

- (3) M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968).  
 (4) M. B. Robin, H. Basch, N. A. Keubler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).  
 (5) T. D. Bouman and A. E. Hansen, *J. Chem. Phys.*, **66**, 3460 (1977).  
 (6) A. Rauk, J. O. Jarvie, H. Shimura, and J. M. Barriol, *J. Am. Chem. Soc.*, **97**, 5656 (1975).  
 (7) G. A. Segal and R. W. Wetmore, *Chem. Phys. Lett.*, **32**, 556 (1975).  
 (8) G. A. Segal, R. W. Wetmore, and K. Wolf, *Chem. Phys.*, in press.  
 (9) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).  
 (10) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1966.  
 (11) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973).  
 (12) O. Ermer, *Angew. Chem.*, **13**, 604 (1974).  
 (13) R. J. Buenker, S. D. Peyerimhoff, and W. E. Kammer, *J. Chem. Phys.*, **55**, 814 (1971).  
 (14) T. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).  
 (15) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).  
 (16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).  
 (17) R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).  
 (18) E. Miron, B. Raz, and J. Jortner, *Chem. Phys. Lett.*, **6**, 563 (1970).  
 (19) M. Krauss and S. R. Mielczarek, *J. Chem. Phys.*, **51**, 5243 (1969).  
 (20) C. F. Bender, T. H. Dunning, Jr., H. F. Schaefer, III, W. A. Goddard, III, and W. J. Hunt, *Chem. Phys. Lett.*, **15**, 171 (1972).  
 (21) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys.*, **9**, 75 (1975).  
 (22) L. E. McMurchie and E. R. Davidson, *J. Chem. Phys.*, **66**, 2959 (1977).

## Theoretical Studies of the Cubane Molecule

Jerome M. Schulman,\*<sup>1a</sup> C. Rutherford Fischer,<sup>1b</sup> Paul Solomon,<sup>1a</sup> and Thomas J. Venanzi<sup>1c</sup>

Contribution from the City University of New York, Department of Chemistry, Queens College, Flushing, New York 11367, the Department of Physics, Queens College, Flushing, New York 11367, and the Department of Chemistry, College of New Rochelle, New Rochelle, New York 10801. Received November 16, 1977

**Abstract:** Molecular orbital calculations were performed on cubane using ab initio STO-3G, SCF-X $\alpha$ , MINDO/3, and INDO methods. The photoelectron ionization energies were calculated from the above by Koopmans' theorem and, in addition, by Slater's transition-state approximation in the SCF-X $\alpha$  method. An analysis of the molecular orbital energy splitting pattern has been made utilizing the concept of interactions between symmetry-adapted combinations of localized CC and CH orbitals.

### I. Introduction

The present study of cubane, (CH)<sub>8</sub> (Figure 1), concludes a set of investigations on the three (CH)<sub>n</sub> molecules whose carbon skeletons form perfect solids, the others being tetrahedrane ( $n = 4$ )<sup>2a</sup> and dodecahedrane ( $n = 20$ ).<sup>2b</sup> Of the three, cubane is especially interesting to chemists since it has already been synthesized<sup>2c</sup> and its  $O_h$  point-group symmetry confirmed.<sup>2d</sup> However, despite these facts cubane has received surprisingly little theoretical consideration.<sup>3</sup> This paper furnishes molecular orbital calculations at the ab initio STO-3G,<sup>4</sup> SCF-X $\alpha$ ,<sup>5,6</sup> MINDO/3,<sup>7</sup> and INDO<sup>8</sup> levels of approximation and applies the SCF-X $\alpha$  method in Slater's transition state approximation to the calculation of the cubane valence-shell vertical ionization energies. The latter may be compared with the photoelectron spectrum,<sup>9</sup> as yet incomplete.

An important consequence of the high cubane point-group symmetry is the fact that several of the molecular orbitals are symmetry determined in a minimal basis set treatment. This invites a novel analysis of the molecular orbital splitting pattern in terms of interactions between localized CC and CH orbitals (LMO's), of the Edmiston-Ruedenberg<sup>10</sup> type, for example, which offers some interesting insights into cubane in particular and hydrocarbons generally.

### II. Molecular Orbital Descriptions

**A. General Aspects.** The present molecular orbital studies utilize a minimal basis of atomic orbitals (AOs), i.e., C 1s, 2s, and 2p and H 1s orbitals. The MINDO/3 and INDO methods ignore the C 1s cores, as we shall do in the present discussion. The three 2p orbitals of each carbon can be chosen to be 2p<sub>r</sub> pointing radially outward from the molecular midpoint and a pair of 2p<sub>t</sub> tangential orbitals perpendicular to 2p<sub>r</sub>. This simplifies the reduction into irreducible representations of the

full atomic orbital reducible representation. Each of the three sets of eight radial functions (C2s, C2p<sub>r</sub>, and H1s) leads to a<sub>1g</sub>, t<sub>2g</sub>, t<sub>1u</sub>, and a<sub>2u</sub> symmetry adapted linear combinations; the 16 AO tangential set furnishes e<sub>g</sub>, t<sub>1g</sub>, t<sub>2g</sub>, e<sub>u</sub>, t<sub>1u</sub>, and t<sub>2u</sub> symmetry orbitals. Thus, in toto, the full valence AO basis contains in type (and number) a<sub>1g</sub>(3), a<sub>2u</sub>(3), e<sub>g</sub>(1), e<sub>u</sub>(1), t<sub>1g</sub>(1), t<sub>2g</sub>(4), t<sub>1u</sub>(4), and t<sub>2u</sub>(1) symmetry orbitals.

