Tetrahedron, 1961, Vol. 15, pp. 87 to 92. Pergamon Press Ltd. Printed in Northern Ireland

CARBON-CARBON AND CARBON-HYDROGEN BOND ENERGIES AND BOND DISTANCES*

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(*Received* 13 *February* 1961; *in revised form* 4 *March* 1961)

Abstract—Two types of mathematical relations are discussed, which represent the connection between carbon-carbon bond energies and carbon-carbon bond distances. They similarly describe the relation between carbon-hydrogen bond energies and the corresponding carbon-hydrogen bond distances.

IN a recent communication[1] the suggestion was made that the relation between carbon–carbon bond energies [B(CC), in kcal] and carbon–carbon distances [R(CC) = r, in Å] could be expressed by a power series of the third degree of the reciprocal distances

$$B(CC) = a/r + b/r^2 + c/r^3 \qquad (1)$$

and

$$B(CH) = A/\rho + B/\rho^2 + C/\rho^3 \qquad (2)$$

where $a = -1140{\cdot}593$, $b = 3252{\cdot}755$ and $c = -1991{\cdot}129$. The corresponding relation between carbon–hydrogen bond energies [B(CH), in kcal] and carbon–hydrogen distances [R(CH) = ρ, in Å] was also considered to be of the same form with the constants: A = 1125·03, B = −2477·006 and C = 1376·444. The authors made the following statement in their paper in reference to the present writer's earlier publications: "We preferred, however, to derive new relations of this kind for CC and CH bonds, since we felt that the published ones were open to criticism".

However, a study of equations (1) and (2) indicates that they have several shortcomings. The most serious difficulty lies in the fact that the summation of the carbon–carbon and carbon–hydrogen bond energies, calculated by means of these equations, does not give the heat of atomization (Qa) for a series of molecules. It is of course a fundamental tenet of bond energy considerations that

$$Qa = l{\cdot}B_1 + m{\cdot}B_2 + ---- \qquad (3)$$

where l = number of B_1-bonds, m = number of B_2-bonds, etc.

The heats of atomization are obtained from the usual heats of formation (Qf at 0°K).[2,3] In the case of hydrocarbons the heat of sublimation of graphite [L(C) = 170·4 kcal, at 0°K] and the heat of dissociation of hydrogen [D(H_2) = 103·24 kcal, at 0°K] are also needed.[3] The authors make their calculations at 25°C. This difference in temperature causes only a change of a few kilocalories. The B(CC) and B(CH)

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* This research is supported by the U.S. Army Office of Ordnance Research under Contract No. DA-31-124-ORD-104.

[1] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 5, 166 (1959).

[2] F. D. Rossini *et al.*, *Selected Values of Properties of Hydrocarbons*. National Bureau of Standards Circular C 461. United States Government Printing Office, Washington, D.C. (1947).

[3] F. D. Rossini *et al.*, *Selected Values of Chemical Thermodynamic Properties*. National Bureau of Standards Circular 500. United States Government Printing Office, Washington, D.C. (1952).

bond energy values reported here were obtained by using equations (3), (4) and (5). These cubic equations were first established in 1958 and are here recalculated.[4]

$$B(CC) = 27{\cdot}00/r - 116{\cdot}00/r^2 + 427{\cdot}533/r^3 \tag{4}$$

and

$$B(CH) = -812{\cdot}61/\rho + 1970{\cdot}90/\rho^2 - 1046{\cdot}71/\rho^3 \tag{5}$$

The numerical values obtained by the use of these equations are shown in Table 1, columns 3 and 6.

TABLE 1.—CARBON CARBON AND CARBON HYDROGEN BOND ENERGIES

	R(CC)	B(CC) kcal		R(CH)	B(CH) kcal	
	Å	G	D · S	Å	G	D : S
C_2H_2	1·207[a]	185·7	170·6	1·06[a]	102·0	109·5
C_3	1·28[b]	154·0	—	—	—	—
C_2	1·315[a]	141·5				
C_2H_4	1·337[c]	134·1	130·4	1·086[c]	99·1	100·5
C_6H_6	1·397[d]	116·7	—	1·090[d]	98·6	—
Graphite	1·421[d]	110·6	—	—	—	—
Graphite	3·354[d]	9·1				
C_2H_6	1·543[d]	85·2	84·5	1·102[d]	97·0	97·0
Diamond	1·5445[d]	84·9	84·6	—		
CH_4				1·094[d]	98·1	98·2

[a] Ref. 5. [b] Ref. 12. [c] Ref. 7. [d] Ref. 8.

