associated with discrete and continuous satellites taken together. Krause, *et al.*, also indicate that the probability is about five times greater for double excitation to a continuum state[55,56] of the second electron than to a discrete state so that only about 3% of the 1s ionizations are associated with discrete shake-up satellites, a value less than that reported[1b] by Siegbahn, *et al.*

We do not calculate the probabilities of the two types of double excitations explicitly but simply associate our computed 15% reduction in the normal hole state probability with a rough measure of combined probabilities for double excitations. Thus our results presented in the previous section assuming a frozen core should correspond more closely to the contribution from a given shell of the neutral to intensities measured by experimental techniques such as X-ray absorption, which include transitions to many different final states of the ion having a hole in a specified core orbital, than to photoelectron spectral intensities, since the latter imply the use of an electron energy analyzer to select a single state of the ion. However, relative values of cross sections computed assuming frozen cores, such as the ratios given in Table VI and others that can easily be calculated from our results, should nevertheless serve as a useful guide to photoelectron spectral intensities for inner shells of atoms and molecules.

Summary

We have presented photoionization cross sections at soft X-ray photon energies for the 1s shell of the elements boron through neon and for the 2s and 2p shells of the elements aluminum through argon. The cross sections were calculated from the exact continuum wave functions of a piecewise Coulombic potential and from reported[41] SCF bound state wave functions. The method for generating the continuum wave functions is very flexible in that various interactions may be added to the potential given in eq 7 before the fitting to a piecewise Coulombic form. Our present use of the method differs from McGuire's[22] in that our fitting is to the purely electrostatic atomic potential generated from SCF charge densities, while his fitting was to Herman–Skillman[19] atomic potentials which include an approximate exchange contribution. Indeed omission of exchange may be a major reason why our 2s cross sections are significantly greater than experimental values at the soft X-ray energies but less than experimental values at lower photon energies. We have found that cross sections for orbitals possessing radial nodes, such as 2s, are more sensitive to changes in the computational method than are cross sections for radially nodeless orbitals, such as 1s and 2p. Calculations including full exchange such as those reported by Kennedy and Manson[21] for noble gases yield results better than ours for the $\sigma(n\mathrm{s})/\sigma(n\mathrm{p})$ ratio. In a future publication we shall present photodetachment cross sections for anions calculated by a modification of the present procedure to include both exchange and polarization contributions to the potential.

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(55) For measurements of shake-off probabilities, see T. A. Carlson, W. E. Moddeman, and M. O. Krause, *Phys. Rev. A*, 1, 1406 (1970).
(56) For calculations of shake-off probabilities, see T. A. Carlson and C. W. Nestor, Jr., *Phys. Rev. A*, 8, 2887 (1973).

A Theoretical Study of the Tetrahedrane Molecule

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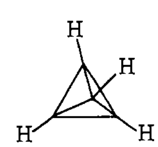
Abstract: An *ab initio* calculation in the extended Gaussian 4-31G basis set has established that tetrahedrane is a local minimum point on the eight-atom C_4H_4 potential energy surface. The CC and CH bond lengths were found to be 1.48 and 1.05 Å, respectively, after extensive geometry search. A normal coordinate analysis performed in the 4-31G basis furnished predictions of the tetrahedrane vibrational frequencies and the relative ir intensities. Also, a barrier of at least 18 kcal/mol for homolytic cleavage of a single bond has been obtained. The calculated heat of formation, hybridization, photoelectron spectrum, and one-bond nuclear spin–spin coupling constants are given.

Tetrahedrane (tricyclo[1.1.0.0^{2,4}]butane), I, is of chemical interest from the viewpoints of: (1) topology, having a carbon framework represented by the simplest connected cubic graph,[2] II; (2) symmetry,[3] having a carbon framework which is the simplest of the five regular polyhedra and one unique skeletal length, four being the largest number of points equidistant on the surface of a sphere; (3) quantum theory, as a strained ring system *par excellence*, the fusion of four



I


II

(1) Alfred P. Sloan Research Fellow.
(2) A. T. Balaban, R. O. Davies, F. Harary, A. Hill, and R. Westwick, *J. Aust. Math. Soc.*, 11, 207 (1970).
(3) H. P. Schultz, *J. Org. Chem.*, 30, 1361 (1965).

cyclopropane rings engendering a strain energy of more than 20 kcal/mol per framework bond;[4] (4) attempted syntheses, dating back more than 50 years[5a] (tetrahedrane has been implicated as an intermediate in carbene insertion reactions[5b,c]).

There have been several theoretical studies of tetrahedrane[6a–g] at various levels of sophistication from electrostatic models to semiempirical to *ab initio* SCF–CI, which have predicted a highly reactive molecule, thermodynamically less stable than the matrix-trapped isomer, cyclobutadiene.[7] Yet, no calculation has determined whether, in fact, C_4H_4 in tetrahedral arrangement is actually a minimum point on the eight-atom potential energy surface. Now a complete study of a potential surface with $3(8) - 6 = 18$ degrees of freedom is unprecedented; however, the high T_d point-group symmetry actually enables such a calculation to be made. The internal vibrational modes of tetrahedrane are $A_1(2)$, $E_2(2)$, $T_1(1)$, and $T_2(3)$ in representation (and number). Thus, a choice of symmetry displacements consisting of one set of orthogonal partners of the degenerate irreducible representations necessitates only 13 independent matrix elements (eight diagonal and five interaction), F_{ij}, of the potential energy. This treatment is performed here using *ab initio* SCF energies calculated in the extended contracted Gaussian 4-31G basis set [8a] and, for comparison, the results obtained in the minimal STO-3G basis[8b] are also included. It is demonstrated that the tetrahedral geometry does indeed represent a local potential energy minimum point.

Another matter of importance is whether this potential is deep enough to allow isolation of tetrahedrane or, at least, its spectroscopic detection. Barriers to concerted rearrangement to cyclobutadiene and retrogression to acetylenes, both undoubtedly exothermic reactions, are suggested by conservation of orbital symmetry as the tetrahedrane ground state correlates with excited states of the latter molecules (it is not *a priori* clear just how large the barriers would be). The process of homolytic cleavage of a single tetrahedrane CC bond is not governed by symmetry arguments and the determination of the barrier is a difficult computational problem. Results of calculations on the bicyclobutyl diradical are presented here which furnish an insight into the height of this barrier.