The ground-state molecular orbital configuration is easily determined by projecting the 12 CC bent  $\sigma$  bonds onto the irreducible representations of  $O_h$ , to give a<sub>1g</sub>(1), e<sub>g</sub>(1), t<sub>2g</sub>(1), t<sub>1u</sub>(1), and t<sub>2u</sub>(1) orbitals; projecting out the eight linear combinations of CH  $\sigma$  bonds gives a<sub>1g</sub>(1), t<sub>2g</sub>(1), t<sub>1u</sub>(1), and a<sub>2u</sub>(1) orbitals. Two important points follow. (1) The e<sub>g</sub> and t<sub>2u</sub> orbitals that occur only once in the occupied set are symmetry-determined combinations of CC LMOs with no CH admixture (they are also symmetry-determined combinations of 2p<sub>t</sub> orbitals with no C2s admixture). (2) The a<sub>2u</sub> orbital is derived from a linear combination of CH LMOs with no CC LMO contribution. Thus, cubane represents the unusual situation where a saturated hydrocarbon has a molecular orbital which is solely CC bonding and another which is solely CH bonding. (By contrast, tetrahedrane and dodecahedrane have symmetry-determined molecular orbitals which are linear combinations of CC LMOs alone, but no orbitals formed exclusively from CH LMOs).

**B. SCF-X $\alpha$  Calculations.** Before citing the results, it is necessary to give some particulars of the SCF-X $\alpha$  calculations performed here since the parameters of the method have not been standardized. For a general description of the method, its philosophy, and applications, the reader is referred to the papers of Slater<sup>5</sup> and Johnson.<sup>6</sup> The quantities specific to the present calculations are (1) the ratio of C to H atomic sphere radii,  $r_C/r_H$ , (2) the percent overlap between atomic spheres, (3) the exchange-term prefactors,  $\alpha_C$  and  $\alpha_H$  for the atomic,

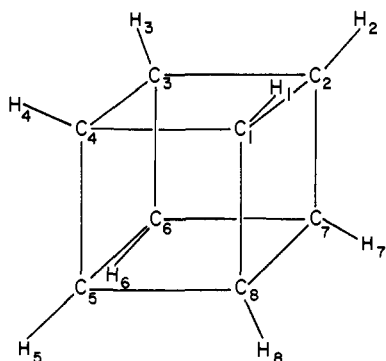


Figure 1. The cubane molecule including the atomic numbering system used here.

interatomic, and outer-sphere regions, and (4) the angular momentum  $l$  values to be used in the inner- and outer-sphere regions.

For the atomic spheres we employed the criterion of Norman<sup>11</sup> that each hydrogen and carbon sphere contain one and six electrons, respectively, when the atomic charge densities were superposed, giving  $r_C/r_H = 1.426$ . The extent of sphere overlap was determined by Norman's condition<sup>11</sup> that the virial theorem be satisfied, which furnished  $r_C = 1.74 \text{ \AA}$  (and  $r_H = 1.22 \text{ \AA}$ ). Overlap of the carbon spheres was 19% of the CC bond length and the carbon-hydrogen sphere overlap was somewhat greater. The outer sphere was made tangent to the hydrogen spheres. Values of  $\alpha_C = 0.75928$  and  $\alpha_H = 0.77725$  were taken from the work of Schwarz<sup>12</sup> and Rosch et al.,<sup>13</sup> while for the intersphere and outer-sphere regions a weighted average,  $\alpha = 0.76185$ , was employed. Finally, as to the choice of angular momentum values, partial waves through  $l = 1$  (p orbitals) were used in the carbon and hydrogen spheres and values through  $l = 4$  were used in the outer-sphere region. A test of d waves ( $l = 2$ ) showed their effect on the orbital energies to be negligible.

**C. Molecular Orbital Energies.** The orbital energies,  $e_i$ , obtained from the STO-3G, SCF- $X\alpha$ , MINDO/3, and INDO calculations are given in Table I. The STO-3G and SCF- $X\alpha$  ordering of the orbital energies was the same:  $e_{1a_{1g}} < e_{1t_{1u}} < e_{1t_{2g}} < e_{2a_{1g}} < e_{1a_{2u}} < e_{2t_{1u}} < e_{1e_g} < e_{1t_{2u}} < e_{2t_{2g}}$ , although the SCF- $X\alpha$  values are ca. 0.2–0.3 eV higher (owing to the particular choice of numerical atomic orbitals). The MINDO/3 method led to the same ordering except for a transposition of the proximate  $1e_g$  and  $2t_{1u}$  orbital energies. On the other hand, the INDO ordering differs significantly from the above because of an unusually stable  $1e_g$  level. The localized orbital analysis of section III reveals the source of this extra stability, and demonstrates that it is anomalous. Thus, aside from a possible transposition of  $2t_{1u}$  and  $1e_g$  orbitals the ordering of the cubane molecular energy levels is established.

