[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

"Acetylenic" Strained Hydrocarbons

BY WILLIAM WELTNER, JR.

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Acetylene, C_4H_4, and C_8H_8 form a series of strained hydrocarbons analogous to the ethylene, cyclopropane, cyclobutane series. The "caged" structures of the two higher members of this series are formed from tetrahedral and cubic configurations of CH groups, respectively. Assuming that these two molecules possess bond lengths corresponding to paraffinic hydrocarbons, the strain energies are calculated by the procedure of Dunitz, Schomaker and Pauling, and by the electron pairing approximation of VB theory, and a comparison made of the results by the two methods. The heats of formation at 0°K. thus derived are compared with the energies of certain isomers of C_4H_4 and C_8H_8, namely, vinylacetylene, cyclobutadiene (as yet unsynthesized), and cycloöctatetraene. Tetrahedral C_4H_4 is found to have a strain energy of about 90 kcal./mole as compared to 59 kcal./mole in vinylacetylene and about 50 kcal./mole in a hypothetical non-resonating model of cyclobutadiene. The true tetrahedral C_4H_4 probably has carbon–carbon bond lengths near 1.48 Å. at which distance the strain energy may be reduced to a value comparable with that of vinylacetylene. Cycloöctatetraene is found to be about 80 kcal./mole more stable than the cubic C_8H_8.

Another series of strained hydrocarbons, besides the familiar series consisting of ethylene, cyclopropane and cyclobutane, might exist in which the corresponding members are built up from CH groups, and not CH_2 groups. The lowest member of this series would be acetylene, and the next higher member C_4H_4 of tetrahedral configuration (see Fig. 1). The next higher homolog, analogous to cyclobutane, would be C_8H_8 in which the carbon atoms are located at the corners of a cube. This series may appropriately be called the "acetylenic" strained hydrocarbons.

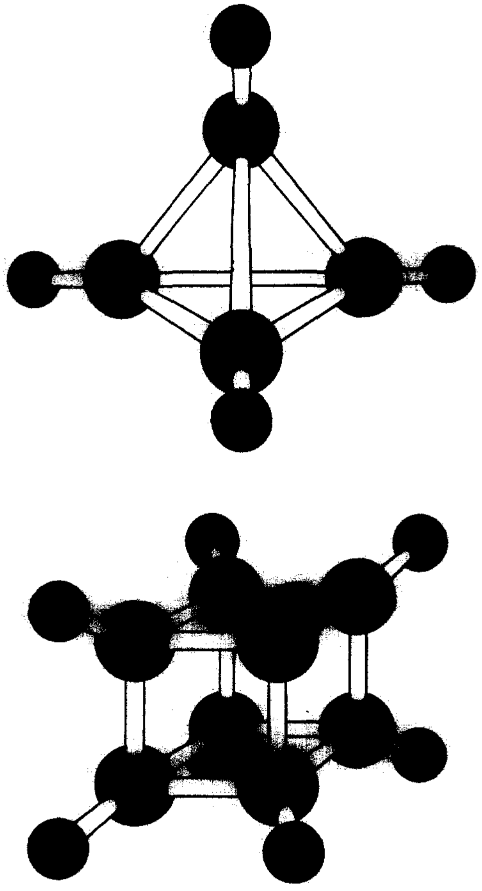

Fig. 1.—Tricyclobutane and tricycloöctane.

The possible existence of C_4H_4 and C_8H_8 having these structures was proposed by Beesley and Thorpe[1] in 1913, when they synthesized the tricarboxymethyl substituted derivative of tetrahedral C_4H_4.[2] C_4H_4 itself has not been synthesized; in fact, since 1920 it seems that no further work has been done in that direction, nor has anyone repeated Beesley and Thorpe's work or prepared further derivatives. For the sake of simplicity the tetrahedral C_4H_4 will here be called tricyclobutane and the cubic form of C_8H_8 will be referred to as tricyloöctane.[3]

It is evident from the unique structures of these two members of the "acetylenic" series that they are relatively highly strained and also that they are isomeric to two other unusual compounds, 1,3-cyclobutadiene and cycloöctatetraene. The synthesis of cyclobutadiene has so far been attempted unsuccessfully[4] and theoretical considerations[5–7] have not been able to determine whether this is to be expected or not. The lack of the planarity and resonance of aromatic compounds makes cycloöctatetraene exceptional. A comparison of the stabilities of these isomers is attempted here by calculation of their relative energies at 0°K. Of equal importance are the comparison of results by different methods of calculation, the carbon atom hybridization in the molecules, and the extent of participation of the various energy terms in determining the hybridization.

Calculation of Strain Energy

The calculation of strain energies in paraffinic cyclic hydrocarbons has been made by Kilpatrick and Spitzer,[8] utilizing Pauling and Sherman's concepts of the energy of hybrid bonds.[9] In their

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(1) R. M. Beesley and J. F. Thorpe, *Proc. Chem. Soc.*, **29**, 346 (1913).

(2) R. M. Beesley and J. F. Thorpe, *Trans. Chem. Soc.*, **117**, 591 (1920).

(3) The full names for these compounds are tricyclo[1.1.0.$0^{2,4}$]butane and tricyclo[4.2.0.$0^{2,5}$.$0^{3,8}0^{4,7}$]öctane according to the system specified in A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publ. Corp., New York, N. Y., 1940.

(4) See, for example, a review of cyclobutadiene chemistry by W. Baker, *J. Chem. Soc.*, 259 (1945).

(5) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949). Dr. Moffitt has, however, pointed out that the application of the Jahn-Teller theorem to account for the instability of cyclobutadiene is only possible in the zeroth order where the MO configuration is degenerate. In first-order theory no degeneracy is present and the Jahn-Teller theorem does not apply.

(6) D. P. Craig, *Proc. Roy. Soc.* (*London*), **A202**, 498 (1950).

(7) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(8) J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946).

(9) L. Pauling and A. Sherman, THIS JOURNAL, **59**, 1450 (1937).

method the minimum of energy of the molecule was determined solely by the C–C bond energy variation with the serious omission of C–H terms except in the final energy calculation. This procedure has recently been modified by Dunitz and Schomaker[10] so that both C–H and C–C bond energy terms determine the minimum. However, the variation of bond energy with degree of hybridization in C–H bonds in this theory is not in agreement with observed data, as pointed out by Mulliken,[11] and Maccoll,[12] so that there is still reason for viewing this procedure skeptically at present.

An alternative procedure of calculating these energies is the electron pairing approximation of the VB method, as employed by Förster[13] and Coulson and Moffitt.[5] The difficulty here lies in obtaining correct values for the necessary integrals involved since those previously theoretically estimated did not reproduce the known strain energy of cyclopropane. This procedure should be capable of more accurate results than the Dunitz–Schomaker–Pauling method if for no other reason than that it involves more determinable parameters.

The Dunitz–Schomaker–Pauling Method.—Calculations, analogous to those made for cyclopropane and cyclobutane,[10] may be made for the "acetylenic" strained hydrocarbons in which the carbon orbital symmetry is C_{3v}. Torkington,[14] for example, has given the hybridized carbon orbital wave functions for C_{3v} symmetry.

