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Multi-Conformational Compounds with Two Absorbing Groups

VI.* Cyclopropane

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Two methods are proposed for dealing with a three-membered ring which is incorporated into a large molecule. The first, an all-valence electron approach, is an iterative CNDO/2 which provides, through bond indices, self-consistent hybridizations and valency angles. The second is compatible with π-electron approaches and aims at the study of conjugation and transmission of conjugation. The methods are illustrated by application to the unsubstituted cyclopropane molecule.

On propose deux méthodes pour étudier les molécules contenant une composante cyclopropanique. La première, qui tient compte de tous les électrons de valence, est une CNDO/2 itérative qui fournit – par l'intermédiaire des indices carrés de liaison – des valeurs auto-cohérentes pour l'hybridation et les angles de valence. L'autre, compatible avec les techniques π-électroniques, a pour but l'étude de la conjugaison et de la transmission de conjugaison. Les méthodes sont illustrées par application au cyclopropane non-substitué.

Es werden zwei Methoden zur Behandlung von Molekülen, die einen Dreiring enthalten, vorgeschlagen. Die eine besteht in der iterativen Anwendung des CNDO/2-Verfahrens mit selbst-konsistenten Hybridisierungen und Valenzwinkeln. Die zweite entspricht etwa einem π-Elektronenverfahren und dient besonders dem Studium von Konjugationseffekten. Illustriert werden beide am Beispiel des einfachen Cyclopropan.

1. Introduction and Summary

In 1916, Robinson observed [2] that certain reactions of substituted cyclopropanes could be rationalized on the assumption that the three-membered ring behaves like a double bond. Ever since, the ability of the cyclopropane ring to participate in, and transmit conjugation has been discussed [3, 4]. Akin to these properties are the addition reactions [5], reminiscent of ethylene, the low dipole moment of chlorocyclopropane [6], and the acidity of cyclopropane hydrogen atoms [7]. Another peculiarity of cyclopropane is the relatively low energy of its valence-shell transitions [8, 9].

Theoretical studies of cyclopropane have employed a variety of methods, including "maximum overlap" (for bibliography, see [10]), "pseudo-pi" [11, 12], all-valence [e.g. 10, 13–15] and all-electron techniques [16–20]. Two theoretical models, equivalent to a unitary transformation [21], have been useful in analyzing the results. The first (Fig. 1), introduced by Sugden [22] and developed by Walsh

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* For Part V, see Ref. [1].

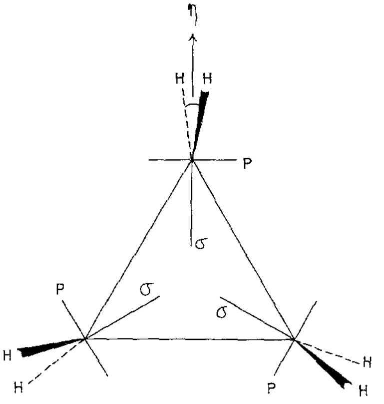

Fig. 1. Sugden-Walsh orbitals

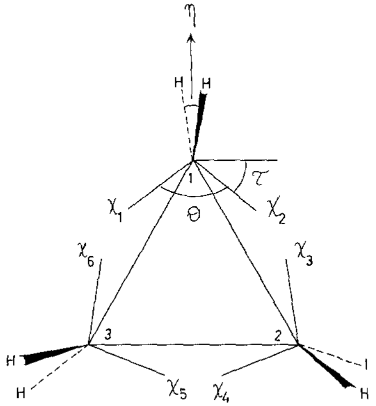

Fig. 2. Coulson-Moffitt orbitals

[23], classifies the basis orbitals as either pure p or $sp^2(\sigma)$, and attributes the above-mentioned properties of cyclopropane to levels that are based on p-type orbitals. The second model [24], developed by Coulson and Moffitt [25], replaces the valence orbitals at each carbon atom by two pairs of combinations, one of *ca.* sp^5 hybridization (χ_i in Fig. 2), the other – of *ca.* sp^2. Hybrids of the first type, which point off the interatomic C–C segments, give rise to the three "bent" C–C linkages which are used to rationalize the particular properties of cyclopropane.