**D. Ionization Energies.** The vertical ionization potentials (IPs) of cubane can be obtained from the ab initio orbital energies by a variant of Koopmans' theorem. By fitting our previous STO-3G eigenvalues of benzene to the observed IPs we obtain the least-squares equation<sup>14</sup>

$$\text{IP} = -20.75e_{\text{STO-3G}} + 3.10 \text{ eV} \quad (1)$$

with a standard deviation over the range of ca. 20 eV of only 0.21 eV. Applying this equation to the calculated STO-3G cubane eigenvalues gives the predicted IPs shown in Table II. An alternate procedure for the IPs is the SCF- $X\alpha$  "transition-state" method of Slater.<sup>5,13</sup> Here, a separate self-consistent-field calculation is performed for each ionized state— $^2T_{2g}$ ,  $^2T_{2u}$ , etc., with the occupation number of the ionized orbital diminished by half an electron. The calculated ionization energy then closely approximates the difference between the total

Table I. Valence Orbital Energies of Cubane Calculated by Several Methods<sup>a</sup>

Orbital	Negative orbital energy, au			
	STO-3G	SCF- $X\alpha$	MINDO/3	INDO
$1a_{1g}$	1.219	0.835	1.709	2.489
$1t_{1u}$	0.947	0.646	1.055	1.467
$1t_{2g}$	0.739	0.522	0.735	0.990
$2a_{1g}$	0.693	0.505	0.641	1.076
$1a_{2u}$	0.617	0.443	0.584	0.769
$2t_{1u}$	0.555	0.378	0.487	0.728
$1e_g$	0.548	0.361	0.528	0.952
$1t_{2u}$	0.350	0.211	0.349	0.494
$2t_{2g}$	0.344	0.188	0.338	0.393

<sup>a</sup>Bond lengths of  $R_{CC} = 1.55 \text{ \AA}$ ,  $R_{CH} = 1.06 \text{ \AA}$  were employed except in the MINDO/3 calculation where the geometry was optimized to  $R_{CC} = 1.568 \text{ \AA}$ ,  $R_{CH} = 1.106 \text{ \AA}$ .

Table II. Ionization Energies of Cubane (eV)<sup>a</sup>

Symmetry of ionized state	STO-3G eq 1	SCF- $X\alpha$ transition-state method
$^2T_{2g}$	10.2	10.2
$^2T_{2u}$	10.4	10.8
$^2E_g$	14.5	14.9
$^2T_{1u}$	14.6	15.4
$^2A_{2u}$	15.9	16.5
$^2A_{1g}$	17.5	18.5
$^2T_{2g}$	18.4	19.9
$^2T_{1u}$	22.8	22.7
$^2A_{1g}$	28.4	28.0

<sup>a</sup>Reference 9 gives observed ionization energies (eV) at 8.74, 13.62, 15.34, 16.87, and 17.26.

energy of the ion, obtained from its own self-consistent-field ("relaxed") orbitals, and the ground state. The transition state ionization energies are also given in Table II. They have been adjusted so as to bring them into agreement with the STO-3G ionization potentials obtained from eq 3. In the transition-state SCF- $x\alpha$  method the spacings between levels are often produced better than their absolute values.

It should be noted that both the ab initio and transition-state calculations assume  $O_h$  symmetry, thus ignoring the nuclear distortions which would remove the degeneracies of the ion energies. For example, it is probable that a  $D_{4h}$  symmetry would arise from first-order Jahn-Teller distortion of the  $^2E_g$  state along an  $E_g$  vibrational mode. Distortions of the  $^2T_{1u}$ ,  $^2T_{2u}$ , and  $^2T_{2g}$  ions should lead to  $D_{4h}$  and  $D_{3d}$  symmetries via  $E_g$  and  $T_{2g}$  vibrations, respectively. The magnitude of the Jahn-Teller splittings, which are ignored in the present treatment, are probably quite small since cubane is a rigid polycyclic hydrocarbon. Indeed, the splittings observed in the  $^2T$  states of methane and neopentane are 0.7<sup>15</sup> and 0.5 eV,<sup>16</sup> respectively, so that splittings of ca. 0.2 eV can be anticipated for cubane.

Although actual band assignments must await the full photoelectron spectrum, it is already clear that the calculated ab initio and transition-state ionization potentials, which are themselves in good agreement, are quite similar to the values reported in the low-resolution He(I) spectrum, given in Table II.<sup>9</sup> In particular, the calculations predict a very large gap of ca. 4 eV between the  $T_{2g}$ - $T_{2u}$  and  $E_g$ - $T_{1u}$  pairs at 9 and 13 eV. In fact, a gap of 4.9 eV does appear in just this region of the spectrum. Cubane is a rather unusual hydrocarbon in having such a band-free region in its PE spectrum. The gap is most likely a consequence of the unique nature of the  $e_g$  and  $t_{2u}$  orbitals which bracket it, and are purely symmetry-determined combinations of carbon  $2p_t$  orbitals.

