Tetrahedron, 1958, Vol. 2, pp. 345–352. Pergamon Press Ltd., London

ELEMENTARY MOLECULAR ORBITAL TREATMENT OF *CYCLO*PROPANE AND *CYCLO*BUTANE

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(*Received* 26 *July* 1957)

Abstract—A theory of binding in *cyclo*propane and *cyclo*butane involving non-orthogonal orbitals is proposed. The theory accounts for the observed auxochromic effects in these molecules in a simple way, and correctly predicts several properties of these molecules.

ONE of the unsatisfactory features of present-day MO theory is the artificiality of its treatment of *cyclo*propane.[1–6] It has long been known that it is impossible to form orthogonal *sp*-hybrids with bond angles of less than 90°, so that current treatments either do not overlap orbitals along the line of centres of carbon atoms, forming so-called "banana" bonds,[1] or else invoke a certain amount of π-bonding in this substance.[2] It is the feeling of the authors that, for some cases at least, the requirement of orthogonality is too stringent. If an MO is formed from LCAO's

$$\Psi = \Sigma a_{ij}\phi_{ij}$$

where ϕ_{ij} represents the *j*th AO on the *i*th atom, then this MO can be interpreted in terms of a bond additivity rule if the AO's on a given atom are orthogonal. If these AO's are not orthogonal, then the MO's so formed are not considered to represent localized bonds,[7] implying the failure of the bond additivity rule for the substance under discussion. Most chemical evidence indicates that bond additivity rules are quite accurate, so that it is reasonable to require orthogonality in most cases. There is, however, some disagreement in the literature as to the value of the C–C bond energy in[8,9] *cyclo*propane. Also, several workers have reported that the replacement of a double bond in a conjugated chain with a *cyclo*propyl group does not completely destroy effects characteristic of conjugation.[10,11] These observations are most easily discussed in terms of nonlocalized electrons, which in turn suggest, in the light of the foregoing, nonorthogonal orbitals. Theory demands the orthogonality of the solutions of Schroedinger's equation for the molecule, of course, but it is strictly speaking not necessary to demand orthogonality of the functions that go to make up the MO. Here they are conveniently described as having the form of AO's, but we shall carry over only those properties that are useful to us.

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[1] T. M. Sugden *Nature, Lond.* **160**, 367 (1947).
[2] A. D. Walsh *Nature, Lond.* **159**, 164 (1947).
[3] R. Robinson *Nature, Lond.* **159**, 400 (1947).
[4] C. A. Coulson and W. E. Moffitt *J. Chem. Phys.* **15**, 151 (1947).
[5] C. A. Coulson and W. E. Moffitt *Phil. Mag.* **40**, 1 (1949).
[6] A. D. Walsh *Trans. Faraday Soc.* **45**, 179 (1949).
[7] C. A. Coulson *Valence.* Oxford Press (1952).
[8] F. H. Seubold *J. Chem. Phys.* **21**, 1616 (1953).
[9] H. O. Pritchard and A. F. Trotman-Dickenson *J. Chem. Phys.* **22**, 944 (1954).
[10] G. W. Perold *J. S. Afr. Chem. Inst.* **6**, 22 (1953).
[11] J. J. Wren *J. Chem. Soc.* 2208 (1956).

Cyclo*propane*

Let us drop the orthogonality requirement for the orbitals that will be used to form C–C bonds and substitute it its place the requirement that the orbitals have maximum bond forming power in the Pauling sense. This latter is suggested, but in no way established, by the fact that the C–C bond length in *cyclo*propane, 1·526 Å,[12] is very close the normal C–C bond length. We form four *sp*-hybrids distributed as follows: two equivalent orbitals in the *xz*-plane, each making an angle of 30° with the $+x$ axis, to be used in forming C–C bonds, and two equivalent orbitals in the *xy*-plane making equal, but not necessarily 30°, angles with the $-x$ axis. For the first and second orbitals, we require a bond forming power, F, of 2. For the third and fourth, we require mutual orthogonality and also orthogonality with the first and second. The required AO's are