As tetrahedrane, if successfully prepared, is likely to be identified in part by vibrational spectroscopy we have calculated approximate ir and Raman frequencies and, in addition, the relative ir intensities. Although they are not of spectroscopic accuracy due to the limitations of contracted basis sets in calculating force constants[9,10] and the need for anharmonicity corrections, these calculated frequencies and intensities may be useful in the interpretation and proof of structure. Moreover, should more extensive calculations of the tetrahedrane be warranted, the present paper provides a framework for carrying them out.

Finally, employing our previous experience in the theory of strained ring hydrocarbons,[11] we predict the tetrahedrane equilibrium geometry, heat of formation, strain energy, photoelectron ionization energies, and directly bonded nuclear spin–spin coupling constants, $^1J_{^{13}CH}$ and $^1J_{^{13}C^{13}C}$.

I. Equilibrium Geometry and Normal Coordinate Analysis

The *ab initio* SCF method with an extended Gaussian 4-31G basis gives hydrocarbon CC and CH equilibrium bond lengths to *ca.* 0.01 Å accuracy[12a] (the STO-3G basis gives almost as good agreement,[10,12b] even for highly strained molecules[11]). Thus, with these basis sets we first sought an energy minimum with respect to totally symmetric (A_1) distortions of the carbon skeleton and CH bond lengths, within T_d symmetry. An equilibrium geometry was indeed obtained with 4-31G CC and CH bond lengths of 1.482 and 1.054 Å, respectively. (The corresponding STO-3G values were 1.472 and 1.069 Å.) The framework bond lengths are rather similar to the experimental values for bicyclobutane ($r_0(C_1C_2) = 1.498$ Å, $r_0(C_1C_3) = 1.487$ Å).[13] The CH bond length of tetrahedrane is similar to that of acetylene, $r_e = 1.061$ Å,[14] for which the 4-31G and STO-3G values are 1.051 and 1.065 Å,[12a] respectively. As will be seen later, the short CH bond length is consistent with the very high s character in the carbon CH hybrid.

The CC and CH bond lengths were found to sufficient precision that contributions to the potential energy, linear in the A_1 distortions, were negligible. With this construction and the fact that the close shell electronic structure of tetrahedrane given in section II precludes degeneracy in the ground-state total energy, the nuclear potential energy becomes a quadratic form in the various symmetry distortions in the harmonic approximation. Thus we formed sets of "external" symmetry coordinates, written in terms of Cartesian atomic displacements, linearly independent and mutally orthogonal, corresponding to the two A_1, two E, three T_2, and T_1 distortions. The symmetry coordinates belonging to the same degenerate representation had the same "orientation," *i.e.*, belonged to the same row or column of the irreducible representation matrices. The set of external symmetry coordinates furnished, *en passant*, a diagonal **G** matrix,[15] which could be transformed fur-

(4) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 773 (1972).
(5) (a) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967; (b) A. P. Wolf and P. B. Shevlin, *J. Amer. Chem. Soc.*, **92**, 406 (1970); (c) L. B. Rodewald and H. Lee, *ibid.*, **95**, 623 (1973).
(6) (a) Z. Maksic, L. Klasinc, and M. Randic, *Theor. Chim. Acta*, **4**, 273 (1966); (b) M. Randic, *Croat. Chim. Acta*, 38, 49 (1966); (c) N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967); (d) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); (e) N. C. Baird, *Tetrahedron*, **26**, 2185 (1970); (f) R. J. Buenker and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **91**, 4342 (1969); (g) I. J. Miller, *Aust. J. Chem.*, 24, 2013 (1971); (h) O. Martensson, *Acta Chem. Scand.*, **25**, 1140 (1971).
(7) (a) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); (b) O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *J. Amer. Chem. Soc.*, **95**, 1337 (1973).
(8) (a) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); (b) W. J. Hehre, R. J. Stewart, and J. A. Pople, *ibid.*, **51**, 2657 (1969).
(9) W. Meyer and P. Pulay, *J. Chem. Phys.*, **56**, 2109 (1972).
(10) M. D. Newton, W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(11) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **96**, 17 (1974).
(12) (a) W. A. Lathan, W. H. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); (b) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971).
(13) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).
(14) W. J. Lafferty and R. J. Thibault, *J. Mol. Spectrosc.*, **14**, 79 (1964).
(15) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

ther to the unit matrix (a change of metric tensor) if the local Cartesian coordinates (*e.g.*, X_1^C, an arbitrary displacement from its equilibrium position of carbon 1 along the X-Cartesian axis) were transformed to mass-weighted coordinates[16] (*e.g.*, $q_{X_1}{}^C = m_C{}^{1/2}X_1{}^C$). In any event, the demonstration that the eigenvalues of the potential energy matrix are greater than zero is sufficient proof of bound motion and the **G** matrix need be used only for determining the normal modes.

Consider, then, a basis of symmetry coordinates for describing the vibrations of tetrahedrane. Two independent and "normalized" A_1 coordinates (E_a, T_{2a}, and T_{1a} coordinates are given in the Appendix) are clearly

$$S_1{}^{A_1} = {}^1/_2(R_1 + R_2 + R_3 + R_4) \qquad (1a)$$

and

$$S_2{}^{A_1} = {}^1/_2(H_1 + H_2 + H_3 + H_4) \qquad (1b)$$

where $R_1 = 3^{-1/2}(X_1{}^C + Y_1{}^C + Z_1{}^C)$, $R_2 = 3^{-1/2}(-X_2{}^C + Y_2{}^C - Z_2{}^C)$, $H_1 = 3^{-1/2}(X_1{}^H + Y_1{}^H + Z_1{}^H)$, etc., are linear combinations of carbon and hydrogen Cartesian displacements from their equilibrium positions. The atomic numberings and location of the Cartesian axes are shown in Figure 1. The two symmetry coordinates correspond to independent expansions of the carbon and hydrogen tetrahedral frames. The $S_1{}^{A_1}$ displacement can also be written as

$$S_1{}^{A_1} = 24^{-1/2}(R_{12} + R_{13} + R_{14} + R_{23} + R_{24} + R_{34}) \qquad (1c)$$

where the R_{ij} are increases in the six CC equilibrium bond lengths. Since the hydrogens remain in place in $S_1{}^{A_1}$, this coordinate contains considerable CH distortion and it will have a large interaction matrix element, $F_{12}{}^{A_1}$, in the A_1 contribution, V^{A_1}, to the potential energy

$$V^{A_1} = V_0 + {}^1/_2[F_{11}{}^{A_1}(S_1{}^{A_1})^2 + F_{22}{}^{A_1}(S_2{}^{A_1})^2 + 2F_{12}{}^{A_1}S_1{}^{A_1}S_2{}^{A_1}]$$