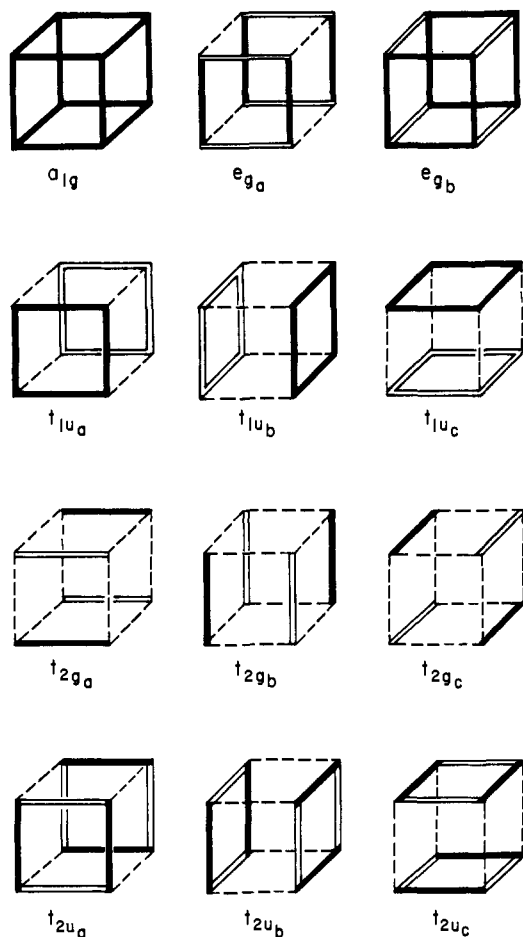


Figure 2. The above are depictions of the symmetry-adapted linear combinations of CC localized orbitals. Filled lines indicate bonds whose contribution to the symmetry function is +1, while unfilled bonds indicate contributions of -1 (excepting  $e_{g_b}$  where the contribution is -2). Dashed bonds do not enter the linear combination of that particular symmetry species.

An interesting question is whether the proximate  $T_{2g}$  and  $T_{2u}$  ionizations, and similarly the  $E_g$  and  $T_{1u}$  ionizations, can be resolved since their calculated energy differences are close to the magnitudes of the Jahn-Teller T-band splittings. A useful experimental approach to this problem would be to obtain the ionization spectrum using He(I) and He(II) or x-ray sources. The latter give relatively high intensities to bands associated with ionizations from orbitals having high s character, while the former leads to intense lines from orbitals having high p character. Thus, the relative intensities of  $T_{2g}$  vs.  $T_{2u}$  and  $E_g$  vs.  $T_{1u}$  bands should vary significantly with the nature of the source.

### III. Localized Orbital Analysis

As has been previously stated, the high point-group symmetry of cubane suggests an interpretation of its orbital energy splitting pattern in terms of symmetry-adapted linear combinations of bond LMOs localized mainly on two centers. In principle, the analysis could utilize either orthogonal LMOs as in the present case (such LMOs are readily obtained computationally by an orthogonal transformation of the canonical molecular orbitals<sup>10</sup>) or nonorthogonal LMOs (e.g., entirely two-center localized).<sup>17</sup>

The 12 symmetry-adapted orbitals obtained by projection of the CC LMOs— $a_{1g}$ ,  $t_{1u}$ ,  $e_g$ ,  $t_{2g}$  and  $t_{2u}$ —are depicted in Figure 2. A bond which makes a positive contribution to the symmetry combination is indicated by a filled solid line, a bond which makes a negative contribution by an unfilled line, and

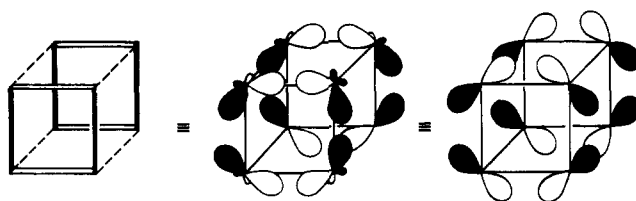


Figure 3. The  $e_{g_a}$  symmetry orbital of Figure 2 depicted in terms of  $sp^3$  hybrids on each carbon, and equivalently in terms of unhybridized p orbitals on each carbon.

a bond which does not contribute to the symmetry-adapted function is dashed. All the magnitudes in the symmetry-adapted functions are unity, except for the negative bonds of the  $e_{g_b}$  orbital which have magnitudes of two. (It might be noted that the  $e_{g_a}$  and  $e_{g_b}$  orbitals transform like  $d_{x^2-y^2}$  and  $d_{2z^2-x^2-y^2}$  orbitals in  $O_h$  symmetry). The symmetry orbitals of Figure 2 are mutually orthogonal.

In terms of the carbon numbering of Figure 1 the LMO between bonded carbons  $i$  and  $j$  is denoted  $b_{ij}$ , and, for example, the normalized algebraic expressions for  $e_{g_a}$  and  $e_{g_b}$  associated with the pictorial representations of Figure 2 are

$$e_{g_a} = 8^{-1/2}(b_{18} - b_{14} + b_{45} - b_{58} + b_{27} - b_{23} + b_{36} - b_{67})$$

$$e_{g_b} = 24^{-1/2}(b_{18} + b_{23} + b_{45} + b_{14} + b_{58} + b_{67} + b_{27} + b_{36} - 2b_{12} - 2b_{56} - 2b_{34} - 2b_{78})$$

The diagrams of Figure 2 are further elaborated on in Figure 3 where the  $e_{g_a}$  orbital is depicted in terms of linear combinations of AO hybrids (ca.  $sp^{3.2}$  in an INDO calculation)<sup>18</sup> or equivalently pure p orbitals. That only p orbitals are sufficient follows immediately from Figure 3 where it can be seen that each carbon contains two equivalent hybrids of opposite sign so that each carbon makes a net zero 2s contribution. A similar situation prevails with the  $t_{2u}$  orbitals which differ from the  $e_{g_a}$  orbital by a rotation of the back face relative to the first, followed by rotation of the entire molecule so as to give either the a, b, or c partner of Figure 2.