Assuming Dunitz and Schomaker's values of 57.6 and 87.3 kcal./mole (based upon the value of 124.1 kcal./mole as the heat of sublimation of graphite) for normal C–C and C–H bonds, respectively, the energy (in kcal./mole) of the tricyclobutane molecule is

$$E = 4E_{\text{CH}} + 6E_{\text{CC}} - P = 174.6S_{\text{CH}} + 86.4S^2_{\text{CC}} - P \qquad (1)$$

where S_{CC} is the angular part of the carbon orbital bonded to carbon, S_{CH} is the angular part of the carbon orbital bonded to hydrogen. P is the energy of promotion of four carbon atoms above the tetrahedral tetravalent state as calculated from Van Vleck's equation[15] using Voge's[16] carbon atom constants. P was not included in Dunitz and Schomaker's calculations on cyclopropane and cyclobutane and perhaps its inclusion here may be thought a refinement which is unwarranted. However, the variation of P with the degree of strain becomes quite significant in tricyclobutane as compared to cyclopropane (compare the $-P$ curve in Fig. 2 with that in Fig. 3), and it was felt that a fair comparison of the D–S–P and the electron pairing approximations necessitated including it in both. Its inclusion has little effect upon the strain energies but does change significantly the state of hybridization of the carbon atoms.

Table I then shows the energy as a function of the strain angle, θ, which is the angle between the carbon orbital direction and the straight line joining the bonded carbon atoms. The maximum occurs at $\theta = 32°$, and the strain energy is then 81 kcal./mole. To this must be added torsional strain[17] estimated as 2 kcal. per opposed CH group or 12 kcal./mole so that the total calculated strain energy is 93 kcal./mole or 23 kcal./CH mole. The resonance energy in the carbon–carbon skeleton is found to be approximately zero by the method to be described below. The C–H bond hybridization corresponding to $\theta = 32°$ is 35% s and 65% p.

TABLE I

TRICYCLOBUTANE ENERGY BY THE DUNITZ–SCHOMAKER–PAULING METHOD

θ	S_{CC}	S_{CH}	P (kcal./mole)	Energy, (kcal./mole)
29	1.795	1.949	11.2	607.6
30	1.786	1.966	7.4	611.4
31	1.776	1.979	4.5	613.5
32	1.765	1.988	2.5	613.8
33	1.753	1.994	1.1	612.7
34	1.741	1.998	0.3	610.5
35	1.728	2.000	0.0	607.0
36	1.714	1.999	0.1	602.9
Tetrahedral unstrained	2.000	2.000	0.0	694.8

With this large strain angle, the notion of a "bent-bond length"[10,18] prescribes that the carbon–carbon distance will be shorter than in other paraffins. Use of the relation,[10] $d = 1.542 \sin \theta/\theta$, yields a value of 1.46 Å. for this bond length. This is a rather large departure from the normal paraffinic distance and indicates that an alteration of the carbon–carbon bond energy used in this procedure is probably necessary to obtain a more reliable strain energy for the molecule than that value given above.

It is to be expected that inclusion of d orbitals to allow formation of non-cylindrical bonds should also be advantageous here as in the similar tetrahedral molecule P_4.[19] A rough calculation will demonstrate this. At the minimum of energy calculated using only s- and p-orbitals the C–H hybridization was found above to be 35% s and 65% p. Assume that this remains the same and allow the d orbitals to participate only in the three carbon orbitals joined to carbon atoms. Proceeding in an analogous way to that of Pauling and Simonetta,[19] then

$$W = -7.20S^2 + 220c^2$$

where W is the energy in kcal./mole per half bond. Here $7.20 = (57.6/2)/4$, where 57.6 is the energy in kcal./mole per tetrahedral carbon–carbon bond and the four is the maximum value of S^2 for sp-hybridization. This amounts to assuming the same proportionality factor for bond strength in spd-hybridization as in sp-hybridization. c^2 is the per cent. d character of the carbon wave function, $\psi = as + bp + cd$. By extrapolation within Moore's tables[20] a probable value of about 380 kcal./mole was obtained for the lowest $2s2p^23d$ state above the $s^2p^2\,{}^3P$ state of carbon. This promotional energy is reduced to 220 kcal./mole when referred to the sp^3 valence state of carbon. Then using the same relation between $a_1, a_2, \ldots, a_9$ as obtained from normalization and orthogonalization conditions for three equivalent orbitals by Pauling and Simonetta, with

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(10) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(11) R. S. Mulliken, THIS JOURNAL, **72**, 4493 (1950).

(12) A. Maccoll, *Trans. Faraday Soc.*, **46**, 369 (1950).

(13) T. Förster, *Z. physik. Chem.*, **B43**, 58 (1939).

(14) P. Torkington, *J. Chem. Phys.*, **19**, 528 (1951).

(15) J. H. Van Vleck, *ibid.*, **2**, 20 (1934).

(16) H. H. Voge, *ibid.*, **16**, 984 (1948). Contrary to Voge's paper, the heat of sublimation of graphite is taken as 170.4 kcal./mole in all of the calculations made in this paper except the *D–S–P* calculations pecified otherwise.

(17) K. S. Pitzer, *Science*, **101**, 672 (1945).

(18) C. N. Copley, *Chemistry and Industry*, 663 (1941); H. J. Bernstein, *J. Chem. Phys.*, **15**, 284 (1947).

(19) L. Pauling and M. Simonetta, *ibid.*, **20**, 29 (1952).

(20) C. E. Moore, "Atomic Energy Levels," Circular 467, Natl. Bur. Standards, 1949.

the added one that $a_1^2 = 0.22$, the wave function having the strongest bonds along the 60° bond angles is found to be

$$\psi = 0.469\ \mathrm{s} + 0.331\ \mathrm{p_z} + 0.060\ \mathrm{d_z} + 0.809\ \mathrm{p_x} + 0.105\ \mathrm{d_{x+z}} + 0.037\ \mathrm{d_{xy}}$$

and $S = 2.025$, $W = -25.99$ kcal./mole. The S_{CH} is here 1.988 and the total energy per molecule is then −656 kcal./mole. The small factor of 2.5 kcal./mole (see Table I) was included in this calculation as promotional energy above the tetrahedral state. The best spd-hybridization of the three orbitals with the C–H hybrid as 25% s is

$$\psi = 0.500\ \mathrm{s} + 0.685\ \mathrm{p_z} + 0.256\ \mathrm{d_z}$$

with $S_{\mathrm{CC}} = 2.505$ and $S_{\mathrm{CH}} = 2.000$ and $W = -30.78$. The total energy per molecule is then −719 kcal./mole. The strain energy is then 63 kcal./mole, a reduction of 18 kcal./mole over that using only sp-hybridization.