$$\phi_a = \frac{1}{2}s + \frac{3}{4}p_x + \frac{\sqrt{3}}{4}p_z$$

$$\phi_b = \frac{1}{2}s + \frac{3}{4}p_x - \frac{\sqrt{3}}{4}p_z$$

$$\phi_c = \frac{3}{\sqrt{26}}s - \frac{\sqrt{2}}{\sqrt{13}}p_x + \frac{1}{\sqrt{2}}p_y$$

$$\phi_d = \frac{3}{\sqrt{26}}s - \frac{\sqrt{2}}{\sqrt{13}}p_x - \frac{1}{\sqrt{2}}p_y$$

It is seen that ϕ_a and ϕ_b are the first pair mentioned above, and ϕ_c and ϕ_d are the second pair.

Two items of immediate interest are the F of ϕ_c and ϕ_d, and the H–C–H angle, 2η (Fig. 1). A straight forward calculation of F_c or F_d gives

$$F_c = F_d = \frac{3}{\sqrt{26}} - \frac{\sqrt{2}}{\sqrt{13}}\sqrt{3}(1) - \frac{\sqrt{2}}{\sqrt{17}} + \frac{1}{\sqrt{2}}3\ (1)\ \frac{\sqrt{13}}{\sqrt{17}} = 1{\cdot}988$$

close to the usual value of 2; $\tan\eta$ is given by the coefficient of p_y divided by the coefficient of p_x in ϕ_c.

$$\tan\eta = \frac{1/\sqrt{2}}{\sqrt{2}/\sqrt{13}} = \frac{\sqrt{13}}{2}$$

$$\eta = 61^\circ$$

$$2\eta = 122^\circ$$

This value is to be compared with 118·2° ± 2·0° found by Bastiansen and Hassel[13] using electron diffraction techniques. A later value is reported by Günthard *et al.*[14] as being just above 120°. The treatment of Coulson referred to above yields $F = 1{\cdot}883$ and an H–C–H angle of 116°.[5]

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[12] L. Pauling and L. O. Brockway *J. Amer. Chem. Soc.* **59**, 1223, (1937).

[13] O. Bastiansen and O. Hassel *Tidsskr. Kemi. Bergv.* **6**, 71 (1946).

[14] H. H. Günthard, R. C. Lord and T. K. McCubbin,.Jr. *J. Chem. Phys.* **25**, 768 (1956).

Since it is not immediately clear how the interaction of nonorthogonal orbitals will affect the energy of our system, we next set up the MO's for the C–C bonds. Labelling the orbitals as indicated in Fig. 2, we have

$$\Psi = C_{1a}\phi_{1a} + C_{1b}\phi_{1b} + C_{2a}\phi_{2a} + \cdots + C_{3b}\phi_{3b}.$$

By symmetry, and using the usual notation and assumptions,

$$H_{1a,1a} = H_{1b,1b} = \ldots = H_{3b,3b} = Q \qquad S_{1a,1a} = \ldots = S_{3b,3b} = 1$$
$$H_{1a,2b} = H_{2a,3b} = H_{3a,1b} = \beta \qquad S_{1a,2b} = S_{2a,3b} = S_{3a,1b} = 0$$
$$H_{1a,1b} = H_{2a,2b} = H_{3a,3b} = X \qquad S_{1a,1b} = S_{2a,2b} = S_{3a,3b} = J$$

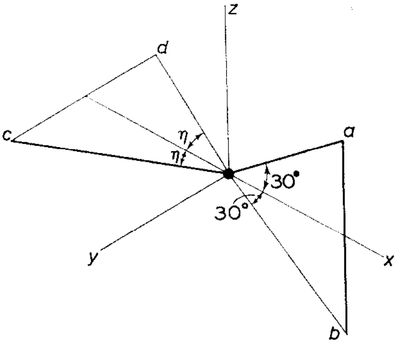

FIG. 1. Disposition of orbitals about carbon atoms in *cyclo*propane.

