

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

On the Length of the Carbon-Carbon Single Bond¹

BY L. S. BARTELL

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Evidence is presented that intramolecular van der Waals forces can affect bond lengths appreciably. The carbon-carbon bond is discussed, in particular, and it is shown that *gauche* repulsions in the conventional reference, diamond, may account for the 0.01 Å. difference between bonds in the diamond and *n*-hydrocarbons. Other factors governing bond lengths in hydrocarbons are discussed briefly.

For several decades the accepted reference distance for the C-C single bond has been 1.544 Å., the distance occurring in the diamond. The recent observation² that the average C-C bond length in the *n*-hydrocarbons butane through heptane is only 1.533 ± 0.003 Å., warrants an explanation. A simple model, based upon an extension of a recent scheme of Pitzer and Catalano,³ is proposed below which considers semi-quantitatively the effects of van der Waals forces. It accounts for the observed difference in bonds and suggests that the conventional reference may plausibly be considered to be too high. It succeeds, additionally, in correlating thermochemical data. Other factors governing bond lengths in hydrocarbons are also discussed.

Assumptions of Model.—Pitzer and Catalano³ showed that isomerization energies of paraffin hydrocarbons can be attributed principally to dispersion force effects between non-bonded atoms. In their scheme, C-C and C-H bond energies were assumed to be independent of the structure. Interactions between all non-bonded pairs of atoms were considered to be attractive, involving r^{-6} dispersion energy terms, except those arising in *gauche* conformations from the well-known *gauche* methyl or methylene repulsions. The extra energy associated with *gauche* repulsions was computed from thermal data. The model of Pitzer and Catalano, with its reasonableness and economy of assumptions, represents a noteworthy advance over earlier highly empirical schemes for computing heats of formation. It seems appropriate to extend it, tentatively, to the diamond crystal itself.

The most conspicuous feature of the diamond crystal, viewed in the above light, is the abundance of *gauche* arrangements, totaling three per C-C bond, which might be expected to expand the diamond lattice. The magnitude of the *gauche* carbon and other non-bonded repulsions, not derivable from the Pitzer and Catalano model, can be estimated if it is assumed that the Lennard-Jones potential

$$V_{ij} = \{ (B/r_m^6) [C(r_m/r)^{12} - (r_m/r)^6] \}_{ij} \quad (1)$$

is applicable. The values of B used below are those of Pitzer and Catalano, and r_m is taken, tentatively, as 3.3, 2.9 and 2.5 Å. for C-C, C-H and H-H interactions, respectively, from considerations of van der Waals radii.⁴ The constant C in the re-

pulsive term is given its conventional value of $1/2$ for non-bonded pairs unless they are bonded to the same atom. For the latter case C arbitrarily was taken as zero in the expectation that the repulsive term is smaller than in normal van der Waals contacts⁴ and approximately constant in the molecules being compared. An additional justification is the fact that the Pitzer and Catalano model, which also assumes C is zero for these closely-spaced pairs, is consistent with thermochemical data.⁵

Implications of Model.—Interatomic forces can be computed from the appropriate differentiated form of eq. 1, together with the measured internuclear distances.² A summation over pairs of atoms shows that the net attractive (r^{-7}) forces across each C-C bond are approximately the same for *n*-hydrocarbons and the diamond. By contrast, repulsive forces in all-*trans* hydrocarbons are small compared with *gauche* repulsions in the diamond. Accordingly, we can balance the diamond *gauche* repulsive force per bond, $3(r_g/r_{cc})(\partial V_g/\partial r_g)$, with the force, $k_{cc} \Delta r_{cc}$, to stretch the bond, and determine Δr_{cc} , the excess C-C bond length in the diamond. Using the spectroscopic value⁶ $k_{cc} = 4.5 \times 10^5$ dynes/cm., we find that $\Delta r_{cc} \sim 0.017$ Å. A more detailed summation yields $\Delta r_{cc} \sim 0.014$ Å., but this result cannot be regarded as much more reliable in view of the approximate nature of the treatment.

In addition to providing a plausible explanation for the difference between C-C bond lengths, the present model also permits a direct calculation of the *trans-gauche* energy difference that was an adjustable parameter in the Pitzer and Catalano method. If the structural model of reference 2 is used with eq. 1, a value of about 0.52 kcal./mole is obtained for an azimuthal angle of 60°, in reasonable agreement with experimental values of 0.6 to 0.8 kcal./mole. The assumption that C-C bonds in hydrocarbons and the diamond are identical, except for effects of dispersion forces, implies that the heat of vaporization of the diamond should be calculable from Pitzer and Catalano bond energies as modified by dispersion and zero-point energies. It is disappointing to find in a preliminary calculation that the calculated value is about 3 kcal. lower than the experimental value of 170 kcal./mole. It should be noted, however, that a modest modification of the constants used in

(5) We are inclined to justify the neglect of the term more on the basis of its approximate independence of whether C or H atoms are involved, than on its absolute smallness. Such repulsions probably play an important role in governing bond angles and force constants for bending vibrations. They may affect bond distances, also, if the number of such contacts is reduced, as in going from isobutane to isobutene.