Assuming no resonance energy and approximately 2 kcal. per opposed CH group for torsional strain, the strain energy in tricyclooöctane is calculated to be 32 + 24 = 56 kcal./mole. The strain angle is here 13° and the CH bond hybridization is $^1/_3$ s, $^2/_3$ p. To this, however, must be added across-the-ring non-bonded repulsions analogous to those pointed out by Dunitz and Schomaker as contributing 13.6 kcal./mole to the strain in cyclobutane. This value is altered to 10.7 kcal./mole when P is included and the strain energy of 23.3 kcal./mole (see section below on cyclobutane) is used for cyclobutane. Assuming that approximately the same distances prevail in each of the six cyclobutane units making up tricyclooöctane as in cyclobutane, 64 kcal./mole of strain must be added to that calculated above, so that the total strain now becomes about 120 kcal./mole or 15 kcal./CH mole.

If Pitzer's[21] bond energies of 80 kcal./mole for a C–C bond and 98.2 kcal./mole for a C–H bond (based upon the value of 170.4 kcal./mole as the heat of sublimation of graphite) are used, the calculated strains by the D–S–P method become 122 kcal./mole for tricyclobutane and 84 kcal./mole for tricyclooöctane. The across-the-ring repulsion was 2.7 kcal./mole in cyclobutane in this case, and cyclopropane was found to have a strain energy of 36 kcal./mole. The C–C bond energy would require lowering by 30 kcal./mole in order to yield the experimental strain energy of 25 kcal./mole for cyclopropane.

The Electron Pairing Approximation.—Application of this procedure to CH_4 by Van Vleck,[22a] Voge[16,22b] and Penney,[23] to CH by Stehn[24] and King,[25] and to benzene, ethane, and ethylene by Penney[26,27] has proved successful at least qualitatively, and in the first instances quantitatively. The approach in all of these cases has been semi-empirical in that the integrals have been determined, in general, from energy or spectroscopic data in simple molecules. The exchange integrals are of two types, $N_{\alpha\beta}$ and $C_{\alpha\beta\gamma\delta}$, the former involving carbon and hydrogen wave functions and thus requiring only two subscripts

$$N_{\alpha\beta} = -\int\int \psi_{\mathrm{H}}(1\mathrm{s}_1)\psi_{\mathrm{C}}(\alpha_2)H\psi_{\mathrm{C}}(\beta_1)\psi_{\mathrm{H}}(1\mathrm{s}_2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$C_{\alpha\beta\gamma\delta} = -\int\int \psi_{\mathrm{C}}(\alpha_1)\psi_{\mathrm{C'}}(\beta_2)H\psi_{\mathrm{C'}}(\gamma_1)\psi_{\mathrm{C}}(\delta_2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$\alpha, \beta, \gamma, \delta$ = 2s, 2pσ, 2pπ, or 2pπ' of carbon atoms C and C′. The inner shell interactions are obtained from Mulliken[28] and some of the symbols used here will be taken from his magic formula.

Determination of $N_{\alpha\beta}$ Integrals.—These integrals have been determined by Van Vleck,[15] Voge,[22a] Stehn,[24] and Penney,[23] the first three authors from energy considerations in methane and CH and the last named author from a vibrational frequency in methane. They are generally in agreement; however, certain assumptions were made in each determination. It was decided here to determine N_{ss}, $N_{\mathrm{s}\sigma}$ and $N_{\sigma\sigma}$ from the dissociation energy of methane, the dissociation energy of the CH molecule, and the fact that the CH molecule energy must be a minimum in the ground state. Hybridization will be allowed in the CH molecule as suggested by Moffitt[29] and Mulliken[28]; however, this introduces a fourth parameter into the calculation requiring the use of Penney's methane frequency equation.

For methane, with the value of D_{e} taken from Voge[16]

$$-D_{\mathrm{e}} = -18.20 = 4M_{\mathrm{ss}} + 4M_{\sigma\sigma} + 8M_{\pi\pi} + N_{\mathrm{ss}}/2 - 5N_{\sigma\sigma}/2 - 3\sqrt{3}N_{\mathrm{s}\sigma} + 4N_{\pi\pi} - R.E. + P + 6K_{\mathrm{hh}} + 4K_{\mathrm{kh}} \quad (2)$$

where the M's are the coulombic integrals

$$M_{\alpha\beta} = \int\int \psi_{\mathrm{C}}(\alpha_1)\psi_{\mathrm{H}}(1\mathrm{s}_2)H\psi_{\mathrm{C}}(\beta_1)\psi_{\mathrm{H}}(1\mathrm{s}_2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

and the N's are the C–H exchange integrals defined above. $R.E.$ is the resonance energy, shown by Voge[22a] to be about 1.3 ev. P is the carbon atom promotional energy to the tetrahedral valence state = 6.97 ev. This may be calculated from Van Vleck's equation[15] using the carbon atomic constants of Voge.[16] The K's are repulsive terms arising from hydrogen–hydrogen interaction and inner shell-hydrogen interaction and are taken to be 0.41 and 0.62 from Mulliken.[28] From Woods'[30] more elaborate calculation on methane, one-fourth the coulombic energy (see Voge[31]) is −2.64 ev., hence

$$M_{\mathrm{ss}} + M_{\sigma\sigma} + 2M_{\pi\pi} = -2.64 \text{ ev.}$$

If the calculated values of these integrals as tabulated by Kotani and Amemiya[32] are used, a value of −2.7 ev. is obtained. Therefore the values for the M integrals are taken from these tables as approximately $M_{\mathrm{ss}} = -0.65$, $M_{\sigma\sigma} = -1.8$, $M_{\mathrm{s}\sigma} = -2.1$, $M_{\pi\pi} = +0.05$ ev. for the CH molecule calculations.

For the CH molecule, with the value of D_{e} taken from Voge[16]

$$-D_{\mathrm{e}} = -3.65 = M_{\pi\pi} + (1 + \beta^2)M_{\mathrm{ss}} - 2\alpha\beta M_{\mathrm{s}\sigma} + (1 + \alpha^2)M_{\sigma\sigma} + (2\beta^2 - 1)(N_{\mathrm{ss}} - N_{\sigma\sigma}) - 4\alpha\beta N_{\mathrm{s}\sigma} + N_{\pi\pi}/2 + P + K_{\mathrm{kh}} - R.E. \quad (3)$$

The resonance enegy ($R.E.$) was here assumed zero and K_{kh} was again taken as 0.62. The promotion energy of carbon in CH has been discussed by Moffitt[29] and Mulliken[33] and may be written (using Voge's 1948 carbon atom constants) as $p = 0.32 + 9.72\,\alpha^2$. α^2 and β^2 are the fractions of s- and p-character, respectively, in the hybridized bond. Differentiating the energy with respect to α and equating to zero to determine the minimum of energy yields

$$(\alpha^2 - \beta^2)/\alpha\beta = [9.72 - 2(N_{\mathrm{ss}} - N_{\sigma\sigma}) + (M_{\mathrm{ss}} + M_{\sigma\sigma})]/(2N_{\mathrm{s}\sigma} + M_{\mathrm{s}\sigma}) \quad (4)$$

similar to Moffitt.[34] If $N_{\pi\pi}$ is taken as −0.8 from the tables

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(21) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

(22) (a) J. H. Van Vleck, *J. Chem. Phys.*, **1**, **177**, 219 (1933); (b) H. H. Voge, *ibid.*, **4**, 581 (1936).

(23) W. G. Penney, *Trans. Faraday Soc.*, **31**, 734 (1935).