It is noteworthy that the two constructions (Figs. 1 and 2) have not been extended quantitatively to *substituted* cyclopropanes. The reason for this is very probably that the concept of hybridization is foreign to the usual molecular-orbital tools of the organic chemist. In order to conserve conceptual clarity, one should treat molecules, in which cyclopropane is but one of several components, by methods that are made malleable enough to incorporate the specific features of this moiety. Stated conversely, the hybridization in three-membered rings has to be formulated in a way that is compatible with the routine molecular-orbital techniques.

In the present paper we propose two complementary ways of doing this. The first is an iterative CNDO/2 that aims at the elucidation of internally-consistent valency angles and bond hybridizations. The iterations, based on "bond indices" [26] are necessary, because CNDO energy-profiles do not contain minima at equilibrium bond angles[1] (at least in the case of cyclopropane and some of its derivatives [29]).

The other method seeks to analyze conjugation phenomena and is made compatible with π-electron approximations, particularly with one version [30–32] that was adapted to handle non-planar delocalization. In extension of the $\sigma-\pi$ separability invoked in the general procedure [33], we consider hybrids involved in C–C bonding as separable from hybrids participating in C–H linkages. The scheme is therefore "carbon-centered", in the sense that the three-membered ring is taken to contribute six orbitals χ_i (Fig. 2) and six electrons to the overall pool.

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[1] Dihedral angles [27] and, to a certain extent [28], interatomic distances can, however, be obtained from CNDO energies.

It differs from previous approaches of a similar nature [11, 12] in being based on the construction of Fig. 2, rather than on Fig. 1.

Deferring the discussion of some substituted cyclopropanes to a later publication, we limit ourselves here to an outline of the methods and a prefatory discussion of the unsubstituted molecule.

Our main results may be stated as follows:

a) The HCH angle in cyclopropane (but not in its derivatives [23]) is calculated as 113.7°, in close agreement with experimental estimations [34, 35]. The hybridization in C–C bonds, 3.69, corresponds to a "bending" angle of 22.6°, intermediate between the two values, 22° and 24.5° obtained by Coulson [25, 36].

b) The C-centered bond orders have features in common with π-electron bond orders of alternant hydrocarbons. A pronounced resemblance to benzene contributes to the understanding of conjugation phenomena. The similarity of each of the C–C bonds to the π-bond in ethylene explains the addition reactions of cyclopropane.

c) Broadening of the HCH angle at one of the apices is expected to weaken the two C–C bonds that emanate from it. This is linked with the observarion [5] that ring-fission in alkyl-substituted cyclopropanes occurs between the carbon atoms that carry the smallest and largest number of substituents.

d) The C-centered molecular orbitals correspond, by symmetry sequence, to those CNDO/2 levels that are poor in hydrogen-orbital contribution. The interpretation, by the two methods, of spectra and symmetry-dependent properties, is thus uniform and complementary.

2. An All-Valence Electron Approach

We use the CNDO/2 method [37] in conjunction with the concept of hybridization [38]. Consider a hydrogen atom I (valence orbital i) linked to a carbon atom K (valence orbitals k), and denote by $p(\mu\nu)$ the elements of the "bond order and charge" matrix. Then [39], in analogy with an argument originally derived for π-electron systems [40],

$$\sum_{j\neq i} p^2(ij) = \sum_{k\in \mathrm{K}} p^2(ik) + \sum_{j\neq i,k} p^2(ij) = p(ii)\,[2-p(ii)]$$

where j varies over all valence orbitals in the molecule. In certain cases it may be permissible to assume

$$p(ii)=1\,, \qquad \sum_{j\neq i,k} p^2(ij)=0 \tag{1}$$

whereupon

$$\sum_{k\in \mathrm{K}} p^2(ik) = p^2(is_k) + \{p^2(ix_k)+p^2(iy_k)+p^2(iz_k)\} = Q_s + Q_p = 1\,.$$

The charge (1 electron) at i is thus partitioned into a part Q_s, involved in bonding with the $2s$ orbital of K, and a part Q_p, involved with its $2p$ orbitals. The index λ^2_{KI},

$$\lambda^2_{\mathrm{KI}} = Q_p/Q_s = [1-p^2(is_k)]/p^2(is_k) \tag{2}$$

may then be taken [cf. 26, 41] to define the hybridization of K in bond K–I and, as such, to be connected with the hybridization at other bonds (K–J, etc.) and with the interorbital angles (IKJ), ...:

$$\sum_{L=\mathrm{I,J},\ldots} [1/(1+\lambda_{\mathrm{KL}}^2)] = 1\,, \qquad (\mathrm{IKJ}) = \arccos(-1/\lambda_{\mathrm{I}}\lambda_{\mathrm{J}})\,. \tag{3}$$