Consider now the matrix elements of the Fock operator,  $F$ , in the symmetry-adapted CC basis. Since the operator is totally symmetric in  $O_h$ , its matrix is fully blocked into one-dimensional matrices, the elements of which may be viewed as the Hartree-Fock energies  $e(\text{CC})$  of the  $a_{1g}$ ,  $t_{1u}$ ,  $t_{2g}$ ,  $e_g$ , and  $t_{2u}$  CC symmetry orbitals. These energies can, in turn, be expressed in terms of the four unique Fock interaction matrix elements between various CC LMOs, i.e., the  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$  matrix elements of Figure 4, in addition to the diagonal CC matrix element  $\alpha$ . (Note that we are using the same symbol,  $\beta$ ,  $\gamma$ , etc., to denote the interacting pair of Figure 4 and its matrix element  $\langle b_{12} | F | b_{23} \rangle$ .) Another way to say this is that we can obtain the Fock matrix elements over atomic orbitals, transform them to matrix elements over canonical molecular orbitals, transform again to matrix elements over LMOs,  $\alpha, \beta, \dots$ , and finally transform to matrix elements over symmetry-adapted LMOs. While this seems rather involved, it is certainly conceptually clear that what we seek is the splitting pattern of the CC symmetry-adapted orbital energies.

In terms of the matrix elements  $\alpha, \beta, \dots$ , which are all negative, these energies are

$$e_{a_{1g}}(\text{CC}) = \alpha + 4\beta + 2\gamma + 4\delta + \epsilon \quad (2a)$$

$$e_{t_{1u}}(\text{CC}) = \alpha + 2\beta - 2\delta - \epsilon \quad (2b)$$

$$e_{t_{2g}}(\text{CC}) = \alpha - 2\gamma + \epsilon \quad (2c)$$

$$e_{e_g}(\text{CC}) = \alpha - 2\beta + 2\gamma - 2\delta + \epsilon \quad (2d)$$

$$e_{t_{2u}}(\text{CC}) = \alpha - 2\beta + 2\delta - \epsilon \quad (2e)$$

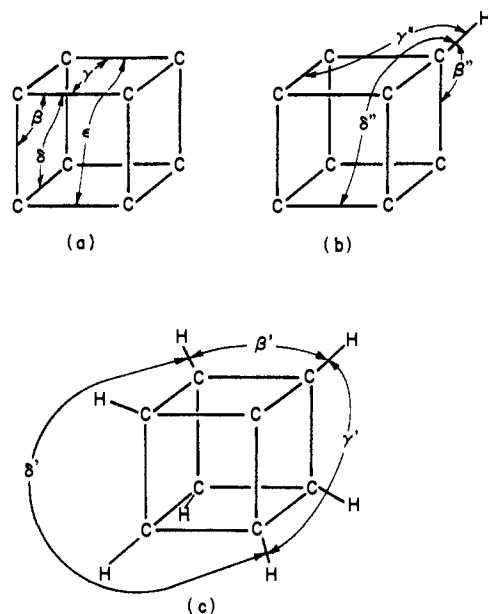


Figure 4. Interactions between CC and CH localized orbitals of cubane. These lead to corresponding matrix elements in the Hartree-Fock operator bearing the same designations in the text.

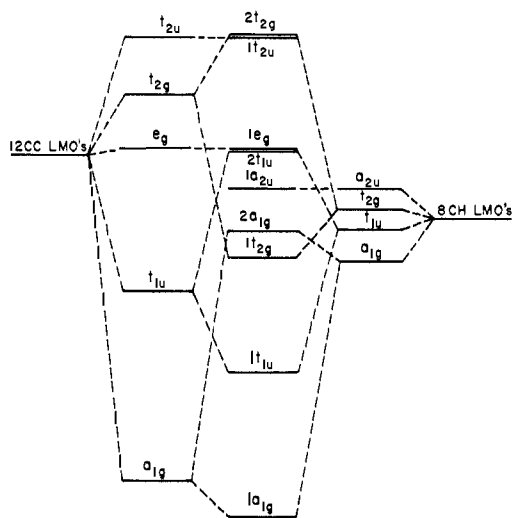


Figure 5. Schematic diagrammatic representation of the cubane orbital energies. On the left, 12 degenerate CC LMOs interact to form five CC energy levels of  $a_{1g}$ ,  $t_{1u}$ ,  $e_g$ ,  $t_{2g}$ , and  $t_{2u}$  symmetries; on the right, eight degenerate CH LMOs interact to form four CH energy levels of  $a_{1g}$ ,  $t_{1u}$ ,  $t_{2g}$ , and  $a_{2u}$  symmetry. In the center the cubane molecular orbital levels are shown. Six are formed from interactions between CC and CH orbitals of like symmetry ( $a_{1g}$ ,  $t_{1u}$ , and  $t_{2g}$ ); the  $e_g$ (CC),  $t_{2u}$ (CC) and  $a_{2u}$ (CH) are symmetry determined. The location of the 12 CC LMO's relative to the 8 CH LMO's is not known with certainty.