(24) J. R. Stehn, *J. Chem. Phys.*, **5**, 186 (1937).

(25) G. W. King, *ibid.*, **6**, 378 (1938).

(26) W. G. Penney, *Proc. Roy. Soc.* (*London*), **A144**, 166 (1934).

(27) W. G. Penney, *ibid.*, **A146**, 223 (1934).

(28) R. S. Mulliken, *J. Phys. Chem.*, **56**, 298 (1952).

(29) W. E. Moffitt, *Proc. Roy. Soc.* (*London*), **202A**, 534 (1950).

(30) H. J. Woods, *Trans. Faraday Soc.*, **28**, 877 (1932).

(31) See reference 22a, p. 589.

(32) M. Kotani and A. Amemiya, *Proc. Phys. Math. Soc. Japan*, **22**, Extra Number 1, June (1940).

(33) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952), Appendix I, Table VIII.

(34) Reference 29, p. 548.

of Kotani and Amemiya,[32] then there remain four unknowns to be determined, N_{ss}, $N_{s\sigma}$, $N_{\sigma\sigma}$ and α^2.

The values of α^2, $N_{s\sigma}$, and $(N_{\sigma\sigma} - N_{ss})$ satisfying the two equations obtained from consideration of the CH molecule are given in Table II.

TABLE II

VALUES OF THE PARAMETERS α^2, $N_{s\sigma}$ AND $(N_{\sigma\sigma} - N_{ss})$ SATISFYING EQUATIONS (3) AND (4)

α^2	$N_{s\sigma}$	$(N_{\sigma\sigma} - N_{ss})$
0.040	1.77	+0.550
.048	1.85	+ .485
.060	1.96	+ .393
.074	2.07	+ .285
.10	2.25	+ .084
.12	2.37	− .072
.13	2.43	− .152
.16	2.58	− .391
.30	3.08	−1.60
.40	3.29	−2.52

The necessary fourth relation is the equation of Penney[23] derived from the ν_2 vibrational frequency in methane.

$$3(N_{\sigma\sigma} - N_{\pi\pi}) + \sqrt{3}N_{s\sigma} = 12.2 \qquad (5)$$

The values $\alpha^2 = 0.074$, $N_{ss} = 1.79$, $N_{s\sigma} = 2.07$, $N_{\sigma\sigma} = 2.08$ were found to fit all four equations. A value of $\alpha^2 = 0.155$ was found by Mulliken[28] to fit the CH molecule best when applying his magic formula. As in his work, the equations here are particularly sensitive to the value of α^2 chosen.

Förster[13] has shown that there is a parallelism between C–H bond energies, as calculated by the electron pairing approximation, and the C–H vibrational frequencies in the series, methane, ethylene and acetylene. More recent work has substantiated this since both force constants[35] and observed bond energies[36] indicate that the CH bond strength increases as the % s character increases through the range of approximately zero to 50% s in the hybrid bond. By the electron pairing approximation the CH bond energy may be expressed as

$$E(\text{C–H}) = Q + \alpha^2 N_{ss} + 2\alpha\beta N_{s\sigma} + \beta^2 N_{\sigma\sigma}$$

Using the values of the N's derived above, it may be seen that the C–H bond energy is an increasing function of α^2, attaining a maximum value at 47% s character, and is therefore in agreement with the known data.

Determination of $C_{\alpha\beta\gamma\delta}$ Integrals.—The values of Penney[37] for those integrals involving only s and σ are

$$C_{ssss} = 1.00,\ C_{sss\sigma} = 1.32,\ (C_{s\sigma\sigma s} + C_{ss\sigma\sigma} + C_{s\sigma s\sigma})/3 = 1.73$$

$$C_{s\sigma\sigma\sigma} = 2.29,\ C_{\sigma\sigma\sigma\sigma} = 3.00$$

With values of about this magnitude for the $C_{s\sigma}$ integrals and $C_{\pi\pi\pi\pi}$ as about 1.0 ev. and other π-integrals assumed small, the strain energy in cyclopropane, on the basis of a "bent bond" model, was calculated[38] to be 7 ev., whereas the observed strain is about 1 ev. This large difference must be attributed to the underestimate of the carbon–carbon energy in the molecule relative to the tetrahedral unstrained configuration. If the procedure is reversed, cyclopropane offers itself as an aid in the evaluation of these $C_{\alpha\beta\gamma\delta}$ integrals since in the calculation of strain energy, the coulombic terms and inner shell repulsions will essentially cancel out. The proper C integrals should then reproduce the strain energy and the degree of hybridization of carbon in the molecule as indicated by the measured HCH angle. The HCH angle in cyclopropane has been reported as 118 ± 2°[39] and the strain energy is 25.2 kcal./mole. The strain energy was calculated from the heat of combustion data of Knowlton and Rossini,[40] corrected to 0°K. by use of Kistiakowsky and Rice's[41] vibrational assignment, in conjunction with Pitzer's[42] values for the bond energies.

As another criterion for the evaluation of the C integrals the ethane molecule may be utilized. If the C–H energy in this molecule is evaluated by the electron pairing approximation using the $N_{\alpha\beta}$ parameters derived above, then the C–C energy must have the proper slope so as to provide a minimum of energy of ethane at approximately tetrahedral hybridization of the carbon atoms.

In order to simplify the calculation, since the large number of C integrals involving s and σ is cumbersome, it was assumed that

$$C_{ssss} = C_{sss\sigma} = C_{s\sigma s\sigma} = C_{s\sigma\sigma s} = C_{ss\sigma\sigma}$$

and that

$$C_{s\sigma\sigma\sigma} = C_{\sigma\sigma\sigma\sigma} \qquad (6)$$

The combinations of C_{ssss} and $C_{\sigma\sigma\sigma\sigma}$ which provided a minimum of energy in ethane at HCH angles equal to 109° 28′ could then be obtained since the ethane calculation involves no π-integrals. Such values, over a limited range, are given in columns 1 and 2 of Table III. The details of the ethane calculations will not be given here since they follow the pattern of cyclopropane discussed in more detail below. Applying these C integrals to the calculation of the strain energy in cyclopropane makes possible the evaluation of the total contribution of the C integrals involving π (symbolized by $(\text{C–C})_\pi$ below) to the energy of cyclopropane at the HCH angle of 118°.

TABLE III

C INTEGRALS DERIVED FROM ETHANE AND CYCLOPROPANE (all units are electron volts)

	C_{ssss}	$C_{\sigma\sigma\sigma\sigma}$	$(\text{C–C})_\pi$[a]	$C_{\pi\pi\pi\pi}$	*R.E.* in cyclopropane
	0.76	0.0			
I	0.9	0.6	1.40	0.55	0.28
II	1.0	1.0	2.26	1.2	0.00
	1.1	1.4			
III	1.2	1.7	3.83	2.0	0.18
IV	1.5	3.0	6.49	3.2	1.0

[a] $(\text{C–C})_\pi$ is given at HCH ∠ = 118° in cyclopropane.

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(35) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947).

(36) A. D. Walsh, *Faraday Society Discussion No. 2*, 18 (1947).