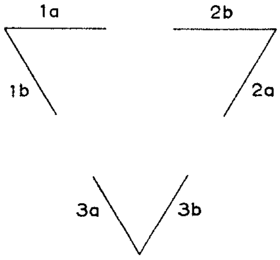

FIG. 2. Labelling of orbitals in *cyclo*propane ring.

All other H's and S's are zero. A straightforward calculation of J from the angular parts of the wave functions, permissible because of the assumed identity of the radial parts, gives $J = 5/8$. X, the corresponding Hamiltonian integral could likewise be evaluated directly, but for simplicity we shall assume $X = JQ$. (See Appendix II.) Setting $Q - E = W$, we have the secular equation

$$\begin{vmatrix} W & \beta & 0 & 0 & 0 & JW \\ \beta & W & JW & 0 & 0 & 0 \\ 0 & JW & W & \beta & 0 & 0 \\ 0 & 0 & \beta & W & JW & 0 \\ 0 & 0 & 0 & JW & W & \beta \\ JW & 0 & 0 & 0 & \beta & W \end{vmatrix} = 0 \qquad (1)$$

This equation may be solved in a variety of ways. (See Appendix I.) The six roots are

$$E_{\alpha+} = E_{\alpha-} = Q + 1{\cdot}9\beta$$
$$E_{0+} = Q + 0{\cdot}62\beta$$
$$E_{\beta+} = E_{\beta-} = Q - 0{\cdot}87\beta$$
$$E_{0-} = Q - 2{\cdot}7\beta$$

Putting six electrons into the three lowest levels and remembering that $\beta < 0$, we find for the total energy

$$E_t = 6Q + 8{\cdot}8\beta$$

A treatment with orthogonal AO's is the same as above with $J = 0$ and β replaced with β'. The determinant now factors, giving three roots $W = \beta'$ and three $W = -\beta'$. The total energy is $6\ W + 6\ \beta'$. Since it is clear that the absolute value of β is a maximum for orbitals that overlap under the best possible conditions, we conclude, to this approximation, that the treatment using nonorthogonal orbitals leads to a somewhat improved energy. A fuller discussion would call attention to the increased interelectronic repulsion and kinetic energy associated with the confinement of the electrons more strictly to the ring. To a considerable extent these are offset by the enhancement of the coulombic attraction and the overlap just mentioned. Appendix II carries the discussion a bit further.

Cyclo*butane*

A similar treatment for cyclobutane can be carried through, assuming 90° instead of 60° orbitals. The four LCAO's for carbon are

$$\phi_a = \frac{1}{2} s + \frac{\sqrt{3}}{\sqrt{8}} p_x + \frac{\sqrt{3}}{\sqrt{8}} p_z$$

$$\phi_b = \frac{1}{2} s + \frac{\sqrt{3}}{\sqrt{8}} p_x - \frac{\sqrt{3}}{\sqrt{8}} p_z$$

$$\phi_c = \frac{\sqrt{3}}{\sqrt{10}} s - \frac{1}{\sqrt{5}} p_x + \frac{1}{\sqrt{2}} p_y$$

$$\phi_d = \frac{\sqrt{3}}{\sqrt{10}} s - \frac{1}{\sqrt{5}} p_x - \frac{1}{\sqrt{2}} p_y$$

Again, the first pair refer to C–C bonds and the second to H–C bonds. As before, we may calculate $F_3 = 1{\cdot}997$ and an H–C–H angle of 115°. Using the same notation as before, $S_{1a,1a} = J = 1/4$. Again solving the secular equation under the same assumptions as before, we find a total energy of $8\ Q + 8{\cdot}2\ \beta$ as compared to $8\ Q + 8\ \beta'$ for the treatment with orthogonal orbitals. The conclusion here is that conjugation is much less important for an interposed *cyclo*butyl group than it is for a *cyclo*propyl group. Recently Wren[11] has measured an auxochromic effect for *cyclo*butyl. The results bear out the above.