$F_{22}{}^{A_1}$ is nearly the force constant for a single CH stretch since interactions between the CH bonds are small. The CC stretching force constant, F_{CC}, may be shown, using (1c), to be approximately

$$F_{CC} = {}^1/_4(F_{11}{}^{A_1} + F_{22}{}^{A_1} + 2F_{12}{}^{A_1}) \qquad (1d)$$

or alternately, if in computing the interaction constant $F_{12}{}^{A_1}$ equal $S_1{}^{A_1}$ and $S_2{}^{A_1}$ displacements are made, the carbon skeleton expands while the CH lengths remain unchanged and F_{CC} may be computed directly from the observed increase in energy.

The various $F_{ij}{}^R$ of each representation R were obtained by distorting the molecule under orthogonal partners of each symmetry species, *e.g.*, $S_1{}^{E_a}$, $S_2{}^{E_a}$, and $S_1{}^{E_a} + E_2{}^{E_a}$, and calculating the matrix elements in the harmonic approximation

$$F_{11}{}^E = 2(V - V_0)/(S_1{}^{E_a})^2 \qquad (2)$$

The denominator contains the square of the magnitude of the displacement and $V - V_0$ is the energy change computed for distortion solely in the symmetry coordinate $S_1{}^{E_a}$, all other $S_i{}^R = 0$. A large number of distortions were made for the calculation of the $F_{ij}{}^R$ which are given for both the 4-31G and STO-3G bases. Small distortions were used, 0.01 to 0.05 Å; however, a few random tests using even larger distortions gave very similar force constants. The $F_{ij}{}^R$ values are averages of very similar values for several displacements and they are given in Table I. No attempt was made to separate out the small anharmonic contributions due to the approximate values of the dominant quadratic terms.

(16) H. Goldstein, "Classical Mechanics," Addison-Wesley, Reading, Mass., 1959, Chapter 10.

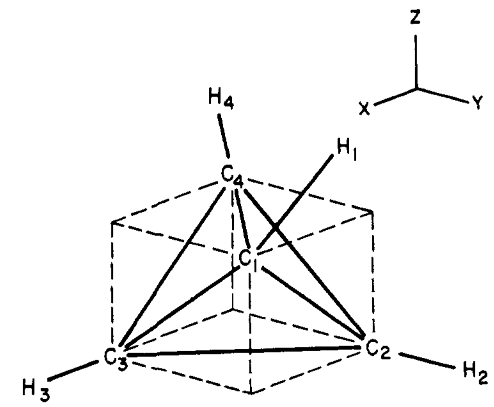


Figure 1. Atomic numberings and coordinate positions of tetrahedrane. Local atomic coordinate systems, *e.g.*, ($X_1{}^C$, $Y_1{}^C$, $Z_1{}^C$), are situated on the various atoms and are parallel to the XYZ axes.

Table I. Potential Energy Matrix Elements, F_{ij} (mdyn/Å), G^{-1} Matrix Elements (amu), and Dipole Moment Derivatives (D/Å)

Symmetry coordinates $(i, j)^a$	$F_{ij}{}^b$ 4-31G	STO-3G	$G_{ij}{}^{-1\,c}$	$\partial\mu/\partial S_i{}^{T_{2a}}$
$S_1{}^{A_1}$	24.5	32.9	12	
$S_2{}^{A_1}$	6.5	7.9	1	
$S_1{}^{A_1}$, $S_2{}^{A_1}$	−6.8	−8.7	0	
$S_1{}^{E_a}$	5.2	8.9	12	
$S_2{}^{E_a}$	0.46	0.49	1	
$S_1{}^{E_a}$, $S_2{}^{E_a}$	0.092	0.27	0	
$S_1{}^{T_{2a}}$	2.6	3.1	12/13	−0.35
$S_2{}^{T_{2a}}$	15.2	21.5	12	−1.37
$S_3{}^{T_{2a}}$	4.7	5.5	1	−0.97
$S_1{}^{T_{2a}}$, $S_2{}^{T_{2a}}$	2.7	3.1	0	
$S_1{}^{T_{2a}}$, $S_3{}^{T_{2a}}$	−2.9	−3.5	0	
$S_2{}^{T_{2a}}$, $S_3{}^{T_{2a}}$	−4.7	−5.5	0	
$S_1{}^{T_{1a}}$	0.73	0.78	1	

[a] A single entry indicates the diagonal potential energy matrix element or force constant, F_{ii}. [b] The conversion factor from atomic units to mdyn/Å is 15.58. [c] The G^{-1} matrix is defined in ref 15.

The CH A_1 stretching force constant in the 4-31G basis was 6.5 mdyn/Å, which is slightly larger than the A_1 force constant for methane in the same basis, 5.8 mdyn/Å (the methane experimental value, without anharmonic correction, is 5.2 mdyn/Å[17]). The STO-3G symmetric CH stretching force constants of tetrahedrane, methane, and acetylene are respectively 7.9, 7.4,[10] and 8.2[10] mdyn/Å, which suggests that the force constant of tetrahedrane is similar to that of acetylene, as is its bond length. (The experimental acetylene

(17) J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964). The experimental value including anharmonic correction is 5.8 mdyn/Å.