The comparison of the two sets of bond energy values is best done by calculating the heats of atomization for the two cases using equation (3). In Table 2 the experimental values of *Qa* are shown in column 2. The present calculated *Qa*-values (column 3) naturally check the experimental ones. However, the *Qa*-values derived by Dewar and Schmeising[1] (not mentioned), show differences of several per cent between calculation and experiment.

TABLE 2.—HEATS OF ATOMIZATION (*Qa*, kcal)

	Expt.	G	D · S
C_2H_2	389·7	389·7[a]	388·6[b]
C_3	320·8[c]	308·0	
C_2	141·2[c]	141·5	
C_2H_4	532·7	530·5	532·5
C_6H_6	1308·1	1293·6	1279·4
Graphite		165·9	
Graphite		4·5	—
C_2H_6	667·2	667·0	666·6
Diamond	169·8	169·8	169·8
CH_4	392·9	392·9	392·7

[a] Equations (3–5). [b] Ref. 14. [c] Refs. 10 and 11.

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[4] Presented at the American Chemical Society Regional Meeting, Richmond, Virginia, 5–7 November 1959.

Another discrepancy should be noted. The values for B(CH) as calculated from equation (2), with the appropriate constants given above, must be multiplied by a factor of ten, in order to yield reasonable values. The *Qa*-values for ethane check then satisfactorily. An entirely different set of empirical constants can of course remove this discrepancy as is noted in equations (4) and (5).

The relations between bond energies and bond distances are shown graphically in Fig. 1 and 2. It is seen that the discrepancy in B(CC, C_2H_2) is due to the fact that the cubic relation[1] has a maximum at 1·15 Å or near to R(CC, C_2H_2) = 1·207 Å. It was found during these calculations that the location of a maximum can be shifted by a relatively small change in internuclear distance. The latter are given in Table 1, column 2.[6–8] In the case of ethylene it is likely that Dewar and Schmeising[1] used the internuclear distances given by Bartell and Bonham[9], which are R(CC, C_2H_4) = 1·334 and R(CH, C_2H_4) = 1·085 Å. The corresponding bond energy values B(CC, C_2H_4) = 134·1 and B(CH, C_2H_4) = 103·6 kcal lead to *Qa*(C_2H_4, calc.) = 548·5 kcal, whereas *Qa*(C_2H_4, expt.) = 532·7 kcal. The calculated value is then only 3 per cent greater than the experimental finding.

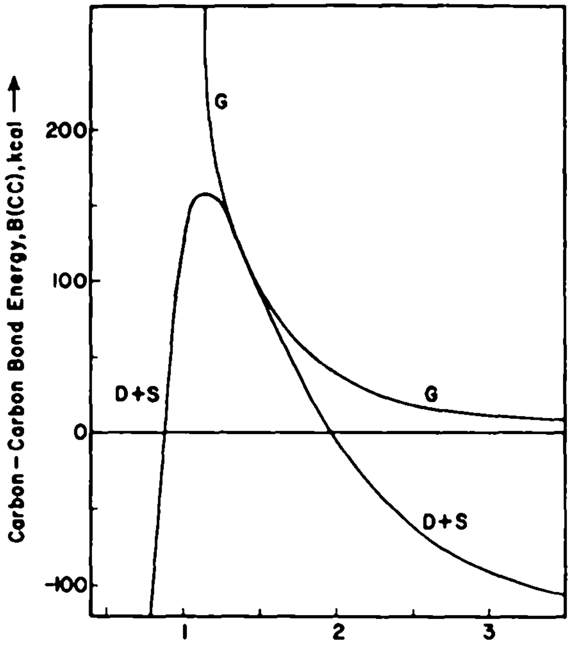

FIG. 1. Relation between carbon-carbon bond energies and carbon-carbon distances. (Equations 1 and 4.)

From Fig. 1 it is seen that the present empirical relation between B(CC) and R(CC), equation (4), includes the interaction energy between the planes in solid

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[5] T. L. Cottrell, *The Strengths of Chemical Bonds*. Academic Press, New York (1954).

[6] A. E. Douglas, *Astrophys. J.* **114**, 466 (1951).

[7] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 703 (1959).

[8] L. E. Sutton, (Editor), *Tables of Interatomic Distances*. The Chemical Society, London (1958).