*Chloro*cyclo*propane*

It is of interest to see how orbitals of this type can be used to describe the observations that chloro*cyclo*propane is very difficult to hydrolyze.[15] Brown *et al.*[16] have explained this by noting that the strain in the transition state, represented by a carbonium ion with the hydrogen atom in the plane of the ring, is even greater than that of the initial state. Let us form such an orbital and calculate its F.

Taking ϕ_a and ϕ_b as before for *cyclo*propane, we now require ϕ_c along the $-x$ axis, orthogonal to ϕ_a and ϕ_b and normalized. Such an orbital is

$$\phi_c = \frac{3}{\sqrt{13}} s - \frac{2}{\sqrt{13}} p_x$$

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[15] J. D. Roberts and V. C. Chambers *J. Amer. Chem. Soc.* 73, 5030 (1951).

[16] H. C. Brown, R. S. Fletcher and R. B. Johannesen *J. Amer. Chem. Soc.* 73, 212 (1951).

For this orbital, $F = 1{\cdot}793$, considerably less than the F of the orbital out of which it is formed in the course of the reaction. Since the transition state involves not only the removal of a chloride ion, but also the weakening of a C–H bond, we conclude that the energy requirements of the transition state are very high and the reaction should proceed very slowly, as indeed it does.

APPENDIX I

Factoring of the secular equation

Equation (1) of the text may be factored by using symmetry orbitals (SO's) rather than the $\phi_{ia,b}$ as basis functions. Determination of the SO's is straightforward using either group theory[17] or alternative methods which do not use explicitly the formalism of group theory.[18]

In determining the SO's we need not employ the full symmetry, since we are concerned only with bonds in the plane of the carbon ring. Thus we use the symmetry group C_{3v} for *cyclo*propane and C_{4v} for *cyclo*butane. We consider first *cyclo*propane.

To find the SO's we must diagonalize appropriate symmetry operators.[18] For *cyclo*propane we can conveniently form SO's which diagonalize the rotations about the threefold axis by taking the linear combinations:

$$\chi = \sum_{k=1}^{3} \epsilon^{-(k-1)j}\, \phi_{ka.b} \qquad (j = 0, \pm 1, \ldots) \tag{1}$$

where $\epsilon^j = \exp j\,(i\,2\pi/p)$, p = order of rotation (in this case 3). For $j = 0$ we have two linear combinations $\phi_{1a} + \phi_{2a} + \phi_{3a}$, $\phi_{1b} + \phi_{2b} + \phi_{3b}$. For $j = 0$, however, another set of symmetry operations, the reflections in the three vertical planes passing through the symmetry axis and the three carbon atoms, may simultaneously be diagonalized. The pair of functions above may be added and subtracted to give SO's which belong to $j = 0$ and are, respectively, symmetric (+) and anti-symmetric (—) with respect to reflections:

$$\chi_{0+} = \frac{1}{N_1}\,[(\phi_{1a} + \phi_{1b}) + (\phi_{2a} + \phi_{2b}) + (\phi_{3a} + \phi_{3b})] \tag{2}$$

$$\chi_{0-} = \frac{1}{N_2}\,[(\phi_{1a} - \phi_{1b}) + (\phi_{2a} - \phi_{2b}) + (\phi_{3a} - \phi_{3b})] \tag{3}$$

The normalizing factors N_1 and N_2 are:

$$N_1 = \sqrt{6(1 + J)}$$

$$N_2 = \sqrt{6(1 - J)}$$

For $j = +1$, we obtain a number of SO's depending on which carbon atom we choose as the initial one in the sum (1), but the only essentially different ones are:

$$\chi_1 = \frac{1}{N_1}\,[(\phi_{1a} + \phi_{1b}) + \gamma^*(\phi_{2a} + \phi_{2b}) + \gamma(\phi_{3a} + \phi_{3b})] \tag{4a}$$

$$\chi'_1 = \frac{1}{N_2}\,[(\phi_{1a} - \phi_{1b}) + \gamma^*(\phi_{2a} - \phi_{2b}) + \gamma(\phi_{3a} - \phi_{3b})] \tag{4b}$$

$$\gamma = e^{2\pi i/3}$$

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[17] M. A. Melvin *Rev. Mod. Phys.* **28**, 18 (1956).