The utility of the foregoing relations becomes clear in the case of cyclopropane, where CNDO/2 fails to detect an energy minimum for HCH angles between 105° and 125°. To obtain a value for this angle, we have assumed[2] that the interorbital (HCH) angle coincides with the geometrical HCH angle (η in Figs. 1 and 2), and we have considered it as a variational parameter. Interatomic distances were as published ($r_{\mathrm{CC}} = 1.510$ Å, $r_{\mathrm{CH}} = 1.089$ Å [34]), somewhat different from those used by previous authors [cf. 13, 16]. By calculation, conditions (1) hold approximately,

$$p(ii) = +0.996\,, \qquad \sum_{j \neq i,k} p^2(ij) = 0.053$$

so that, by Eqs. (2) and (3),

$$\lambda_{\mathrm{CH}}^2 = -1/\cos\eta \tag{4a}$$

$$\lambda_{\mathrm{CC}}^2 = (1 - 3\cos\eta)/(1 + \cos\eta)\,. \tag{4b}$$

To obtain internally-consistent quantities, one starts with a trial index λ_{CH}^2(input), derives (Eq. (4a)) an initial η, and carries out a CNDO/2 treatment; the computed bond orders lead (Eq. (2)) to a new index λ_{CH}^2(output) and a new value for η. Iterating to self-consistence final values for $\lambda_{\mathrm{CH}}^2, \eta$ and (Eq. (4b)) λ_{CC}^2, as well as for other quantities, are determined.

Results

In Fig. 3, the input/output relationship is used as background for a tracing of the iterated steps. It is noteworthy that λ_{CH}^2(output) is almost insensitive to the input value, being confined, at an input range as wide as 1.8–2.8, to the narrow domain of 2.37–2.52. Convergence is therefore very rapid (4 iterations to 10^{-2}).

The self-consistent hybridization at C–H is $sp^{2.49}$ (to be compared with the schematic [21] sp^2); this corresponds to $\eta = 113.67°$, in better agreement with the NMR (114.4°, 113.6° [34]) and electron diffraction (115.1° ± 1.0 [35]) data than the values used (118–120° [e. g. 10, 13, 16]) or computed (119° [42]) in previous studies. By Eqs. (3), the hybridization in C–C bonds is $sp^{3.69}$ (vs. the schematic sp^5) and the interorbital (CCC) angle $\theta = 105.7°$, thus bent by $2 \times 22.6°$ from 60° (Fig. 2). This value is intermediate between the energy-minimization (22° [25]) and the maximum-overlap (24.5° [36]) predictions. Experimental electron density in cyclopropane derivatives has been matched with a bending angle of about 20° [43, 44].

The molecular orbitals are classified in Table 1 as "CC" or "CH", according to the contribution, low or high, of hydrogen 1*s* orbitals. It may be noted that the ordering of occupied levels conforms with that obtained (Ref. [13], cited in Table 1)

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[2] This assumption, explicit or implicit in former treatments, can be traced back to the paper by Coulson and Moffitt [25]. It has been discussed by Veillard and Del Re [42].