In order to get some numerical estimate of these splittings we obtained  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\dots$ , from the INDO calculation, its orbitals being convenient to localize. The values calculated were (au)  $\alpha = -0.96$ ,  $\beta = -0.23$ ,  $\gamma = -0.23$ ,  $\delta = -0.03$ , and  $\epsilon = -0.06$ . It can be seen that the diagonal CC LMO matrix element,  $\alpha$ , is the most negative and that the algebraic increase in the interaction elements tends to correlate with decreasing LMO overlap. The only exception is the vicinal interaction energy,  $\gamma$ , which is as negative as the geminal value,  $\beta$ , even though the vicinal bonds are somewhat further apart. This illustrates an inadequacy of the INDO method. By observing that  $\frac{1}{2}(e_{t_{2u}}(\text{CC}) - e_{e_g}(\text{CC})) = -\gamma + 2\delta - \epsilon \approx -\gamma$  and recalling that both the  $t_{2u}$  and  $e_g$  orbitals are symmetry determined, we can obtain values of  $-\gamma$  from the SCF orbital

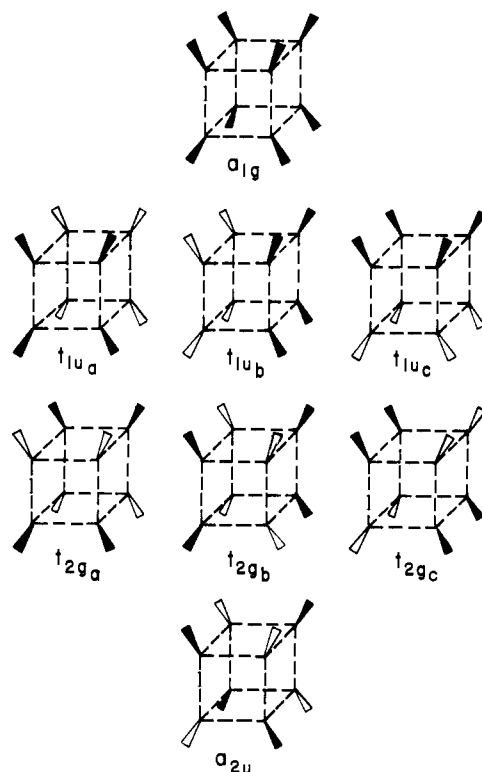


Figure 6. Symmetry-adapted linear combinations of CH localized orbitals. Filled and unfilled lines indicate contributions of +1 and -1, respectively.

energies  $e_{t_{2u}}$  and  $e_{e_g}$  (which are identical with  $e_{t_{2u}}(\text{CC})$  and  $e_{e_g}(\text{CC})$ ). The values of  $\frac{1}{2}(e_{t_{2u}} - e_{e_g})$  found from the STO-3G, SCF-X $\alpha$ , and MINDO/3 methods are 0.099, 0.075, and 0.090 au, respectively, whereas the INDO value is more than twice as large, 0.229 au. Thus, the INDO method produces too negative a  $\gamma$ , i.e., it overemphasize the  $\pi$ -like interactions between front and back carbons in Figure 3.

If we accept as approximate values of the parameters  $\beta = -0.2$ ,  $\gamma = -0.15$ ,  $\delta = -0.03$ , and  $\epsilon = -0.06$ , it is easily verified that the CC energies in order of increasing values are  $e_{a_{1g}}(\text{CC}) < e_{t_{1u}}(\text{CC}) < e_{e_g}(\text{CC}) < e_{t_{2g}}(\text{CC}) < e_{t_{2u}}(\text{CC})$ . These are depicted schematically on the left-hand side of the orbital interaction diagram, Figure 5, with the set of 12 "degenerate" CC LMO energies (at the center of gravity of this splitting pattern) further to the left, yet.

We now turn to the corresponding splitting pattern for the eight CH LMOs. The latter, when projected onto the  $O_h$  irreducible representations, furnish species of symmetry  $a_{1g}$ ,  $t_{1u}$ ,  $t_{2g}$ , and  $a_{2u}$ , once each. These are shown in Figure 6, where positive CH contributions to the symmetry combinations are indicated by filled lines and negative contributions by unfilled lines. In order to compute the CH Hartree-Fock energies we require the three unique Fock interaction matrix elements,  $\beta'$ ,  $\gamma'$ , and  $\delta'$  of Figure 4, along with  $\alpha'$ , the diagonal CH matrix element. The splitting pattern is readily obtained as