(37) See reference 23 and footnote 11 of R. Serber, *J. Chem. Phys.*, **3**, 81 (1935).

(38) See reference 5. In the course of this work an error was found in the integral γ in the cyclopropane calculation of Coulson and Moffitt. This has been confirmed by these authors. γ should be +1.4 instead of +10. This value of the integral reduces the calculated resonance energy of cyclopropane from 3.3 ev. to about 0.0 ev.

(39) O. Bastiansen and O. Hassel, *Tids. Kjemi Bergvesen Met.*, **6**, 71 (1946).

(40) J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards*, **43**, 113 (1949).

(41) G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940).

(42) K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

Reference may be made to Coulson and Moffitt[5] for the details of the electron pairing calculation as applied to cyclopropane. Retaining their symbolism along with that of Mulliken,[28] the energy of cyclopropane, relative to the ^{3}P ground state of carbon, is

$$E(\theta) = Q - (\text{C–C}) - (\text{C–H}) + P - R.E. + T.S. \quad (7)$$

where Q = coulombic energy

$$(\text{C–C}) = (\text{C–C})_{s\sigma} + (\text{C–C})_{\pi}$$

$$\begin{aligned}(\text{C–C})_{s\sigma} = 4.5\, l^4[&C_{ssss} + 4\lambda\cos\theta C_{ss\sigma s} + 2\lambda^2\cos^2\theta\,(C_{s\sigma\sigma s} + \\ &C_{s\sigma s\sigma} + C_{ss\sigma\sigma}) + 4\lambda^3\cos^3\theta\, C_{s\sigma\sigma\sigma} + \lambda^4\cos^4\theta C_{\sigma\sigma\sigma\sigma}]\end{aligned}$$

$$\begin{aligned}(\text{C–C})_{\pi} = 4.5\, l^4[&\lambda^4\sin^4\theta C_{\pi\pi\pi\pi} + 2\lambda^2\sin^2\theta(C_{ss\pi\pi} + C_{s\pi\pi s} + \\ &C_{s\pi s\pi}) + 4\lambda^3\sin^2\theta\cos\theta(C_{s\pi\sigma\pi} + C_{s\pi\pi\sigma} + \qquad (8) \\ &C_{s\sigma\pi\pi}) + 2\lambda^4\sin^2\theta\cos^2\theta(C_{\pi\pi\sigma\sigma} + C_{\pi\sigma\sigma\pi} + C_{\pi\sigma\pi\sigma})]\end{aligned}$$

$$(\text{C–H}) = 9m^2[N_{ss} + 2\mu N_{s\sigma} + \mu^2 N_{\sigma\sigma}]$$

P = promotional energy of 3 carbon atoms, $R.E.$ = resonance energy of the carbon–carbon skeleton as given by Coulson and Moffitt's secular equation,[5] $T.S.$ = torsional strain.[17] The promotional energy of the carbon atoms is determined by Van Vleck's equation[15] as a function of the HCH angle or, what is an equivalent parameter, the strain angle, θ. This is the angle between a carbon orbital and the line joining the carbon centers. When the HCH angle in cyclopropane varies from 90 to 109°28′ to 120° to 180°, θ varies from 60 to 24°44′ to 20°46′ to 15°. The assumption has been made that the resonance energy in each CH$_2$ group is the same regardless of the carbon hybridization so that this may be included in Q as a constant term. Torsional strain may be taken to be 2 kcal./opposed CH$_2$ group in cyclopropane, or 6 kcal./mole.

Substitution of $\theta = 0$, $l^2 = m^2 = {}^1/_4\, l^2\lambda^2 = m^2\mu^2 = {}^3/_4$, P = 3 (6.97) ev., $R.E. = 0$, $T.S. = 0$, yields the value of the energy for the tetrahedral unstrained model. The difference between $E(\theta)$ and E(tetrahedral unstrained) is the strain energy which is 25 kcal./mole or 1.09 ev. for cyclopropane. Substituting the N integrals derived above and the $C_{s\sigma}$ integrals given by relation (6) in conjunction with the values of C_{ssss} and $C_{\sigma\sigma\sigma\sigma}$ in columns 1 and 2 of Table III, yields the (C–C)$_\pi$ values in column 3 at θ = 21°22′ (HCH angle = 118°) if it is assumed that $R.E.$ = 0 for cyclopropane. Consideration must now be given to the relative values expected for these C integrals.

The $C_{s\sigma}$ integrals have been generally taken from Penney[26,27] by all authors. The C_π integrals have been discussed by Coulson and Moffitt[5] and by Gorin, Walter and Eyring.[43] If the integrals are calculated exactly using Kopineck's[44] tables at R = 1.54 Å., ZR/a_0 = 10, the values obtained are

$$\begin{array}{llll}
C_{ssss} & = +0.68 & C_{\pi\pi'\pi\pi'} & = +0.15 \\
C_{sss\sigma} & = +0.97 & C_{ss\pi\pi} & = -0.15 \\
C_{s\sigma s\sigma} & = +0.51 & C_{s\pi\pi s} & = -0.16 \\
C_{ss\sigma\sigma} & = +1.35 & C_{s\pi s\pi} & = +0.32 \\
C_{s\sigma\sigma s} & = +0.61 & C_{s\pi\pi\sigma} & = -0.21 \\
C_{\sigma\sigma\sigma s} & = +0.11 & C_{s\sigma\pi\pi} & = -0.18 \\
C_{\sigma\sigma\sigma\sigma} & = -0.03 & C_{s\pi\sigma\pi} & = +0.49 \\
C_{\pi\pi\pi\pi} & = +0.11 & C_{\sigma\sigma\pi\pi} & = -0.20 \\
C_{\pi\pi\pi'\pi'} & = -0.02 & C_{\pi\sigma\sigma\pi} & = -0.28 \\
C_{\pi\pi'\pi'\pi} & = -0.02 & C_{\sigma\pi\sigma\pi} & = +0.28
\end{array}$$

From the screening and overlap considerations employed by Penney, the most reasonable values of the $C_{s\sigma}$ integrals are considered to lie somewhere between $C_{ssss} = 0.9$, $C_{\sigma\sigma\sigma\sigma} = 0.6$, and $C_{ssss} = 1.5$, $C_{\sigma\sigma\sigma\sigma} = 3.0$ as given in Table III. It was assumed that

$$C_{\pi\pi\pi\pi} = C_{\pi\pi'\pi\pi'} = C_{s\pi s\pi} = C_{s\pi\sigma\pi} = C_{\sigma\pi\sigma\pi} \quad (9)$$

since it is to be expected that the π-electrons would be less screened, and thus increase the $C_{\pi\pi\pi\pi}$ and $C_{\pi\pi'\pi\pi'}$ values relative to the others calculated from Kopineck's tables. Also from overlap considerations one might expect a minimum C_π integral among these to be $C_{s\pi s\pi}$ but to this approximation they were taken as equal. The remaining C integrals were taken as zero since they involve only electrostatic repulsion and would be expected to be relatively small negative terms. With these relations and the value of (C–C)$_\pi$ at θ = 21°22′ in cyclopropane, (C–C)$_\pi$ may be calculated as a function of the strain angle θ for each set of values of C_{ssss} and $C_{\sigma\sigma\sigma\sigma}$ given in Table III. When this is done it is found that the minimum of energy in cyclopropane occurs in each instance at θ = 23 to 24° (HCH angle = 114 to 111°), and this minimum cannot be shifted to lower values of θ except by making the slope of (C–C)$_\pi$ zero or negative with respect to θ. These slopes require that the C integrals involved in the first two terms of (C–C)$_\pi$, that is, $C_{\pi\pi\pi\pi}$ and $(C_{s\pi s\pi} + C_{ss\pi\pi} + C_{s\pi\pi s})$, have large negative values. This seemed very unlikely and the minimum was allowed to remain near θ = 23°, the values of $C_{\pi\pi\pi\pi}$ being altered slightly by this change. The resonance energy in cyclopropane was calculated using the values of the C integrals thus derived, and since it in turn altered the value of the C integrals used, an iterative calculation was made until the $R.E.$ and C integrals, when substituted into equation (7), yielded the correct strain energy.