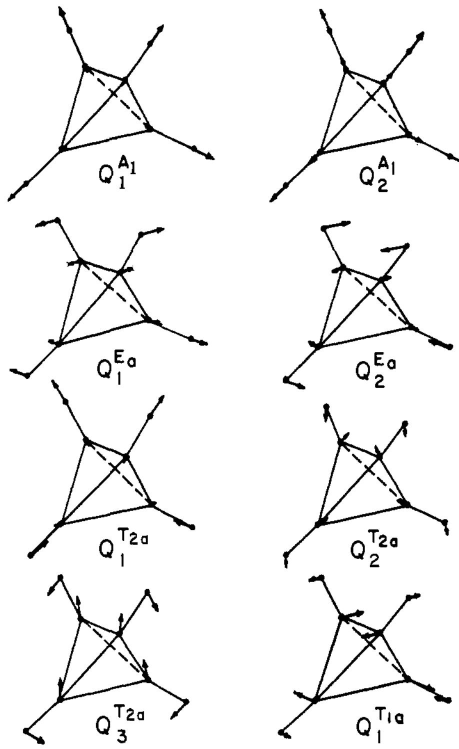


Figure 2. The normal modes of tetrahedrane. As drawn, the T_{2a} modes contain translation of the center of mass in the vertical (Z) direction, which can be eliminated by a suitable Z translation of each atom by the same amount. Similarly, $Q_1^{T_{1a}}$ contains total angular momentum, which can be eliminated by a suitable clockwise rotation of the molecule about the Z axis.

symmetric stretching constant is 6.3 mdyn/Å, 6.0 without anharmonic correction.[18])

The force constant for the framework stretch per CC bond is calculated to be 4.6 mdyn/Å in the 4-31G basis, which agrees with the *ab initio* SCF value reported by Buenker and Peyerimhoff,[6f] 4.6 mdyn/Å (4.4 after CI) obtained in a Gaussian lobe basis.[19] (The STO-3G value is 5.8 mdyn/Å.) These results clearly depict the tetrahedrane CC bond as similar to other CC single bonds. For example, in ethane the CC stretch is 4.6 mdyn/Å[18] and the STO-3G value is 6.5 mdyn/Å;[10] the corresponding ethylene and acetylene values are much larger. One further basis for comparison is the stable P_4 molecule whose force constant is 2.19 mdyn/Å,[20] significantly smaller than that found for tetrahedrane.

The smallest force constant in Table I is that for the hydrogen E_a symmetry distortion. However, it led to a reasonable frequency of vibration and, more important, it was found to be positive, a necessary condition for bound motion.

Using the **F** and $\mathbf{G}^{-1}$ matrix elements of Table I the small vibrations problem $\mathbf{GF} - \lambda I = 0$[15] was solved. Roots of the eigenvalues furnished the harmonic frequencies and the eigenvectors gave the matrix mapping normal coordinates into symmetry coordinates. The frequencies and normal coordinates are given in Table II and the normal modes are depicted in Figure 2. It seems likely that the frequencies are too large by

Table II. Approximate Vibrational Frequencies and Normal Modes of Tetrahedrane Calculated in the Gaussian 4-31G Basis

Normal mode[a]	Vib freq,[b] cm^{-1}	Symmetry coordinates as linear combinations of normal coordinates
$Q_1^{A_1}$	3520	$S_1^{A_1} = 0.10Q_1^{A_1} + 0.27Q_2^{A_1}$
$Q_2^{A_1}$	1550	$S_2^{A_1} = -0.94Q_1^{A_1} + 0.35Q_2^{A_1}$
$Q_1^{E_a}$	900	$S_1^{E_a} = 0.14Q_1^{E_a} + 0.25Q_2^{E_a}$
$Q_2^{E_a}$	840	$S_2^{E_a} = 0.87Q_1^{E_a} - 0.49Q_2^{E_a}$
$Q_1^{T_{2a}}$	3540	$S_1^{T_{2a}} = -0.60Q_1^{T_{2a}} + 0.48Q_2^{T_{2a}} + 0.70Q_3^{T_{2a}}$
$Q_2^{T_{2a}}$	1260	$S_2^{T_{2a}} = -0.072Q_1^{T_{2a}} - 0.26Q_2^{T_{2a}} + 0.11Q_3^{T_{2a}}$
$Q_3^{T_{2a}}$	940	$S_3^{T_{2a}} = 0.78Q_1^{T_{2a}} + 0.059Q_2^{T_{2a}} + 0.62Q_3^{T_{2a}}$
$Q_1^{T_{1a}}$	1110	$S_1^{T_{1a}} = Q_1^{T_{1a}}$

[a] The degenerate modes E, T_2, and T_1 also contain the partners $Q_1^{E_b}$, $Q_2^{E_b}$, etc., not explicitly tabulated. [b] The corresponding STO-3G frequencies are: A_1, 3890, 1710; E, 1140, 890; T_2, 3840, 1520, 970; T_1, 1150 all in cm^{-1}.

10–20%; for example, the symmetric CH stretch is calculated to be 3520 cm^{-1}, whereas the acetylene value is 3374 cm^{-1}.[21] Nonetheless, the 4-31G basis is clearly a considerable improvement over the STO-3G set, for which the CH stretch is computed be 3880 cm^{-1} (Table II), and the 4-31G force constants and frequencies are quite acceptable for an *ab initio* calculation on a molecule of this size. Most striking is the fact that the calculated frequencies are in the range anticipated for a hydrocarbon and there is no indication that tetrahedrane is a particularly weakly bound molecule in the vicinity of its energy minimum.

Since the calculated frequencies give no indication of Fermi resonances with overtones or combination bands, the relative intensities of the three allowed (T_2) transitions can be computed from the squares of the dipole derivatives with respect to the normal modes, $\partial\mu/\partial Q_i^{T_{2a}}$ (i = 1, 3). In turn, these may be computed from the $\partial S_i^{T_{2a}}/\partial Q_j^{T_{2a}}$ obtained from the symmetry coordinates as given in Table II and the dipole derivatives with respect to the symmetry coordinates, $\partial\mu/\partial S_i^{T_{2a}}$, calculated by the INDO method. The INDO values for the dipole derivatives can be quite accurate when its two contributions (point dipole and polarization terms) do not cancel.[22] An example is methane for which the symmetry coordinate for CH stretching was taken to be

$$S_1^{T_{2a}} = {}^1/_2(H_1 - H_2 - H_3 + H_4)$$

with the H_i being displacements from the INDO equilibrium bond length, 1.088 Å (the experimental value is 1.093 Å[17]). Using finite differences, $\partial\mu/\partial S_1^{T_{2a}}$ was computed to be −0.82 D/Å, in good agreement with experiment, −0.83 D/Å (cited in ref 22; the corresponding CNDO value was −0.63 D/Å).