[9] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957).

graphite. It is well known that the heat of sublimation of diamond [L(C, dia) = 169·8 kcal = 2 B(CC, dia)]. If the bond energy values in graphite are given by B(CC, 1·421) within the planes and B(CC, 3·354) between the planes, then

$$1{\cdot}5\ \mathrm{B(CC,}\ 1{\cdot}421) + 0{\cdot}5\ \mathrm{B(CC,}\ 3{\cdot}354) = 170{\cdot}4\ \mathrm{kcal} \tag{6}$$

The cubic relations (equations 4 and 5) include equation (6), whereas relation (1) is not applicable since it gives negative values beyond about R(CC) $\doteq$ 2 Å.

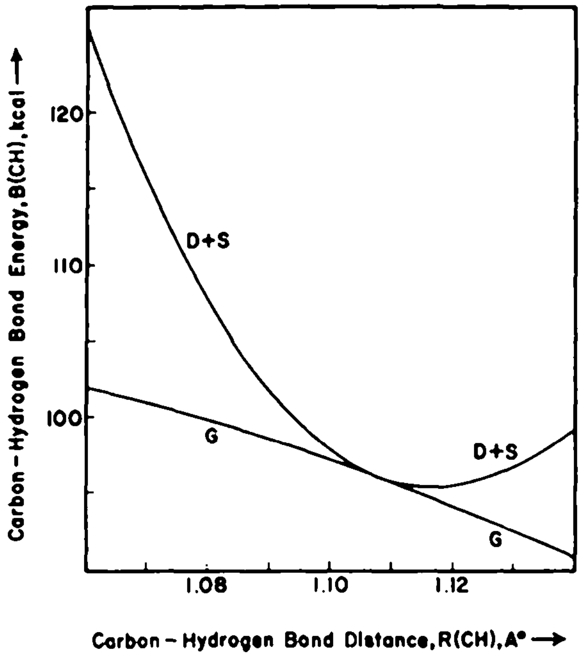

FIG. 2. Relation between carbon–hydrogen bond energies and carbon–hydrogen distances. (Equations 2 and 5.)

The average bond energy of the C_3-molecule from mass-spectroscopy is 160·4 kcal.[10] When calculated from the heat of sublimation of graphite [L(C) = 170·4 kcal], the enthalpy of the C_3-molecule [$\Delta H_0^0 = 186{\cdot}7 \pm 1{\cdot}5$ kcal (second law) and $188{\cdot}1 \pm 2{\cdot}3$ kcal (third law)]. Pitzer and Clementi[11] give 186·5 kcal. From these values and from the relation

$$3\mathrm{L(C)} - \Delta H_0^0 = 2\mathrm{B(CC,}\ C_3) \tag{7}$$

B(CC, C_3) is found to be 162·0 kcal. From the cubic equation (4), the corresponding distance is found to be 1·26 Å, whereas relation (1) yields no result since the maximum carbon–carbon bond energy is 158·6 kcal at 1·15 Å for this equation. However, Kiess and Broida[12] have lately found the rotational constant for the C_3-molecule to be 0·4280 whence R(CC, C_3) = 1·281 Å. This distance implies B(CC, C_3) = 144·5 kcal from equation (1) and 153·8 kcal from equation (3). Hence a discrepancy exists

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[10] J. Drowart, R. P. Burns, G. De Maria and M. J. Inghram, *J. Chem. Phys.* **31**, 1131 (1959).

[11] K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.* **81**, 4477 (1959).

[12] N. H. Kiess and H. P. Broida, *Canad. J. Phys.* **34**, 1971 (1956).

in the case of both relations (1) and (3) and depends entirely on the value of the rotational constant (B).

On the other hand, equation (3) yields B(CC, C_2) = 141·5 kcal with R(CC, C_2) = 1·315 Å[13] in good agreement with B(CC, C_2) = 142·9 kcal derived from mass-spectroscopy.[10] The latter value was obtained from the enthalpy of the C_2-molecule [$\Delta H_0{}^0$ = 195·8 (second law), 198·0 (third law)][10] and 200·0 kcal.[10] The average value is $\Delta H_0{}^0$ = 197·9 kcal. It yields B(CC, C_2) = 142·9 kcal, using L(C) = 170·4 kcal and the relation