At the paraffinic hydrocarbon bond distances considered here the last two values of $C_{\pi\pi\pi\pi}$ in Table III appear to be too large when compared with the accompanying C_{ssss} and $C_{\sigma\sigma\sigma\sigma}$ values. Also, other estimates[5,45] of $C_{\pi\pi\pi\pi}$ place it in the neighborhood of 1 ev. However since no unequivocal choice can be made among the integrals, the calculations on other molecules were made using all four sets. In order to illustrate the behavior of the various energy terms in cyclopropane as calculated by the electron pairing approximation the set with C_{ssss} = 1.0 was used to obtain the curves shown in Fig. 2. For comparison the terms as calculated by the D–S–P method are also shown.

Cyclobutane.—The configuration of this molecule has not been definitely established as planar or puckered.[10] Only the planar form will be considered here for the purpose of calculating approximately the amount of strain due to across-the-ring repulsions for use in the treatment of tricyclooctane. This was previously calculated by Dunitz and Schomaker and amounted to 13.6 kcal./mole by their method. The electron pairing approximation, using the parameters derived above, yields the most stable HCH angle as approximately tetrahedral (strain angle, θ = 9.5°) for each of the four sets of C integrals in Table III. In making the calculations the resonance energy was taken equal to zero and the torsional strain assumed to be 2 kcal./mole per opposed CH group. The strain energies calculated were (I) 13.8, (II) 10.8, (III) 13.0, (IV) 16.6 kcal./mole, where the Roman numerals refer to Table III. The observed strain energy in cyclobutane as obtained from the heat of combustion of Coops and Kaarsemaker,[46] the thermodynamic functions as given by Cottrell,[47] and Pitzer's bond energies, is found to be 23.3 kcal./mole. The across-the-ring repulsion, obtained by difference for each of the four cases, is (I) 9.5, (II) 12.5, (III) 10.3, (IV) 6.7 kcal./mole.

"Acetylenic" Strained Hydrocarbons

Tricyclobutane.—The energy of tricyclobutane in this approximation is obtained in the same way as in the cyclopropane calculation except for the use of

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[43] E. Gorin, J. Walter and H. Eyring, THIS JOURNAL, **61**, 1876 (1939).

[44] H. Kopineck, *Z. Naturforsch.*, **5a**, 420 (1950).

[45] S. L. Altmann, *Proc. Roy. Soc.* (*London*), **A210**, 327 (1951); C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.*, **48**, 293 (1952).

[46] J. Coops and Sj. Kaarsemaker, *Rec. trav. chim.*, **69**, 1364 (1950).

[47] T. L. Cottrell, *Trans. Faraday Soc.*, **44**, 716 (1948).

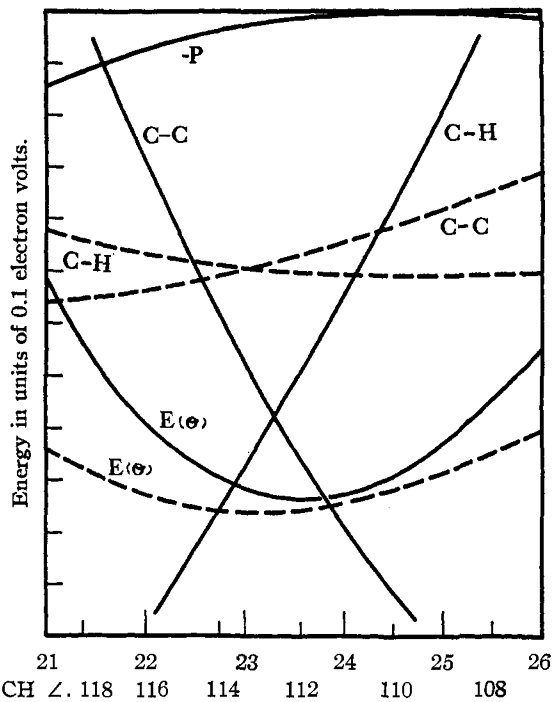

Fig. 2.—Energy terms in cyclopropane. Solid lines refer to calculations by the electron pairing approximation using the *C* integrals designated as II in Table III. Symbolism is that of equation (7). Dashed lines are corresponding terms in the D-S-P method. The top of the graph is zero for *P*. The relative positions of all of the other curves on the energy scale have no meaning since they had to be shifted vertically in order to place them on one graph.

hybrid carbon wave functions having C_{3v} symmetry.[14] The result, relative to the ^3P state of carbon, is given by equation (7) with

$$(\text{C–C}) = 2\,(\text{C–C for cyclopropane})$$
$$(\text{C–H}) = 2\,(\text{C–H for cyclopropane})/3$$

where $l = \operatorname{cosec} \chi(-{}^2/_3 \cos \varphi)^{1/2}$, $\lambda = (-\cos \varphi)^{-1/2}$, $m = -\sqrt{2} \cot \chi$, $\mu = -(-\cos \varphi)^{1/2}/\cos \chi$. χ is the angle between the C–H carbon orbital and any other carbon orbital on the same carbon atom, φ is the angle between any two C–C carbon orbitals on the same carbon atom. The torsional strain was assumed to be about 2 kcal. per opposed group. *P* is obtained from Van Vleck's equation[15] and again the resonance energy within each CH group in its state of hybridization is assumed the same as in the tetrahedral hybrid. The resonance energy (*R.E.*) of the carbon–carbon tetrahedral skeleton cannot be calculated accurately since the calculation would involve 132 bonding structures. If only the 16 structures involving 6 and 4 "good" bonds are considered, a cubic secular equation is obtained[48] which when expanded yields

$$13x^3 + (-25u/4 + 9w/2 + 7v)x^2 + (-3uv/8 + 9vw/4 - 130u^2/4)x - 81u^2v/8 = 0$$

where

$$x = R + 9\alpha;\ u = 4\beta - 2\gamma - 2\varphi;\ v = 8\delta - 8\alpha;\ w = 8\beta - 8\alpha$$

The symbolism is that of Moffitt[48] who made an analogous calculation for the P_4 molecule. His work may be referred to for details.