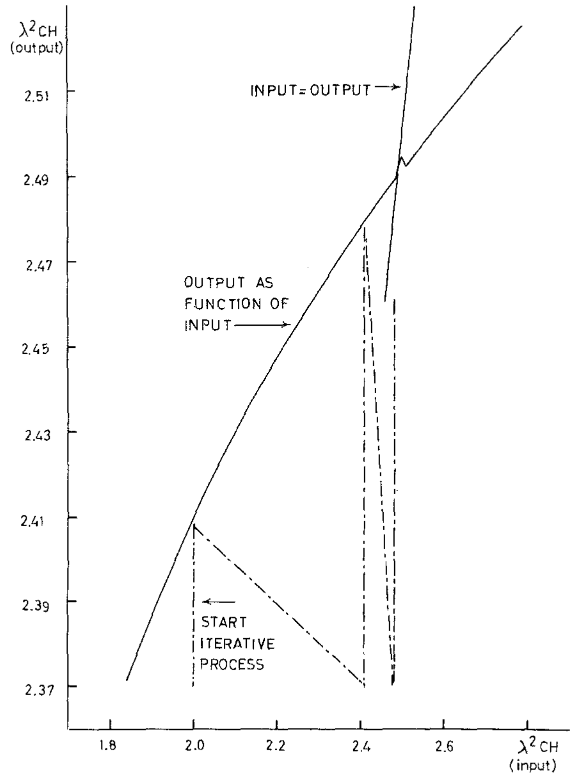

Fig. 3. Iterative CNDO/2 process

Table 1. CNDO *energy levels*

Level[a]	Eigenvalue[b]	Type[c]	Symmetry[d]	Former study[e]
1 2	12.329	CC(7)	E'	E''
3 4	10.674	CH(39)	E''	E'
5	8.345	CC(0)	A_2'	A_1'
6	8.303	CH(53)	A_1'	A_2''
7 8	7.842	CH(46)	E'	E'
9	6.912	CH(64)	A_2''	A_2'
10 11	−15.484	CC(11)	E'	E'
12 13	−16.642	CH(61)	E''	E''
14	−22.132	CH(32)	A_1'	A_1'
15	−27.604	CH(36)	A_2''	A_2''
16 17	−29.154	CH(36)	E'	E'
18	−47.286	CC(15)	A_1'	A_1'

[a] $\phi_9 \equiv$ LVMO, ϕ_{10}, $\phi_{11} \equiv$ HOMO's. Calculations at HCH angle = 113.67°, $r_{CC} = 1.510$ Å, $r_{CH} = 1.089$ Å.

[b] In electronvolt.

[c] See text. In parentheses: percentage contribution of hydrogen 1*s* orbitals.

[d] D_{3h}, $C_3 = z$.

[e] Parametrized CNDO, Ref. [13].

in a parameter-fitting CNDO procedure, and also with the results of *ab initio* approaches (e. g. [16]). The virtual orbitals, however, are ordered differently by the various techniques.

The lowest excitation that may be considered as CC→CC* ($\phi_{10}, \phi_{11} \rightarrow \phi_5 \in E'$) is not separable from the E' components of CC→CH* (e. g. $\phi_{10}, \phi_{11} \rightarrow \phi_7, \phi_8 \in A'_1, A'_2, E'$) and CH→CH* (e. g. $\phi_{12}, \phi_{13} \rightarrow \phi_9 \in E'$) transitions. However, when hydrogen atoms are excluded from the calculation (Sect. 3) this would become a *pure* CC→CC*, the allowed lowest-energy singlet-singlet transition. We identify it with the strong absorption detected at *ca.* 8.55 eV [9], assigned as CC→CC* (though not $e' \rightarrow a'_2$) also by previous authors [18]. It is thus intermediate in energy between CC→CC* in ethane (*ca.* 9.3 eV [9]) and in ethylene (*ca.* 6.9 eV [45]). The identification of the first CC→CC*, which is E', with the first strong absorption, is not affected by the results of the modified CNDO [13], because this has a forbidden A'_2 as the lowest excitation.

3. A C-Centered Approach

In this section, we adapt the previously developed [30–32] π-electronic scheme to the study of carbon-centered bonding in cyclopropane. The valence orbitals, contributed by each of the three carbon atoms, are replaced by four hybrids, of which two are needed. We use the construction of Fig. 2, disposing altogether of three pairs of equivalent orbitals, $\chi_1 \ldots, \chi_6$,

$$\lambda^2(\chi_i) = (1 - 3\cos\eta)/(1 + \cos\eta)\,. \qquad \text{(cf. Eq. (4b))}$$

The necessary integrals are developed as sums of quantities over atomic orbitals. Monocentric integrals are treated within the coordinate system of Fig. 4, whence

$$\chi_1 = K[s + \lambda(Rx - Sy)]\,, \quad \chi_2 = K[s + \lambda(Rx + Sy)]\,, \quad S_{12} \equiv 0\,,$$