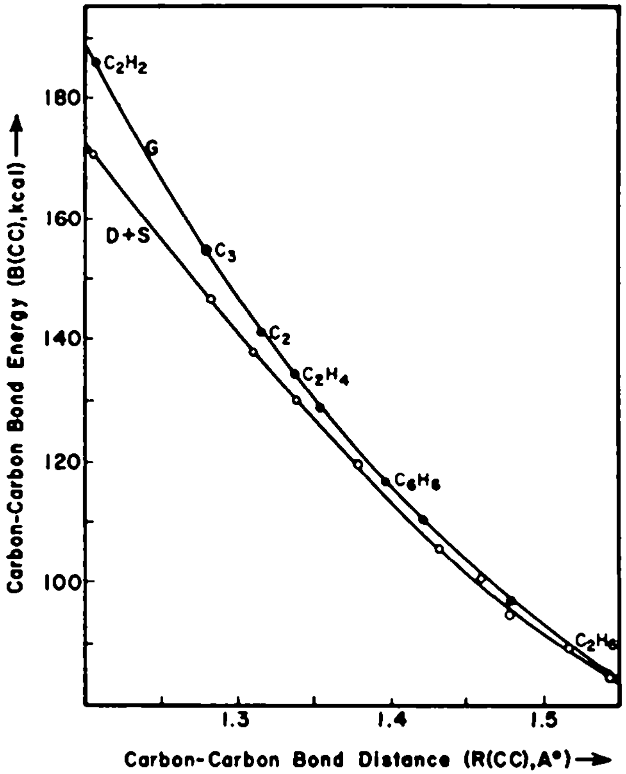

FIG. 3. Relation between carbon–carbon bond energies and carbon carbon distances. (Equation 4; ref. 14, Tables 6 and 7.)

$$2L(C) + \Delta H_0{}^0 = B(CC, C_2) \tag{8}$$

Equation (1) yields 138·0 kcal at R(CC) = 1·315 Å.

Other cubic relations were studied involving small variations of the internuclear distances. They showed no improvement over the case presented here.

In a later communication[14] another relation between the energies and distances of the carbon–carbon bonds is proposed. It is called a tractrix and contains logarithmic terms. These new results are here compared with the present author's cubic as shown in Tables 1 and 2 and Figs. 3 and 4. The two relations now yield comparable values

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[13] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules.* Van Nostrand, New York (1950).

[14] M. J. Dewar and H. N. Schmeising, *Tetrahedron* 11, 96 (1960).

for the carbon–carbon bond energies from ethane to ethylene, but then the respective curves diverge. It is seen that for acetylene the differences in the bond energies in the two cases are relatively large. When however the C_3 and C_2 molecules are considered it would appear that the higher values of the present cubic equation are the more likely ones.

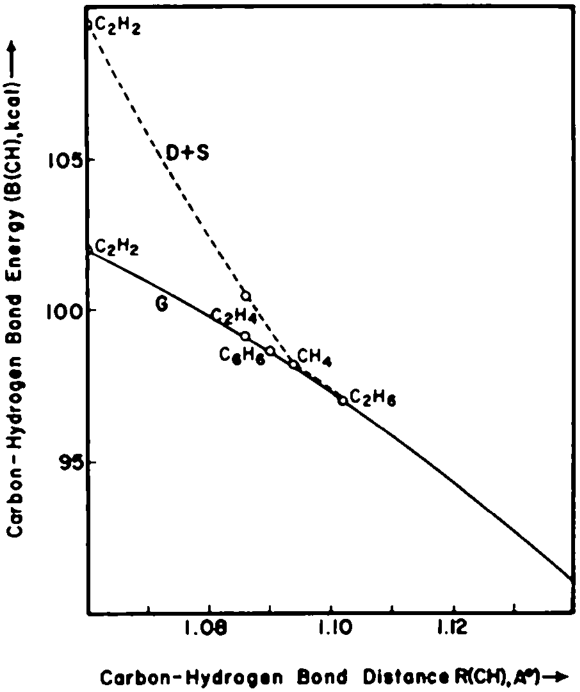

FIG. 4. Relation between carbon-hydrogen bond energies and carbon hydrogen distances. (Equation 5; ref. 14, Tables 6 and 7.)

It is of interest to note that the heat of atomization of benzene [$Qa(C_6H_6) = 1293{\cdot}6$ kcal; Table 2] when calculated by equations (4) and (5). It is given as 1279·4 kcal by Dewar and Schmeising (Table 7). The respective resonance energies are then 14·5 and 28·7 kcal respectively, since the experimental value of the heat of atomization is 1308·1 kcal. On page 111, ref. 14 it is stated that the true resonance energy of benzene probably lies in the range 5–15 kcal/l mole.