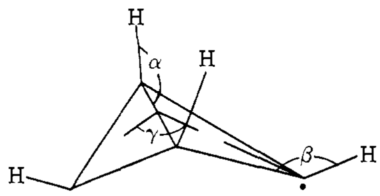
For tetrahedrane it was possible to obtain values for all three $\partial\mu/\partial S_i^{T_{2a}}$ without the cancellation problem arising. These values, obtained by finite differences from the INDO equilibrium geometry of tetrahedrane (R_{CH} = 1.11 Å, R_{CC} = 1.49 Å), are given in Table I. Thus, the dipole derivatives with respect to the three 4-31G normal coordinates were computed to be $\partial\mu/\partial Q_i^{T_{2a}}$ = −0.44, +0.13, and −1.0 D/Å for i = 1–3, in order of decreasing frequency. The allowed vibrational bands of tetrahedrane are thus anticipated to be

(18) J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964). Anharmonic CC corrections are small.
(19) R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, **46**, 2029 (1967).
(20) R. S. McDowell, *Spectrochim. Acta, Part A*, **27**, 773 (1971).
(21) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945.
(22) G. A. Segal and M. L. Klein, *J. Chem. Phys.*, **47**, 4236 (1967). This is a CNDO study.

approximately in the ratio $I_{Q_1}/I_{Q_2}/I_{Q_3}$ = 0.18/0.017/1.0. Since the CNDO method is in appreciably larger error for acetylenic CH stretching and bending dipole derivatives than for those of methane,[22] these estimated intensity ratios may be somewhat crude.

II. The Barrier to Cleavage of a Tetrahedrane Single Bond

We have previously noted that the concerted rearrangement of tetrahedrane to cyclobutadiene and its disproportionation to acetylene are symmetry forbidden reactions. On the other hand, homolytic cleavage of a tetrahedrane single bond to a bicyclobutyl diradical, III, is not. Determination of the barrier for the latter



III

reaction is complicated by the large number of framework and (CH) parameters potentially involved in the reaction coordinate, the possibility of a low-lying diradical triplet state, and the practical difficulty of ascertaining the above and also obtaining a suitable reaction barrier in a basis of manageable size. While completely definitive answers to these questions, which demand appreciable computer time, cannot be given at present, the selected calculations described here give some insight into the probable existence of a barrier.

To start with, the reaction coordinate for breaking the C_2C_3 bond (Figure 1) must, by hypothesis, involve the C_2C_3 distance ($R_{C_2C_3}$). It is further reasonable to assume that regardless of what other geometric parameters participate in the reaction coordinate, *e.g.*, CC bond lengths, HCC angles, etc., the reaction coordinate is a monotonic function of $R_{C_2C_3}$ at early stages of the reaction. While concentrating on a point on the reaction coordinate near to tetrahedrane itself will not give the barrier (which occurs further along), it will furnish a lower bound to it and, moreover, it will tend to simplify some aspects of the computational problem such as minimizing the differential effects of correlation energy and the inadequacy of the *ab initio* basis along the reaction coordinate.

Thus, the present discussion focuses on that point of the reaction coordinate at which $R_{C_2C_3}$ = 1.812 Å (*vs.* the equilibrium 4-31G bond length, 1.482 Å), corresponding to a dihedral angle, γ of III, roughly 20° larger than the tetrahedral equilibrium value, 70° 52′. Working first on the problem of optimizing the geometry of the distorted tetrahedrane, the STO-3G basis was employed. With the framework parameters held fixed, the angles α and β were changed from their tetrahedrane values (α = 160°, β = 145°) to 128° (the bicyclobutane bridgehead value[13]) and 180° (to give a planar radical), respectively. These changes in the hydrogen positions decreased the STO-3G SCF energy at $R_{C_2C_3}$ = 1.812 Å from 50 to 39 kcal/mol above that of tetrahedrane. The angle β was the most important of the two parameters, providing 9 of the 11 kcal/mol stabilization.

With the hydrogens at these new angles the carbon framework was optimized by varying the central bond (C_1C_4), the side bonds (C_1C_2, C_1C_3, etc.), and both side and central bonds together. Almost no further stabilization was obtained by this parameter search. The energy decreased by only 0.4 kcal/mol, and the optimal central and side bond lengths became 0.02 and 0.01 Å larger, respectively. (Optimizing β at this new framework geometry furnished β = 196° and a 2.5 kcal/mol further lowering of the energy.) Thus, at this early stage in the reaction the only major change in geometry appears to be at the two radical centers, C_2 and C_3. If the bicyclobutyl diradical ever evolves into cyclobutadiene, it does so further along the reaction coordinate. This study thus completed our search for a point on the reaction coordinate at $R_{C_2C_3}$ = 1.812 Å.

As a next step, a restricted Hartree–Fock calculation was performed on the $(7a_1)^1(4b_2)^1$ triplet state in the STO-3G basis using the optimized singlet geometry. The triplet energy was found to lie 45 kcal/mol above the singlet state and the triplet therefore need not be considered further at this stage of the reaction, although additional calculations show that it does eventually cross the singlet state when the dihedral angle is *ca.* 110° ($R_{C_2C_3}$ = 2.1 Å).

For a final calculation at $R_{C_2C_3}$ = 1.812 Å the 4-31G basis was employed. For the geometry, the hydrogen angles α = 128° and β = 180° were employed, and the bond lengths now used were the optimized values for tetrahedrane in the extended basis, which are slightly larger than the STO-3G-optimized values. In the 4-31G basis, the energy of distorted tetrahedrane was higher than that of tetrahedrane itself by 23 kcal/mol. This was somewhat less than the 38-kcal/mol value found for the distortion in the STO-3G basis but not surprising as the latter basis is known to overestimate the stability of strained rings.[4,23] Moreover, the value of 23 kcal/mol is still a substantial contribution to the barrier, especially for a point at so early a stage of the reaction, and the only question remaining is how effective configuration interaction will be in reducing the 23 kcal/mol. The most important contribution to the differential amount of configuration interaction between tetrahedrane and distorted tetrahedrane is probably the mixing of the $(7a_1)^2$ ground-state configuration with the $(4b_2)^2$ virtual excited state configuration. This is analogous to the problem of the hydrogen molecule at large internuclear separations where σ_g^2–σ_u^2 mixing is required to correctly describe the diradical. A similar situation was encountered and treated successfully by such a CI treatment in [2.2.2]propellane.[24] In the present problem the 2 × 2 CI calculation in the 4-31G basis led to only a 5 kcal/mol relative stabilization of the distorted tetrahedrane over tetrahedrane itself. This indicates that the energy required for this distortion of tetrahedrane is *ca.* 18 kcal/mol (*i.e.*, to stretch the C_2C_3 bond to 1.812 Å). It presages that the barrier corresponding to the transition state will be even higher, perhaps substantially so.