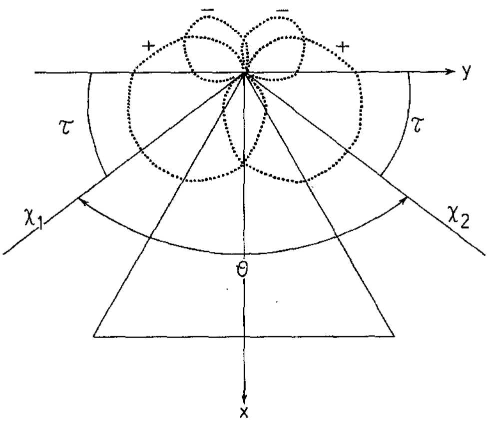

Fig. 4. Monocentric coordinate system

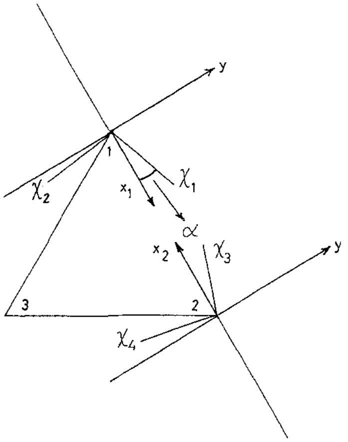

Fig. 5. Bicentric coordinate system

where K is the normalization factor, $K=(1+\lambda^2)^{-(1/2)}$, $\theta=\arccos[(1+\cos\eta)/(3\cos\eta-1)]$ (interorbital angle; cf. Eqs. (3))

$$\tau=(\pi-\theta)/2\,, \qquad R=\sin\tau\,, \qquad S=\cos\tau$$

and s is a $2s$, x and $y-2p$ orbitals, directed as x and y. This leads to expressions such as

$$(\chi_1\chi_1, \chi_2\chi_2)=K^4[(ss,ss)+2\lambda^2(ss,xx)-4(sx,sx)$$
$$+\lambda^4(1-2R^2S^2)(xx,xx)+2\lambda^4R^2S^2(xx,yy)-4\lambda^4R^2S^2(xy,xy)].$$

For bicentric integrals we use the coordinates of Fig. 5, by which

$$\chi_1=K[s_1+\lambda(Mx_1-Ny_1)]\,, \qquad \chi_2=K[s_1+\lambda(Vx_1+Uy_1)]\,,$$
$$\chi_3=K[s_2+\lambda(Vx_2+Uy_2)]\,, \qquad \chi_4=K[s_2+\lambda(Mx_2-Ny_2)]$$

where $\alpha=[\theta-(\pi/3)]/2$, $U=\sin\alpha$, $V=\cos\alpha$

$$M=(1/2)V-(\sqrt{3}/2)U\,, \qquad N=(\sqrt{3}/2)U+(1/2)V$$

so that, e. g.,

$$(\chi_2\chi_2, \chi_3\chi_3)=K^4[(ss,ss)+2\lambda^2V^2(ss,xx)+2\lambda^2U^2(ss,yy)$$
$$+\lambda^4V^4(xx,xx)+2\lambda^4U^2V^2(xx,yy)+\lambda^4U^4(yy,yy)]\ .$$

For compatibility with the π-electronic scheme [20], bielectronic integrals are calculated [46] with an effective exponent (0.927). The Slater exponent (1.625) was used for the overlaps [47], required in the computation of dipole-length [31] and monoelectronic-bicentric integrals:

$$\mu_{ij}=(1/2)S_{ij}(r_i+r_j)\,, \qquad \beta_{ij}=-kS_{ij}\,.$$

Table 2. *Integrals over χ-orbitals*

Integral[a]	$sp^{3.7}$	sp^5
Overlap		
(1, 2)	0.0	0.0
(1, 3)	0.204	0.194
(1, 4)	0.274	0.275
(1, 6)	0.604	0.583
Bielectronic		
(11, 11)	10.960 eV	10.781 eV
(11, 22)	8.625	8.722
(11, 33)	7.380	7.394
(11, 44)	7.152	7.158
(11, 66)	8.012	8.100
(11, 12)	0.376	0.352
(11, 34)	0.033	0.042
(11, 56)	0.152	0.177
(12, 12)	0.833	0.824
(12, 34)	0.038	0.041

[a] Numbering as in Fig. 2.