[18] John C. Slater *Electronic Structure of Atoms and Molecules.* Technical Report No. 3, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts.

These functions do not have the property of being either symmetric or antisymmetric with respect to reflections. Indeed reflection in the plane through carbon atom 1 converts (4a) and (4b) respectively into

$$\chi_{-1} = \frac{1}{N_1}[(\phi_{1a} + \phi_{1b}) + \gamma(\phi_{2a} + \phi_{2b}) + \gamma^*(\phi_{3a} + \phi_{3b})] \tag{5a}$$

$$\chi'_{-1} = -\frac{1}{N_2}[(\phi_{1a} - \phi_{1b}) + \gamma(\phi_{2a} - \phi_{2b}) + \gamma(\phi_{3a} - \phi_{3b})] \tag{5b}$$

where, as the notation indicates, χ_{-1} and χ'_{-1} are the symmetry orbitals obtained by substituting $j = -1$ into (1). We conclude that χ_1 and χ_{-1} are degenerate as are χ'_1 and χ'_{-1}.

Using these symmetry orbitals as our basis functions rather than the atomic orbitals $\phi_{1a,b}$, we conclude that χ_{0+} and χ_{0-} are already MO's, since they can combine only with SO's having the same symmetry and there are no other such linearly-independent SO's formed from the $\phi_{ia,b}$. However, χ_1 and χ'_1 do have the same symmetry and yield a quadratic secular equation; χ_{-1} and χ'_{-1} give the same quadratic equation. The correct linear combinations are of the form

$$\left.\begin{array}{l}\sqrt{1-\delta^2}\,\chi_1 - i\,\delta\,\chi'_1 \\ \sqrt{1-\delta^2}\,\chi_{-1} + i\,\delta\,\chi'_{-1}\end{array}\right\} E_{\alpha\pm}$$

$$\left.\begin{array}{l}i\,\delta\chi_1 - \sqrt{1-\delta^2}\,\chi'_1 \\ i\,\delta\chi_{-1} + \sqrt{1-\delta^2}\,\chi'_{-1}\end{array}\right\} E_{\beta\pm}$$

where δ is a numerical coefficient. By adding and subtracting the degenerate pairs we can obtain the MO's in real form. In this form the functions have the property of being either symmetric or antisymmetric to reflection in the plane passing through carbon atom 1.

We list the molecular orbitals so obtained along with those of equations (2) and (3) thereby obtaining the complete set of six orbitals for *cyclo*propane. They are in order of increasing energy:

$$\left.\begin{array}{l}\Psi_{\alpha+} = -0{\cdot}21(\phi_{1a} + \phi_{1b}) + 0{\cdot}83(\phi_{2a} + \phi_{3b}) - 0{\cdot}62(\phi_{3a} + \phi_{2b}) \\ \Psi_{\alpha-} = -0{\cdot}84(\phi_{1a} - \phi_{1b}) + 0{\cdot}24(\phi_{2a} - \phi_{3b}) - 0{\cdot}60(\phi_{2b} - \phi_{3a})\end{array}\right\}$$

$$\Psi_{0+} = \frac{1}{3{\cdot}1}[(\phi_{1a} + \phi_{1b}) + (\phi_{2a} + \phi_{2b}) + (\phi_{3a} + \phi_{3b})]$$