III. Calculated Properties of Tetrahedrane

(A) Thermochemical Properties. The heats of formation of strained ring molecules such as bicyclobutane

(23) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(24) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 4391 (1972).

and bicyclo[1.1.1]pentane were accurately obtained from calculated heats of reaction in the 4-31G basis set.[4] In such a treatment, molecules with similar total strain energies are balanced against each other.[23] To obtain the heat of formation of tetrahedrane we employed the hypothetical disproportionation reactions

$$\text{2(bicyclo[1.1.1]pentane)} \longrightarrow \text{2(cyclopropane)} + \text{tetrahedrane} \quad (3a)$$

$$\text{2(bicyclo[1.1.0]butane)} \longrightarrow \text{tetrahedrane} + \text{cyclobutane} \quad (3b)$$

The heats of reaction of (3a) and (3b) were calculated to be 64.5 and 29.8 kcal/mol, respectively, in the 4-31G basis. The former value, when combined with the known heats of formation[25] of cyclopropane (16.8 kcal/mol) and bicyclo[1.1.1]pentane (53 kcal/mol) furnished a ΔH_f for tetrahedrane of 136.9 kcal/mol (at 0°K). The heat of reaction for (3b) and the heats of formation of cyclobutane (12.5 kcal/mol) and bicyclobutane (56.0 kcal/mol) gave a ΔH_f = 129.3 kcal. The small difference, 6.1 kcal/mol, between these two independent thermochemical cycles each involving the heat of formation of tetrahedrane is the size of the error usually found for this procedure.[4,23] Moreover, the ΔH_f values, 129 and 137 kcal/mol, are in good agreement with the semiempirical MINDO value, 135.2 kcal/mol, obtained by Baird.[6e]

The strain energy of tetrahedrane can be calculated once a model hypothetical unstrained C_4H_4 analog is chosen. For a molecule composed of four methine (CH) groups, Franklin's tables[26] furnish ΔH_f = 0.72 kcal/mol. Thus, the strain energy of tetrahedrane is *ca.* 129 to 137 kcal/mol or 21–23 kcal/mol per framework CC bond.

(B) Orbital Energies and Valence Ionization Potentials. The STO 4-31G orbital energies, when scaled by the factor −0.9, have given good estimates (to within 0.6 eV) of the vertical ionization potentials of bicyclobutane[11] as shown in Table III. The corresponding tetrahedrane orbital energies and predicted ionization potentials are also given in Table III. The orbital energies of the two molecules differ by: (1) the splitting, in C_{2v} symmetry, of the tetrahedrane t_2 orbitals into a b_2, a_1, and b_1 triple and the splitting of the occupied e orbital into an a_2 and a_1 pair; (2) the fact that bicyclobutane contains an additional occupied orbital, $4b_2$, involved partially in CH_2 bonding and not filled either in tetrahedrane or the diradical, III, in which two methylene hydrogens are missing. The highest occupied orbital of tetrahedrane, 1e ($7a_1$ in C_{2v} symmetry), is entirely carbon–carbon bonding. Thus, the dominant change in orbital structure in going from bicyclobutane to tetrahedrane is the cleavage of two CH bonds, which utilized the $7a_1$, $4b_2$ pair, and with the $4b_2$ orbital now unoccupied the dihedral angle decreases as a result of the new $7a_1$ orbital which forms the C_2C_3 bond (and the absence of the $4b_2$ CC antibonding orbital). It is clear, incidentally, that the hypothetical dehydrogenation of bicyclobutane to tetrahedrane and H_2 is symmetry forbidden since the former molecule utilizes symmetric and antisymmetric (with respect to a bisecting mirror plane) linear combinations of local CH orbitals, while the latter molecules fill two symmetric orbitals (CC and HH).

(25) The relevant heats of formation at 0°K are cited in ref 4.
(26) J. C. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1959).

Table III. Tetrahedrane and Bicyclobutane Orbital Energies in the 4-31G Basis and Predicted Valence Ionization Energies

Tetrahedrane			Bicyclobutane			
Orbital	Orbital energy, au[a]	IP, eV	Orbital	Orbital energy, au	IP, eV	Exptl[b]
$1a_1$	−11.227		$1a_1$	−11.223		
			$1b_2$	−11.223		
$1t_2$	−11.226		$2a_1$	−11.220		
			$1b_1$	−11.219		
$2a_1$	−1.306		$3a_1$	−1.231		
			$2b_2$	−0.931	22.8	22.1
$2t_2$	−0.804	19.7	$4a_1$	−0.786	19.3	18.91
			$2b_1$	−0.784	19.2	18.91
$3a_1$	−0.711	17.4	$5a_1$	−0.696	17.0	16.86
			$3b_2$	−0.583	14.3	14.85
$3t_2$	−0.536	13.1	$6a_1$	−0.580	14.2	14.51
			$4b_2$	−0.515	12.6	12.87
			$3b_1$	−0.463	11.3	11.23
1e	−0.335	8.20	$1a_2$	−0.436	10.7	11.23
			$7a_1$	−0.343	8.48	9.14
$4a_1$	+0.274		$8a_1$	+0.249		
$4t_2$	+0.294		$4b_1$	0.264		
$1t_1$	+0.340					
The total tetrahedrane energy = −153.3414 au						

[a] The STO-3G orbital energies are −11.037, −1.037, −1.240, −0.762, −0.668, −0.495, and −0.285. The two lowest unoccupied levels have energies 0.521 ($1t_1$) and 0.598 ($4t_2$). These values are for the STO-3G optimized geometry. [b] K. B. Wiberg, G. B. Ellison, M. B. Robin, and C. R. Brundle, as cited in ref 11.