The proportionality factor k was put equal to 9.70 eV, so that the calculated lowest excitation energies (8.51 and 8.70 eV) coincide with the measured transition (8.5–8.7 eV [9]); the π-electron value ($k = 10.14$ eV [30]) would have led to somewhat higher energies (8.85 and 9.04 eV).

The numerical evaluation of the Coulomb integral ("α") is obviously redundant. Still, for adaptability in later calculations, we put [30]

$$\alpha = W - \sum_{j \neq i} (ii, jj) + 0.5(12, 21)$$

and assign to W a value (-8.386 eV) to match the HOMO eigenvalue (-10.530 eV), at $\lambda^2 = 3.7$, with the ionization potential of cyclopropane [18].

For comparison with other results, we give in Table 2 a list of integrals, for both the schematic (sp^5) and the actually computed ($sp^{3.7}$) hybridizations.

SCF molecular orbitals were obtained through the Hartree-Fock Hamiltonian operator [48] $\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{G}$, of matrix elements

$$H_{ii} = \alpha_i, \; H_{ij} = \beta_{ij}$$

$$G_{ij} = \sum_k \sum_l \left\{ [2(ij, kl) - (ik, jl)] \sum_m C_{km} C_{lm} \right\}.$$

(Clearly, no assumption akin to the ZDO approximation [49] can be made.)

Results

The computed molecular orbitals ($\phi_i = \sum (i) \chi_i$) are arranged, by descending eigenvalues, in Table 3, and their sequence is seen to correspond, by symmetry species, to the ordering of those all-valence electron orbitals (Table 1) that contain

Table 3. *C-centered energy levels*

Level[a]	Eigenvalue[b]	Symmetry	Corresponding CNDO/2 level[c]
1 2	+ 8.489	E'	1 2
3	+ 4.722	A'_2	5
4 5	−10.530	E'	10 11
6	−19.128	A'_1	18

[a] $\phi_3 \equiv$ LVMO, ϕ_4, $\phi_5 \equiv$ HOMO's. Geometry as in Table 1. $\lambda^2 = 3.7$.
[b] In electronvolt.
[c] cf. Table 1.

Table 4. *Transition energies in cyclopropane*[a]

Main contribution[b]	Symmetry	Singlets	Oscillator strength	Triplets	Exp.[c]
4, 5→3	E'	8.510	0.39	6.930	6.45–7.07
		8.696		7.100	7.81
					8.5 –8.7
					10.16
4, 5→1, 2	A'_2	11.746	0.0	10.384	
	E'	11.813	0.16	10.942	
				11.006	
	A'_1	11.841	0.0	11.532	

[a] Results of CI treatment. Energies in eV.
[b] Numbering as in Table 3.
[c] Ref. [9].

low $1s_h$ percentages. We have equally verified that the number of nodes decreases by steps [50] as one passes from ϕ_1 to ϕ_6. The LVMO is thus assigned, by both criteria, as A'_2 (*not* the degenerate E' pair; cf. [11]), and there is no motive to examine other arrangements, e. g. A'_2, E', E', A'_1 (obtainable by setting $\beta_{12} \neq 0$) [11] or A'_2, E', A'_1, E' (by $\beta_{12} > 0$).

Theoretical transition energies and oscillator strengths, reported in Table 4, were obtained by a configurational-interaction treatment, including all monoexcitations.

4. Discussion of the Unsubstituted Molecule

In Sects. 2 and 3 we have proposed two approaches to the study of conjugation and transmission of conjugation in cyclopropane derivatives. In this section we analyze some of the results obtained for the unsubstituted molecule.

Turning first to the C-centered results, we note that the elements of the "bond order and charge matrix" (Table 5) have features in common with the corresponding quantities in alternant π-electron systems [40]: not only $p(\mu\mu) = 1$, but also $p(\mu\nu) = 0$ for $\nu = \mu + 2$ and $\nu = \mu + 4$ (mod 6). An even closer analogy can be drawn with the π-system of benzene, equally based on six atomic orbitals and consisting

Table 5. *Elements of the "bond order and charge" matrix*

Element[a]		Type	Cyclopropane	Benzene	Ethylene
1	1		1.0	1.0	1.0
1	2	Geminal	−0.235	0.667	
1	3		0.0	0.0	
1	4	Non-vicinal	0.316	0.333	
1	5		0.0	0.0	
1	6	Contingent	0.919	0.667	1.0

[a] Numbering as in Fig. 2.

of two non-degenerate and two pairs of degenerate levels. Indeed, the C-centered system in cyclopropane (D_{3h}) may be considered as derivable, through reduction in symmetry, from the π-system of benzene (D_{6h}). The only significant difference between the bond orders of the two molecules concerns the vicinal quantities (see Table 5), which are large and positive in benzene but smaller and negative in cyclopropane.