$$e_{a_{1g}}(\text{CH}) = \alpha' + 3\beta' + 3\gamma' + \delta' \quad (3a)$$

$$e_{t_{1u}}(\text{CH}) = \alpha' + \beta' - \gamma' - \delta' \quad (3b)$$

$$e_{t_{2g}}(\text{CH}) = \alpha' - \beta' - \gamma' + \delta' \quad (3c)$$

$$e_{a_{2u}}(\text{CH}) = \alpha' - 3\beta' + 3\gamma' - \delta' \quad (3d)$$

Numerical estimates obtained by localizing the INDO nonlocal orbitals are (au)  $\alpha' = -0.88$ ,  $\beta' = -0.05$ ,  $\gamma' = -0.01$ , and  $\delta' = -0.002$ . Again there is found a correlation between the interaction matrix elements and the distance between the corresponding CH LMOs. In order of increasing energy we

obtain  $e_{a_{1g}}(\text{CH}) < e_{t_{1u}}(\text{CH}) < e_{t_{2g}}(\text{CH}) < e_{a_{2u}}(\text{CH})$ . The splitting pattern is depicted on the right-hand side of Figure 5 with the eight "degenerate" CH LMO energies (at the center of gravity) further to the right.

It is interesting to compare the unprimed and primed interaction matrix elements. Thus, we see that  $\alpha \approx \alpha'$ , the INDO "energy" of a CC orbital is approximately equal to that of a CH orbital. This result probably holds true for hydrocarbons in general, since, although cubane has a strained framework, the strain energy is distributed over 12 bonds. Comparison of the interaction matrix elements shows that the CH  $\beta'$ , which describes a vicinal interaction, is of the same order of magnitude as  $\gamma$  and  $\delta$ , the two CC vicinal interactions. Note also that the vicinal interactions depend on dihedral angle since this geometrical parameter largely determines the distance between centroids.

Since there are no geminal CH interactions (which would require at least a CH<sub>2</sub> unit) the range of the CH splittings is somewhat smaller than the CC splittings. Moreover, it is easy to locate the least stable of the CH symmetry-orbital energies,  $e_{a_{2u}}(\text{CH})$ , since this orbital is symmetry determined. Actually, the determination by symmetry here is a somewhat weaker condition than for the  $t_{2u}$  and  $e_g$  orbitals since in a minimal basis there is only one orbital of each of the latter symmetries in both the occupied and virtual molecular orbital set. While there is only one occupied CH orbital which is ascribed to the symmetry-adapted combination of CH bonds, there are three unoccupied  $a_{2u}$  orbitals (also originating from the C 2s, C 2p<sub>r</sub>, and H 1s basis functions) and the detailed form of the occupied  $a_{2u}$  orbital can only be determined after the SCF calculation has been made.

In order to complete the cubane molecular orbital energy scheme and obtain an accounting for the origin of the molecular orbitals, the three CC-CH interaction energies  $\beta''$ ,  $\gamma''$ , and  $\delta''$  of Figure 4 are required. In terms of them the Fock interaction elements between CC and CH symmetry-adapted functions of the same symmetry are

$$V(a_{1g}) = 6^{+1/2}(\beta'' + 2\gamma'' + \delta'') \quad (4a)$$

$$V(t_{1u}) = 2(\beta'' - \delta'') \quad (4b)$$

$$V(t_{2g}) = 2^{+1/2}(\beta'' - 2\gamma'' + \delta'') \quad (4c)$$

The  $2 \times 2$  matrixes for these three symmetries are now known. They can be diagonalized to obtain the Hartree-Fock orbital energies or their solutions can be approximated by the perturbation-theory expression for the splitting (symmetric about the average). INDO calculations yield (au)  $\beta'' = -0.13$ ,  $\gamma'' = -0.04$ , and  $\delta'' = -0.02$ . The largest splitting is obtained for the  $t_{1u}$  case, with smaller splittings for  $a_{1g}$  and  $t_{2g}$ . The split levels and the dashed connecting lines to the interacting CH and CC levels are depicted in the center of Figure 5.

The following characterizations of the cubane molecular orbitals can now be made. The  $1a_{1g}$  orbital is predominantly CC bonding and  $2a_{1g}$  is mostly CH. The  $1t_{1u}$  and  $2t_{2g}$  orbitals are mixtures of CC and CH bonds, with the former predominating, while the  $2t_{1u}$  and  $1t_{2g}$  are mixtures with more CH than CC. Finally, the  $e_g$  and  $t_{2u}$  orbitals are CC by symmetry, and the  $a_{2u}$  orbital is CH. Such a detailed characterization does not appear to have been made for other molecules.

In view of this fact it is worth considering how cubane would be described by an empirical method. The higher ionization potentials of hydrocarbons have been described by a Hückel (one-electron, nearest-neighbor) treatment employing a C 2s orbital basis with an empirical  $\alpha = 21.3$  eV (for a methine carbon) and a 2s-2s interaction energy,  $\beta = 1.85$  eV.<sup>19</sup> The mixing of the eight cubane C 2s functions in this description leads to eight symmetry-adapted linear combinations— $a_{1g}$ ,

$t_{1u}$ ,  $t_{2g}$ , and  $a_{2u}$ —which should correspond approximately to the observed photoionization energies for these symmetries. The results of such a calculation can be readily found from the isomorphic CH splitting pattern, eq 3a-d, by dropping the primes and setting  $\gamma$  and  $\delta$  to zero. We obtain equally spaced levels of separation  $2\beta$  or 3.7 eV. This prediction conforms to some extent with the calculated photoionization energies of the SCF-X $\alpha$  transition-state calculation which furnishes spacings of 3.4 eV for  $A_{2u}$ - $T_{2g}$ , 2.8 eV for  $T_{2g}$ - $T_{1u}$ , and 5.3 eV for  $T_{1u}$ - $A_{1g}$ .