The valence orbitals of tetrahedrane increase with increasing CH and CC bond lengths. The $2a_1$ orbital contains almost no hydrogen contribution and is best described as formed from sp hybrids on each carbon pointing radially inward. The $3a_1$ orbital is entirely CH bonding, formed from overlap of the hydrogen s orbitals with the outward-directed sp hybrids on the carbons. The $2t_2$ and $3t_2$ orbitals are both CH bonding, and the latter is CC (π) bonding, having little C_{2s} character (carbon s orbitals in the t_2 representation have twice as many antibonding as bonding interactions). Perhaps most interesting of all is the fact that the highest occupied orbital of tetrahedrane, 1e, contains no s contributions since the s orbitals do not form a basis for an e representation; the 1e is thus entirely CC π bonding.

The lowest unoccupied orbital in the 4-31G basis is the $4a_1$ (ϵ = +0.27 au) and it is CH antibonding, having nodes between the carbons and hydrogens. Its orbital energy decreases with CH elongation and increases with CC elongation. The $4t_2$ orbitals are CC antibonding (their orbital energies decrease with CC elongation) and CH bonding, both results not surprising since $4t_2$ contains the $4b_2$ orbital in C_{2v} symmetry. The $1t_1$ unoccupied orbital is CC antibonding and CH nonbonding.

(C) Hybridization and Spin–Spin Coupling Constants. The hybridizations in tetrahedrane can be compared with those found in other strained ring hydrocarbons. An INDO calculation performed at the STO-3G equilibrium geometry furnished delocalized (canonical) orbitals which were then transformed to a set of localized molecular orbitals (LMO's), minimizing the coulomb self-repulsion energy.[27] Six equivalent two-center CC LMO's were obtained with $sp^{4.99}$ hy-

(27) C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, 43, S97 (1965).

bridization,[28] equivalent to 83% p character. The hybrids were bent outward from the CC bond vector by 38.8°. Four two-center CH LMO's of $sp^{1.21}$ hybridization (45% p character) were also obtained. The latter clearly supports the short CH bond length and high force constant described previously.

The p character of the CC hybrids is larger than that calculated for other strained ring systems containing cyclopropane rings,[29] *e.g.*, cyclopropane, $sp^{4.16}$, and the bicyclobutane side bond, C_1C_2, $sp^{2.65}$; however, it is less than the 94% p character in the C_1C_3 bond of bicyclobutane. The s character in the carbon CH hybrids ($sp^{1.21}$) is larger than that in the bridgehead CH bond of bicyclobutane, $sp^{1.58}$, or the olefinic CH bond of cyclopropene, $sp^{1.31}$.[11] The tetrahedrane hybridizations may be used in our previously determined least-squares equations for nuclear spin-spin coupling constants[11]

$$J_{\mathrm{CH}} = 5.70(\%\mathrm{S}) - 18.4\ \mathrm{Hz}$$

and

$$J_{\mathrm{C_AC_B}} = 0.0621(\%\mathrm{S_A})(\%\mathrm{S_B}) - 10.2\ \mathrm{Hz}$$

This results in the prediction $J_{\mathrm{CH}} = 240$ Hz and $J_{\mathrm{CC}} = 7.1$ Hz. The J_{CH} value lies between those of cyclopropene, 220 Hz,[30] and acetylene, 251 Hz;[31] a J_{CH} of 229 Hz has been predicted by Mislow.[32] The J_{CC} value, 7.1 Hz, is slightly smaller than that found in cyclopropane, 10.0 Hz,[33] and considerably smaller than that in the side bond of bicyclobutane, 21.0 Hz.[34]

V. Discussion

The present study has located a tetrahedral equilibrium geometry for tetrahedrane such that small distortions along the various symmetry coordinates increase the molecular potential energy. Since an arbitrary small distortion can be written as a linear combination of the symmetry distortions (which form a complete set of coordinates), it follows that tetrahedrane is a local minimum on the C_4H_4 18-dimensional potential energy surface. Moreover, since the approximate force constants and frequencies of vibration seem to be of the order of magnitude found generally for hydrocarbons, it is reasonable to assume that tetrahedrane is capable of supporting one, and perhaps several, bound vibrational states. It would seem that tetrahedrane is a highly energetic molecule which could possess a finite lifetime and might be amenable to spectroscopic detection and, perhaps, isolation.

Tetrahedrane is metastable in the sense of being a local minimum of, as yet, unknown depth on its potential energy surface. It is not, of course, thermodynamically stable with respect to its possible isomers. However, it should be recalled that the four known valence isomers of benzene are markedly less stable than benzene itself (which, in turn, is unstable with respect to hydrogen molecules and graphite). From the heat of formation calculated in section III, tetrahedrane should be 18–26 kcal/mol higher in energy than two acetylene molecules (at 25°K). This estimate is plausible since the tetrahedrane 0°K strain energy, 129–137 kcal/mol, is slightly more than twice the strain energy of bicyclobutane (63 kcal/mol, 0°K), which has half as many fused cyclopropane rings. Tetrahedrane has also been estimated to be 70–84 kcal/mol less stable than cyclobutadiene.[6f,35] This would then furnish the following ordering of C_nH_n molecules in increasing molar energy: $^2/_3$(benzene) < $^2/_3$(Dewar benzene) $\sim$ $^2/_3$(benzvalene) < $^2/_3$(prismane) $\sim$ cyclobutadiene < 2(acetylenes) < tetrahedrane. Thus, the energy of two acetylenes lies between that of cyclobutadiene and tetrahedrane. There is some evidence that (vibrationally hot) tetrahedrane fragments in this way,[5b,c] whereas cyclobutadiene does not.