We find the data of Table 5 useful in the rationalization of the conjugative properties of cyclopropane. First, the geometrical requirements for optimal conjugation should differ from cyclopropane to benzene, because C-centered orbitals in the former molecule are perpendicular, while p-orbitals in the latter are parallel to the main axis of symmetry. Secondly, the conjugation is much attenuated in cyclopropane: while contingent and non-vicinal bond orders (defined in Table 5) are positive, as in benzene, geminal orders, unlike in benzene, are negative. Third, the negative geminal quantities can be considered, in certain contexts, as dividing the molecule into three loosely-interacting "islands" (C_1C_2; C_2C_3; C_1C_3), intermediate between σ and π linkages. The bond order in each "island" is 0.92, very close to the ethylene value (1). Ethylene-like reactions of cyclopropane [5] such as ring-fission with hydrogen, addition of hydrohalic acids, etc. (Fig. 6), can be discussed in these terms.

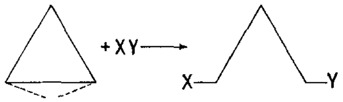

Fig. 6

Some insight into the finer details of chemical reactivity is provided by the CNDO/2 results concerning the unsubstituted molecule. Consider the dependence of the Mulliken overlap populations P on the HCH angle η (Fig. 7). We find that $P(CC)$ decreases while $P(CH)$ augments with η. In other words, angle-broadening at one apex of cyclopropane weakens the two bonds that emanate from it. One obvious cause for such broadening is bulky substitution, so that the experimental counterpart of the foregoing relation comes to mind immediately: it is well-known [5] that reductive ring-opening in alkyl-substituted cyclopropane occurs preponderantly between the carbons that carry the smallest and largest number of alkyl groups (Fig. 8). Put differently, among three linkages, two are relatively weak and prone to attack (C_1C_2 and C_1C_3 in Fig. 8); between these, the reagent chooses the one (C_1C_2) that is more accessible sterically.

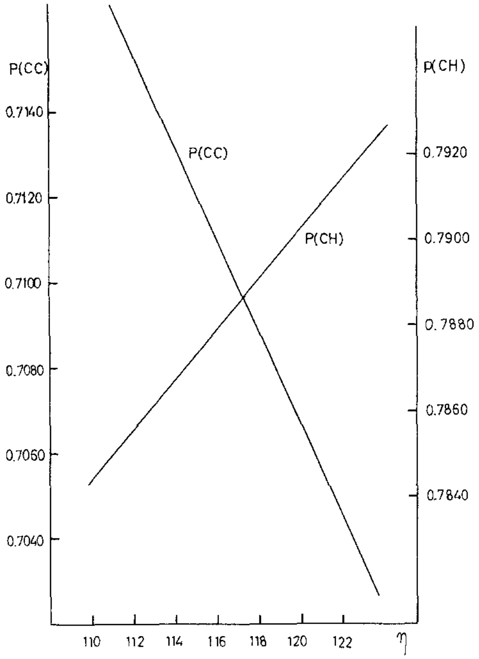

Fig. 7. CNDO/2 population analysis

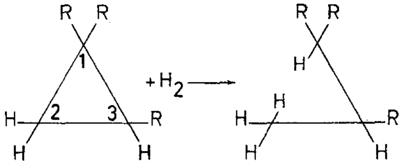

Fig. 8

We would like to close this discussion with a brief outline of cyclopropane transition energies (Table 4). The very weak absorption, observed at 6.45–7.07 eV [9], is probably a singlet-triplet excitation (calc.: 6.9–7.1 eV), while the next absorption (~7.81 eV) seems to belong to a Rydberg series [18]. Then comes an allowed CC→CC*, centered around 8.55 eV. No other CC→CC* excitation is predicted beneath 11.7 eV, in agreement with other evidence [9] that the strong absorption, around 10.16 eV, involves CH bonds.

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