Then for the four sets of *C* integrals the results are

I: $\theta_m = 32°$, *R.E.* = 16 kcal./mole, strain = 92 kcal./mole
II: $\theta_m = 33°$, *R.E.* = 0 kcal./mole, strain = 87 kcal./mole
III: $\theta_m = 33°$, *R.E.* = 15 kcal./mole, strain = 90 kcal./mole
IV: $\theta_m = 32°$, *R.E.* = 51 kcal./mole, strain = 117 kcal./mole

θ_m indicates the value of the strain angle at the minimum of energy. The C–H hybridization is 35% s and 65% p at $\theta = 32°$, 32% s and 68% p at $\theta = 33°$, and the C–C bonds are about 22% s, 78% p.

Case II has been plotted in Fig. 3 as being representative of the variation of energy terms in tricyclobutane at normal paraffinic bond distances.

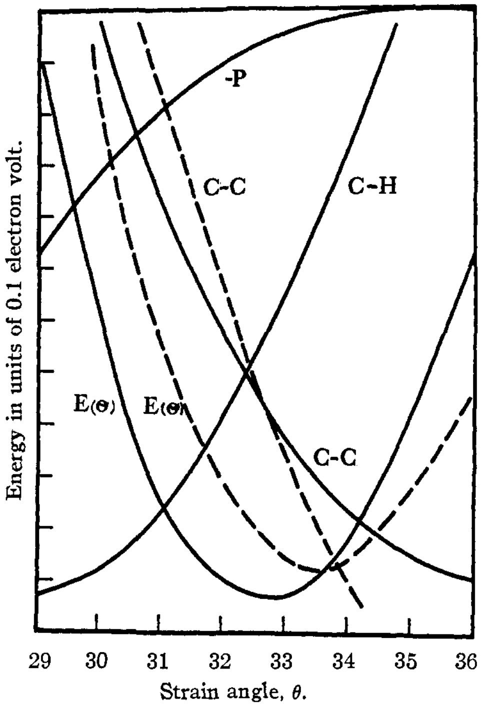

Fig. 3.—Energy terms in tricyclobutane. Solid lines refer to calculations by the electron pairing approximation for a carbon–carbon distance of 1.54 Å. Dashed lines indicate approximate effect of shortening this distance to 1.48 Å. Symbolism is that of equation (7). The top of the graph is zero for *P*. The relative positions of all of the other curves on the energy scale have no meaning since they were shifted vertically in order to place them on one graph.

Bond Shortening in Tricyclobutane.—It is to be expected that there will be a shortening of the carbon–carbon bonds in this molecule as in the other cycloparaffins,[10] however, in order to evaluate it by the electron pairing approximation, the variation of the *C* integrals with bond distance must be estimated. This variation for $C_{\pi\pi\pi\pi}$ may be taken from Coulson and Altmann's[45] work ($C_{\pi\pi\pi\pi}$ corresponds to their $\mathcal{E}_{\pi\pi}$), and for the relatively small

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[48] The secular equation derived here did not agree with that of W. E. Moffitt, *Trans. Faraday Soc.*, **44**, 987 (1948), and for that reason is given again.

alterations in bond length considered here, the $s\sigma$ part of the carbon–carbon terms is assumed to obey a Morse function. The force constant is taken as 4.50×10^5 dynes/cm. and $D_e = 80$ kcal./mole so that Morse's parameter a is 2.84 Å.$^{-1}$. All other terms are assumed to vary linearly with distance: $R = R' + q(r - 1.54)$, where R' is the extra interaction between two carbon atoms bonded at $r = 1.54$ Å. (thus neglecting hydrogen interactions and other non-bonded terms), and q is a parameter which can be determined from cyclopropane and will be assumed independent of the strain angle θ. This energy is $3R$ in cyclopropane, and the value of q may be derived from the fact that a minimum of energy in cyclopropane occurs at $r = 1.53$ Å. For these calculations the set of C integrals designated by II in Table III have been used. For the 24° strain angle in cyclopropane q is found to be 4.05. Applying this value of q to a similar calculation for 33° tricyclobutane involving $6R$ determines the minimum of energy to occur at the carbon–carbon bond distance of 1.48 Å. Then the C integrals become $C_{ssss} = C_{\sigma\sigma\sigma\sigma} = 0.97$, $C_{\pi\pi\pi\pi} = 1.62$ and the strain energy, exclusive of torsional strain and resonance energy, is 58 kcal./mole, a reduction of 17 kcal./mole over that value obtained above. The resonance energy calculated from these C integrals and relations (6) and (9) amounts to 0.38 ev. so that the total strain energy is then lowered to 61 kcal./mole. The shift in slope and minimum of energy in tricyclobutane due to bond shortening is shown by the dashed lines in Fig. 3 when calculated by the very approximate method outlined here.

Tricycloöctane.—The resonance energy will be assumed zero in this molecule, as in cyclobutane. The energy expression is then the same as in tricyclobutane except that all terms are multiplied by two because there are twice the number of CH groups. If 24 kcal./mole is attributed to torsional strain, the strain energy is calculated to be (I) 67, (II) 55, (III) 61, (IV) 88 kcal./mole. In every case the minimum occurs at $\theta = 14°30'$ where the C–H hybridization is 29% s, 71% p and the C–C hybridization is 24% s, 76% p. To this strain energy must be added that due to across-the-ring repulsion in each of the six cyclobutane units of which the molecule is composed. If these are assumed the same as in cyclobutane, then the total strain becomes (I) 124, (II) 130, (III) 123, (IV) 129 kcal./mole.

Discussion

A summary of the calculated properties of these molecules, as obtained by the two methods, is given in Table IV.

The agreement is rather startling and certainly fortuitous in view of the comparison shown in Fig. 2 for cyclopropane. The slopes of the C–C and C–H energies in the figure indicate that these two terms have exchanged roles in the two methods. This is a consequence of Pauling's index of bond strength which places the maximum CH hybrid bond strength at the tetrahedral carbon hybridization whereas that maximum occurs near 50% s hybridization in the electron pairing scheme. The observed data appear to support the latter, as pointed out above when discussing the $N_{\alpha\beta}$ integrals.

TABLE IV

RESULTS OF CALCULATIONS

	D–S–P Method			Electron pairing approximation		
Molecule	Strain energy, (kcal./mole)	Strain angle (degrees)	C–H hybrid % s character	Strain energy, (kcal./mole)	Strain angle, (degrees)	C–H hybrid % s character
Cyclopropane[a]	28	23	28	(25)	23	28
Cyclobutane[a]	(23)	9	26	(23)	10	25
Tricyclobutane	93	32	35	90	33	32
				60[b]	34[b]	29[b]
Tricycloöctane	120	13	33	130	14.5	29

[a] Observed values of the strain energy in these two molecules are: cyclopropane, 25 kcal./mole; cyclobutane, 23 kcal./mole. [b] Approximate calculation for carbon–carbon distance = 1.48 Å.