$$\left.\begin{array}{l}\Psi_{\beta+} = 0{\cdot}40(\phi_{1a} + \phi_{1b}) + 0{\cdot}17(\phi_{2a} + \phi_{3b}) - 0{\cdot}57(\phi_{3a} + \phi_{2b}) \\ \Psi_{\beta-} = -0{\cdot}43(\phi_{1a} - \phi_{1b}) + 0{\cdot}56(\phi_{2a} - \phi_{3b}) + 0{\cdot}13(\phi_{2b} - \phi_{3a})\end{array}\right\}$$

$$\Psi_{0-} = \frac{1}{1{\cdot}5}[(\phi_{1a} - \phi_{1b}) + (\phi_{2a} - \phi_{2b}) + (\phi_{3a} - \phi_{3b})]$$

The bracketed functions are degenerate pairs.

The procedure for *cyclo*butane is similar except that the treatment of C_{4v} symmetry is in some respects simpler. The MO's are in order of increasing energy:

$$\Psi_{0+-} = \frac{1}{\sqrt{6}}\,[(\phi_{1a} - \phi_{1b}) - (\phi_{2a} - \phi_{2b}) + (\phi_{3a} - \phi_{3b}) - (\phi_{4a} - \phi_{4b})]$$

$$\left.\begin{aligned} \Psi_{\alpha+} &= 0{\cdot}51(-\phi_{1a} - \phi_{2b} + \phi_{3a} + \phi_{4b}) + 0{\cdot}07(\phi_{1b} + \phi_{2a} - \phi_{3b} + \phi_{4a})] \\ \Psi_{\alpha-} &= 0{\cdot}07(-\phi_{1a} + \phi_{2b} + \phi_{3a} - \phi_{4b}) + 0{\cdot}51(\phi_{1b} - \phi_{2a} - \phi_{3b} + \phi_{4a})] \end{aligned}\right\}$$

$$\Psi_{0++} = \frac{1}{\sqrt{10}}\,[(\phi_{1a} + \phi_{1b}) + (\phi_{2a} + \phi_{2b}) + (\phi_{3a} + \phi_{3b}) + (\phi_{4a} + \phi_{4b})]$$

$$\Psi_{0-+} = \frac{1}{\sqrt{10}}\,(\phi_{1a} + \phi_{1b}) - (\phi_{2a} + \phi_{2b}) + (\phi_{3a} + \phi_{3b}) - (\phi_{4a} + \phi_{4b})]$$

$$\left.\begin{aligned} \Psi_{\beta+} &= 0{\cdot}07(\phi_{1a} + \phi_{2b} - \phi_{3a} - \phi_{4b}) + 0{\cdot}51(-\phi_{1b} - \phi_{2a} + \phi_{3b} + \phi_{4a}) \\ \Psi_{\beta-} &= 0{\cdot}51(\phi_{1a} - \phi_{2b} - \phi_{3a} + \phi_{4b}) + 0{\cdot}07(-\phi_{1b} + \phi_{2a} + \phi_{3b} - \phi_{4a}) \end{aligned}\right\}$$

$$\Psi_{0--} = \frac{1}{\sqrt{6}}\,[(\phi_{1a} - \phi_{1b}) + (\phi_{2a} - \phi_{2b}) + (\phi_{3a} - \phi_{3b}) + (\phi_{4a} - \phi_{4b})]$$

APPENDIX II

Approximations

Several matters touched upon in the main text deserve a somewhat extended discussion. Probably the most important such point is the assumption of $F = 2$ for the orbitals a and b. The necessity for a new assumption arises, of course, from the abandonment of orthogonality, which, in effect, had fixed one constant of the problem. Fig. 3 is a graph of various parameters of the system against F for orbital a or b. It is seen that, while the bond forming strength of orbitals c and d varies only slowly in the region of interest with F_a, the H–C–H angle, 2η varies quite rapidly. J is also seen to vary, though not sufficiently rapidly to vitiate the general argument. On the basis of this, then F_a was chosen to be 2. Any change in the measured H–C–H angle, necessitating a change in F_a, would cause only insignificant changes in the other parameters.