The behavior of a tetrahedral X_4 molecule in an A_1 electronic state under A_1, E, and T_2 distortions is rather interesting. If we expand the potential energy, V, of X_4 about its value, V_0, in a tetrahedral arrangement, the linear term is totally symmetric since $\langle \partial H/\partial S\rangle$ is nonzero only if S is the totally symmetric normal coordinate (in X_4 the normal coordinates are fully symmetry determined). If a point is found such that $\langle \partial H/\partial S^{A_1}\rangle$ is equal to zero the force field through quadratic terms is[36]

$$V = V_0 + {}^1/_2k_1\sum R_{ij}^2 + k_2\sum R_{ij}R_{ik} + k_3\sum R_{ij}R_{kl}$$

where the R_{ij}, the increases in the six X_iX_j bonds, form a complete set of internal coordinates. Now it is readily shown[36] that the ratios of the three harmonic frequencies of X_4 are

$$\nu_{\mathrm{A}}:\nu_{\mathrm{E}}:\nu_{\mathrm{T2}} = 2(k_1 + 4k_2 + k_3)^{1/2}:(k_1 - 2k_2 + k_3)^{1/2}:\sqrt{2}(k_1 - k_3)^{1/2}$$

On physical grounds one anticipates that $k_1 \gg k_2$ and k_3 (for P_4 the ratio is about 20:1),[20] since k_1 is a diagonal matrix element or bond stretching constant while the latter two are interaction constants between bonds. Thus, if k_1 dominates the three frequencies and is positive it follows that all the vibrations correspond to bound motion. This argument shows that if X_4 is bound with respect to any one vibration it is probably bound with respect to the others. N_4 appears to be such a case.[37] Moreover, to the extent that the carbon–hydrogen motions do *not* facilitate tetrahedral fragmentation through the mixing of their symmetry coordinates with those of the carbon skeleton the tetrahedrane molecule, $(CH)_4$ is another. Thus, it can be said that the fact that tetrahedrane is a local minimum on the C_4H_4 potential energy surface is intimately related to its A_1 stability.

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(28) The coefficients of the C_1 atomic orbitals in the C_1C_2 bond were $c_{2s} = 0.238$, $c_{2p_x} = c_{2p_z} = -0.358$, $c_{2p_y} = +0.393$; coefficients in C_1H_1 were $c_{2s} = 0.476$, $c_{2p} = 0.305$.

(29) M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 767 (1972).

(30) G. C. Closs, *Proc. Chem. Soc., London*, 152 (1962).

(31) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

(32) K. Mislow, *Tetrahedron Lett.*, **22**, 1415 (1964). This calculation assumes that hybrids on the same center are orthogonal.

(33) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **94**, 6021 (1972).

(34) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Amer. Chem. Soc.*, **94**, 997 (1972).

(35) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

(36) N. B. Slater, *Trans. Faraday Soc.*, **50**, 207 (1954).

(37) J. M. Schulman and T. Venanzi, to be submitted for publication.

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Appendix

We consider here symmetry coordinates for the E, T_2, and T_1 vibrational modes of tetrahedrane. The notation corresponds to Figure 1.

Two normalized E_a distortions were chosen to be

$$S_1^{E_a} = 8^{-1/2}(-X_1^C + Y_1^C + X_2^C + Y_2^C - X_3^C - Y_3^C + X_4^C - Y_4^C) \quad (A1)$$

and

$$S_2^{E_a} = 8^{-1/2}(-X_1^H + Y_1^H + X_2^H + Y_2^H - X_3^H - Y_3^H + X_4^H - Y_4^H) \quad (A2)$$

An alternative form for $S_1^{E_a}$ is

$$S_1^{E_a} = {}^1/_2(R_{13} + R_{24} - R_{12} - R_{34}) \quad (A3)$$

The $S_1^{E_a}$ symmetry distortion may be considered to be small counterclockwise rotations of carbons 1 and 4 and clockwise rotations of carbons 2 and 3 about the Z axis. A similar interpretation may be given to the hydrogen motions in $S_2^{E_a}$.

A T_{1a} external coordinate was constructed by forming the linear combination of Cartesian displacements which is orthogonal to pure rotation (of each atom) about the Z axis as the pure rotation is also of T_{1a} symmetry. Thus, it is given by

$$S^{T_{1a}} = N[L_H(X_1^C + X_2^C - X_3^C - X_4^C - Y_1^C + Y_2^C - Y_3^C + Y_4^C) - L_C(X_1^H + X_2^H - X_3^H - X_4^H - Y_1^H + Y_2^H - Y_3^H + Y_4^H)] \quad (A4)$$

where

$$N = [2(L_H^2 + 12L_C^2)/3]^{-1/2}$$

and L_C and L_H are the C_1 and H_1 equilibrium Cartesian coordinates. Clearly, $S^{T_{1a}}$ is a length-weighted combination of counterclockwise carbon rotations and clockwise hydrogen rotations, about the Z axis.

Finally, three independent T_{2a} symmetry coordinates were chosen as

$$S_1^{T_{2a}} = {}^1/_2\sum_{i=1}^{4}(Z_i^C - Z_i^H) \quad (A5)$$

$$S_2^{T_{2a}} = 8^{-1/2}(X_1^C + Y_1^C + X_2^C - Y_2^C - X_3^C + Y_3^C - X_4^C - Y_4^C) \quad (A6)$$

and

$$S_3^{T_{2a}} = 8^{-1/2}(X_1^H + Y_1^H + X_2^H - Y_2^H - X_3^H + Y_3^H - X_4^H - Y_4^H) \quad (A7)$$

The first of these corresponds to equal but opposite translations of the two tetrahedral frames in the vertical plane (Figure 1). It is the analog of the internal coordinate in the two-body problem, the interparticle separation, and G_{11}^{-1} is just the reduced mass, $m_C m_H/(m_C + m_H)$. The T_{2a} representation includes translation of the center of mass of tetrahedrane and it might be noted that $S_1^{T_{2a}}$ is not orthogonal to the center of mass coordinate

$$S_{C_m}^{T_{2a}} = \sum_{i=1}^{4}(m_C Z_i^C + m_H Z_i^H) \quad (A8)$$

which it need not be. Of course, if desired, the center of mass motion can be eliminated by using in place of (A5) the distortion $\Sigma_{i=1}^{4} m_H Z_i^C - m_C Z_i^H$ which is orthogonal to (A8). This motion is then analogous to the 3c T_2 symmetry coordinate given by Herzberg for methane.[21]

The symmetry coordinates $S_2^{T_{2a}}$ and $S_3^{T_{2a}}$ correspond to motions of carbons 2 and 3 (hydrogens 2 and 3) toward each other along their bond vector, while carbons 1 and 4 (hydrogens 1 and 4) move apart along their bond vector. These motions are analogous to the 4c T_2 vibration of methane.[21]