The steepness of the slope for the C–C and C–H curves in the electron-pairing approximation in Fig. 2 depends essentially upon the determination of the C–H parameters, the $N_{\alpha\beta}$ integrals, and these cannot be seriously in error. The curvature in the neighborhood of the minimum, that is, the bending force constant, is too large by either theory but the flatter D–S–P curve is the more correct one. The force constant for HCH bending in cyclopropane[49] is about 0.4×10^{-11} ergs/rad^2 and the value obtained from the solid-line minimum of Fig. 2 is about 10 times this value. The relative curvature of the component curves is extremely critical in determining the curvature at the minimum and for this simple theory and this complex a molecule the inclusion of further refinements in order to reproduce the exact force constant did not seem warranted.

Tricyclobutane has the two possible isomers; vinylacetylene, which exists and is stable, and the planar form, 1,3-cyclobutadiene, which has not as yet been synthesized. The strain energy in vinylacetylene may be determined to be 59 kcal./mole from Stamm, Halverson and Whalen's[50] thermodynamic considerations and Pitzer's[42] bond energies. The planar configuration, cyclobutadiene, is however in a rather anomalous position. Theory indicates that the molecule may have a triplet group state and it seems rather certain that it possesses a relatively small amount of resonance energy. Strain in the ring is generally believed to play only a small part in determining its instability. If, because of a small resonance energy, cyclobutadiene is inferred to have unequal bond lengths in the ring as Craig[7] has suggested, the strain energy in the single carbon–carbon bonds may be calculated by the electron pairing method to be about 5 to 10 kcal./mole. The molecule was conceived of as just two ethylene molecules pushed together to a distance of 1.54 Å. thus making the strain angle 30° for each 33% s hybrid carbon orbital. For this model there should also be added an estimated 15 kcal./mole for across-the-ring repulsion so that the strain is about 22 kcal./mole exclusive of that in the two double bonds. The strain then becomes 47 kcal./mole if about 5 kcal./mole is

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(49) k_4' of B. D. Saksena, *Proc. Ind. Acad. Sci.*, **10A**, 449 (1940).

(50) R. F. Stamm, F. Halverson and J. J. Whalen, *J. Chem. Phys.*, **17**, 104 (1949).

allowed for any stabilizing hyperconjugation. A similar calculation by the D–S–P method yields 62 kcal./mole as the strain. Presumably these represent maximum values since alteration of bond length and angles would tend to reduce the strain but a large error would not be expected. Hence it appears that the three possible isomers are all of comparable stability if, of course, cyclobutadiene has a stable ground state.

The heat of formation at 0°K. of hypothetical tricyclooöctane may be calculated to be 160 kcal./mole from Pitzer's bond energies and the strain energy of 130 kcal./mole. The heat of formation of cyclooöctatetraene as obtained from heat of combustion data by Person, Pimentel and Pitzer[51] is 76.3 kcal./mole. The approximate nature of the calculated value for tricyclooöctane can hardly account for this large a difference and it appears that the cubic structure is thermodynamically highly unstable with respect to cyclooöctatetraene.

It does not appear that the rate of transition of tricyclobutane to the more stable isomers considered here would be rapid at room temperature. These isomerizations involve the breaking of carbon–carbon bonds and the difference in strain energy between the isomers does not appear large enough to lower the activation energy sufficiently for a rapid reaction to occur. Tricyclooöctane is a more dubious case and may or may not be capable of synthesis.

BALTIMORE, MARYLAND

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[51] W. B. Person, G. C. Pimentel and K. S. Pitzer, THIS JOURNAL, **74**, 3437 (1952).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

The General Nature of the Proportionality of Polar Effects of Substituent Groups in Organic Chemistry

BY ROBERT W. TAFT, JR.

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Rates or equilibria for a number of reactions involving bulky groups adjacent to the reaction center have been found to fit an equation, (2) log k/k_0 (or K/K_0) = $\sigma^*\rho^*$. The polar substituent constants, σ^*, are those determined previously from rates of acidic and basic esterification and hydrolysis of esters.[2b] The σ^*-values for aliphatic groups are shown to be additive. The correlations of eq. (2) serve to demonstrate the general nature of the proportionality of polar effects of substituents. If steric factors are variable in a reaction series, eq. (2) is not followed, but the polar contributions to the logarithms of rates or equilibria, $P\sigma$, follow a similar equation, (3) $P\sigma = \sigma^*\rho^*$. Physical properties, such as dipole moments, have been found in a number of cases to follow eq. (3). Applications of the basic principle of proportionality of polar effects in reaction rates and equilibria of this type are discussed and examples given.

Rates and equilibria for a great number of reactions of meta and para substituted benzene derivatives have been found to fit with reasonable precision the Hammett eq.[1a]

$$\log k/k_0 \text{ (or } K/K_0) = \sigma\rho \qquad (1)$$

where k refers to the rate of a reaction of a *m*- or *p*-substituted benzene derivative. K refers to the equilibrium constant for such a reaction.

The subscript zero refers to the corresponding unsubstituted derivative. σ is a substituent constant, measuring the polarity of a given substituent relative to hydrogen. The definition of σ is $\sigma \equiv \log K/K_0$ for the ionization of substituted benzoic acids in water at 25°. ρ is a proportionality constant. It is a measure of the susceptibility of a given reaction series to polar substituents.

Equation (1) demonstrates that the corresponding polar effects of substituents on free energy differences are proportional from one reaction series to another—a relationship which is independent of reaction mechanism, attacking reagent, solvent, temperature or nature of the functional groups involved in the initial or final states of the process. That is, although these variables determine the value of the reaction constant, ρ, the fit of the data to the eq. (1) is independent of these.

The same may not be said for reactions of ortho substituted benzene derivatives or the multitude of various reactions in the aliphatic series. Rates and equilibria do not generally follow eq. (1).[1] A typical illustration is given in Fig. 1. The relatively few cases where proportionality exists between the corresponding effects of substituents on free energies are definitely determined by the nature of the above-mentioned variables.[2a]

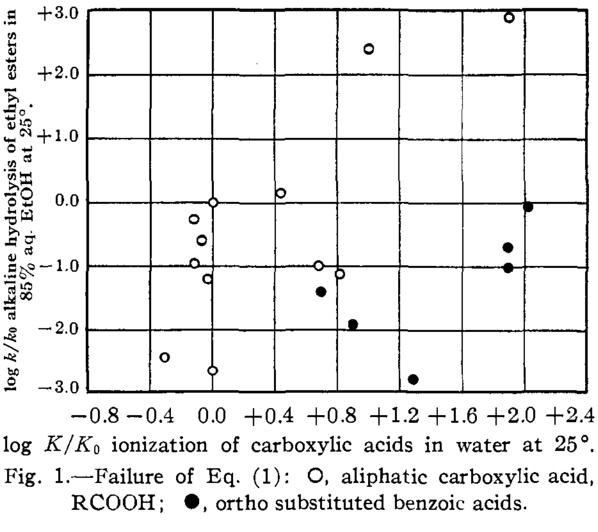

Fig. 1.—Failure of Eq. (1): ○, aliphatic carboxylic acid, RCOOH; ●, ortho substituted benzoic acids.

The failure of eq. (1) to apply to this important class of reactions must depend on one or both of the

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[1] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc, New York, N. Y., 1940, pp. 186–193; (b) p. 222.

[2] (a) R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952); (b) **74**, 3126 (1952).