Another item requiring some justification is the assumption $X = JQ$. We may write the one electron Hamiltonian for the system as

$$H = H^1 + K$$

where H^1 is the atomic Hamiltonian for atom 1 and K is the coulombic effect of the other two centers. K is even with respect to the XY plane and negative everywhere. Now

$$H^1\phi_{1a} = E^1\phi_{1a}$$

$$H^1\phi_{1b} = E^1\phi_{1b}$$

as ϕ_{1a} and ϕ_{1b} are assumed to be degenerate solutions of the atomic problem. Multiply both of the equations by ϕ^*_{1a}, and integrate

$$\int\phi^*_{1a}H^1\phi_{1a} = E^1$$

$$\int\phi^*_{1a}H^1\phi_{1b} = E^1\int\phi^*_{1a}\phi_{1b} = JE^1$$

We require

$$\int \phi_{1a}^{*} H \phi_{1a} = E^1 + K_{1a,1a} = Q$$

and

$$\int \phi_{1a}^{*} H \phi_{1b} = JE^1 + K_{1a,1b} = X$$

Eliminating E^1,

$$X = JQ + K_{1a,1b} - JK_{1a,1b}$$

Since $K_{1a,1a}$ and $K_{1a,1b}$ have the same sign and are of the same order of magnitude, we expect $|K_{1a,1b} - JK_{1a,1a}| \sim |K_{1a,1b}|$, so that the approximation is almost certainly not any more serious for the non-orthogonal case than for the orthogonal. In calculating the improvement caused by the abandonment of orthogonality, the error should roughly subtract out.

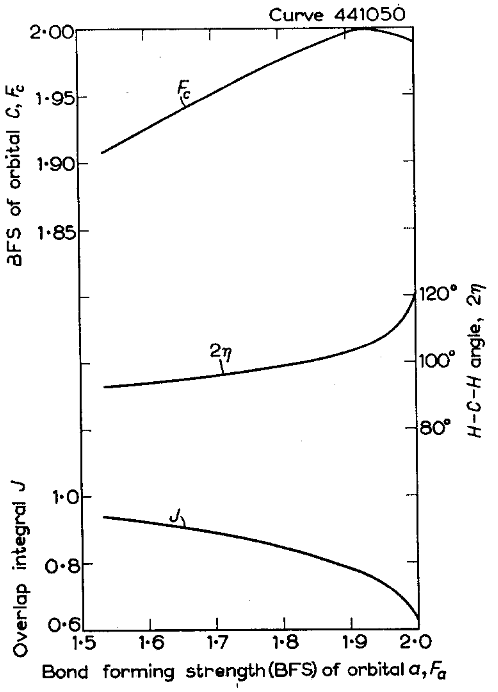

FIG. 3. Various atomic parameters of *cyclo*propane.

A final point concerning non-orthogonality. It may be shown that the energy calculated in the fashion usually employed in these very simple MO pictures decreases without limit as $J \rightarrow 1$, that is, as overlap becomes complete. The fault lies in the fact that the usual procedure of putting two electrons into each state implies a product wave function, whereas we know that the Pauli Principle does not permit simple product functions. The state of affairs here may be easily seen by referring to Appendix I. As $J \rightarrow 1$, we are left only three linearly independent AO's rather than six, so that we may form only three MO's. The SO's χ_{0-}, χ_1^1, and χ_{-1}^1 approach zero so that $\Psi'_{\alpha+} \rightarrow \Psi'_{\alpha-}$, $\Psi'_{\beta+} \rightarrow \Psi'_{\beta-}$, and $\Psi'_{0-} \rightarrow 0$. Since we are dealing with the three lowest states, $E_{\alpha+}$, $E_{\alpha-}$, and E_{0+}, a determinant constructed out of these functions would vanish as $J \rightarrow 1$. In other words, the Pauli Principle would not permit the "catastrophe" to take place.