Presumably the difference between the two models involves inclusion of the 2s-2s matrix elements  $\gamma$  and  $\delta$ <sup>20</sup> since the Hückel spacing would then go, in the order cited above as  $2\beta - 4\gamma + 2\delta$ ;  $2\beta - 2\delta$ ;  $2\beta + 4\gamma + 2\delta$ , which are more in accord with the transition state method spacings. The first treatment presented in this paper, however, seems more appealing in that it is a model involving interacting bonds. In fact, it might be possible to use it for hydrocarbons generally for a simple prediction of the splitting pattern via the various unprimed, primed, and double-primed (i.e., CC-CC, CH-CH, and CC-CH) matrix elements in a one-electron treatment (assuming transferability). This will be the subject of future investigations.

**Acknowledgments.** The authors wish to acknowledge grants-in-aid from the CUNY Research Foundation (No. 11634 to J.M.S. and No. 10647 to C.R.F.). Helpful discussions with Professor R. L. Disch are gratefully acknowledged as well.

## References and Notes

- (1) (a) City University of New York, Department of Chemistry, Queens College; (b) Department of Physics, Queens College; (c) College of New Rochelle.
- (2) (a) J. M. Schulman and T. J. Venanzi, *J. Am. Chem. Soc.*, **96**, 4739 (1974). (b) J. M. Schulman, T. Venanzi, and R. L. Disch, *ibid.*, **97**, 5335 (1975). Note that the pairs of numbers (3,4) and (7,8) in the cubane graph have been inadvertently transposed. (c) P. E. Eaton and T. V. Cole, Jr., *ibid.*, **86**, 3157 (1964). (d) E. B. Fleischer, *ibid.*, **86**, 3889 (1964).
- (3) Various theoretical aspects of cubane have been discussed, however, by (a) H. Preuss and R. Janoschek, *J. Mol. Struct.*, **3**, 423 (1969); (b) O. Martensson, *Acta Chem. Scand.*, **24**, 1495 (1970); (c) H. Iwamura, K. Morio, M. Oki, and T. Kunii, *Tetrahedron Lett.*, **52**, 4575 (1970); (d) N. C. Baird, *Tetrahedron*, **26**, 2185 (1970); (e) K. Shimizu, H. Morimoto, H. Kato, and T. Yonezawa, *Nippon Kagaku Zasshi*, **90**, 865 (1969); (f) K. Kovacevic, M. E. Maksic, and Z. B. Maksic, *Croat. Chim. Acta*, **46**, 249 (1974); (g) K. Kovacevic and Z. B. Maksic, *J. Org. Chem.*, **39**, 539 (1974); (h) Z. B. Maksic, K. Kovacevic, and M. E. Maksic, *Tetrahedron Lett.*, **2**, 101 (1975).
- (4) W. J. Ehre, R. J. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (5) J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972).
- (6) K. H. Johnson, *Adv. Quantum Chem.*, **7**, 143 (1973).
- (7) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
- (8) J. A. Pople and D. L. Beveridge, "Approximate Molecular orbital Theory," McGraw-Hill, New York, N.Y., 1970.
- (9) (a) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969); (b) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, **92**, 19 (1970).
- (10) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965).
- (11) J. G. Norman, Jr., *J. Chem. Phys.*, **61**, 4630 (1974).
- (12) K. Schwarz, *Phys. Rev. B*, **5**, 2466 (1971).
- (13) N. Rosch, W. G. Klempner, and K. H. Johnson, *Chem. Phys. Lett.*, **23**, 149 (1973).
- (14) A similar procedure has been applied more extensively to ab initio 4-31G eigenvalues of hydrocarbons by K. B. Wiberg, G. B. Ellison, C. R. Brundle, and N. A. Kuebler, *Chem. Phys. Lett.*, **41**, 36 (1976). The result of eq 3 then implies that the STO-3G and 4-31G eigenvalues are linearly related. In fact, we find  $\epsilon_{4-31G} = 1.011\epsilon_{\text{STO-3G}} - 1.176$  eV with a standard deviation of 0.25 eV.
- (15) A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 285 (1968).
- (16) S. E. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maler, *J. Chem. Soc., Faraday Trans. 2*, **68**, 905 (1972).
- (17) P. W. Payne, *J. Am. Chem. Soc.*, **99**, 3787 (1977). This reference gives  $-0.853$  au for the energy eigenvalue of a localized CH orbital in ethane, which is similar in magnitude to the value obtained here in INDO theory.
- (18) J. M. Schulman and M. D. Newton, *J. Am. Chem. Soc.*, **96**, 6295 (1974).
- (19) A. W. Potts and D. G. Streets, *J. Chem. Soc., Faraday Trans. 2*, **70**, 875, 1505 (1974).
- (20) It is by no means clear how such matrix elements would be obtained.