH_3$, absorbs at 214 nm (12,300) [20b].

The absorptions in a non-polar solvent are: I, 225 nm (14,200); II, 241 (6,400) [15, 22]. Umbellulone (III) has not been studied in a non-polar medium but, judging from the solvent-effect in the other two cases, its absorption may be estimated as ca. 249 nm.

As a model for compound II, we have calculated the simplified structure IV.[3] A plausible geometry was first derived for II by molecular-mechanical techniques [19], and the three methyl groups were then replaced by hydrogens. Cyclobutane ring-puckering was obtained as 35°, in line with an experimental estimate, $34° \pm 8$, for a germane molecule [23].

By calculation, the (HOMO, HOMO-1)-reversal has taken place in IV. Here, the first two occupied MO's extend mainly on C=C–C=O, but contain some contribution from cyclobutane C–C bonding. Then come two MO's that are derived from the *e*-pair in the four-membered ring (14, 15 in Table 1), with eigenvalues computed as -11.21 and -11.69 eV. The first of these is based to 73% on cyclobutane, of which 49% are C–C; the corresponding numbers for the second are 72 and 46%. In other words, the cyclobutane portion of these orbitals contains only about 65% C–C bonding. The lowest-vacant MO (pi*) is based to 92% on C=C–C=O.

To check this picture – and, incidentally, the computational scheme – we compare the calculated with the observed location of the pi-pi* band. For IV, pi-pi* is computed at 225 nm ($f = 0.62$). The theoretical value for II, which has an additional methyl on the double bond, would then be around 237 nm. The corresponding numbers for I and III are 226 ($f \sim 0.75$) and 242 ($f \sim 0.4$), respectively. The agreement with available data, as regards the absorption wavelength and the sequence of intensities, is thus very good.

Effects of the type above are not encountered when dealing with rings larger than cyclobutane. From Table 1, cyclohexane does have a high-lying orbital-pair (e_g) which is based to 51% on carbon-frame bonding. This number seems to fall beneath a required threshold: even if interaction is allowed, the effect demands the participation of charge-clouds on the physically remote C–H bonds. Moreover, the proximity of the substituent would split e_g (in D_{3d}) into a' and a'' (in C_s). Pilot calculations, on the two conformers of methylcyclohexane, suggest that a' would drift to the top and get the *lower* share of C–C bonding. In other words: the interacting orbital in cyclohexane would be based on its carbon-frame to an even lower degree than Table 1 indicates. The actual numbers we get, for the six-membered ring in methylcyclohexane, is 32% C–C bonding in a'.

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[3] Compound II itself could not be studied because of computer-memory and time limitations.

6. Conclusion

The structure of cyclopropane is such that spectral transitions are assignable to zones within the molecule (carbon frame, C–H bonds) or to transfers (CC → CH*, CH → CC*), and the CC → CC* transition is pushed to low energy. The zone structure becomes progressively blurred as one goes to cyclobutane and cyclohexane.

The auxochromic effect of these rings has been found to evolve in line with the carbon-frame content in their highest degenerate level. This is maximal in the three-membered ring, and insignificant – to practical purposes – in cyclohexane.

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