(6) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 193.

(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) R. A. Bonham and L. S. Bartell, THIS JOURNAL, **81**, 3491 (1959).

(3) K. S. Pitzer and E. Catalano, *ibid.*, **78**, 4844 (1956).

(4) The values of r_m and C chosen were selected principally on the basis of a discussion by L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, pp. 187-195.

eq. 1, well within the range of their uncertainty, could bring about agreement. Such modification would not affect the interpretation or general magnitude either of the isomerization energies or of the shift in bond distances.

Of the alternative factors responsible for the difference between hydrocarbons and the diamond, purely electrostatic effects should be small. It seems unprofitable to invoke second-order hyperconjugation because effects of first-order hyperconjugation are not clearly evident in a variety of recently determined ground state structures of molecules. Similarly, it appears unnecessary to attribute the differences to a change of hybridization possibly associated with the 3° difference in the C-C-C angles. The relationship between bond angles and hybridization seems less direct than popularly supposed, presumably because of bond bending due to non-bonded repulsions. It is interesting to note, in this connection, that in the n -hydrocarbons (tetrahedral bonds) the C-C-C angles, which are increased by steric strain, are almost the same as in isobutene (trigonal bonds) where the Me-C-Me angle is decreased by steric strain, and where the C-C bond is appreciably shorter.⁷ According to the scheme of Dunitz and Schomaker,⁸ the bending of the bonds in n -hydrocarbons should have a negligible effect on the C-C distance.

The n -hydrocarbon C-C distance of $1.533 \pm$

(7) R. A. Bonham and L. S. Bartell (to be published).

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

0.003 Å. appears in some respects a more suitable reference for saturated molecules than the diamond distance. It should be pointed out, however, that neither distance seems a satisfactory reference for conventional estimations of bond orders in conjugated systems with trigonal bonds. A single bond distance of about 1.48 Å. for cases in which both C atoms participate in double bonding is suggested by the value of 1.506 Å. for the single bond in isobutene.⁷ For reasons to be discussed elsewhere,⁷ we prefer to regard the single bond in isobutene as a pure single bond, shortened by effects of hybridization and relaxation of non-bonded repulsions but altered very little by hyperconjugative effects.

Much of the present work on internuclear distances is inaccurate or confused by the different operational definitions of bond lengths associated with various spectroscopic and diffraction methods, so that an extensive comparison now is difficult. Preliminary comparisons indicate that the above approach may prove generally useful in correlating precise molecular structures as well as energies of formation.

MORE ADDED IN PROOF.—It is now apparent that the dependence on r assumed above for the H-H term is too extreme and, accordingly, the result for the *trans-gauche* energy difference is somewhat fortuitous. An improved potential function to be described elsewhere, coupled with corrections for deformation and zero-point effects, has led to a better value of the energy difference.

AMES, IOWA

[CONTRIBUTION FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

Variation of the Thermodynamic Ideal Temperature in the Polystyrene-Cyclohexane System¹

BY DONALD MCINTYRE, J. H. O'MARA AND B. C. KONOUCK

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The second virial coefficients of cyclohexane solutions of several fractions of polystyrene prepared in slightly different ways have been determined by light scattering and osmometry near the theta, or ideal, temperature. The results indicate that the ideal temperature is increased as the molecular weight is decreased. The larger increase is due to small but increasingly effective chemical interactions when an n -butyl mercaptan group is incorporated in the chain. A much smaller effect appears to exist even when the chain is apparently uniform.

According to the earlier theories of Flory,² for solutions of all molecular weights of a given polymer in a particular solvent there is a temperature, called the theta temperature, at which the solvent-polymer segment interaction allows the penetration of polymer segments among each other freely. Consequently the equations relating the experimental quantities of osmotic pressure, turbidity and concentration gradient in centrifugation to the molecular weight and concentration at the theta temperature would be written without the second virial term in equations 1, 2 and 3. The terms are the same as those used by Flory.² In

$$\pi/c = RT/M + A_{2c} + \dots \quad (1)$$

$$Hc/\tau = 1/MP(\theta) + 2A_{2c} + \dots \quad (2)$$

(1) Presented at the 132nd Meeting of the American Chemical Society in New York, N. Y., on September 9, 1957.

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XII.

$$(H_u/RT)(c_x/(dc/dx)) = 1/M_x + 2A_{2c} + \dots \quad (3)$$

this case the osmotic pressure yields the familiar van't Hoff relation which would correspond to an ideal solution. In this sense the theta temperature may also be referred to as an ideal temperature.

By working under these ideal conditions the measurement of the molecular weights of high polymers can be facilitated. Thus in an effort to determine accurate molecular weights of fractions of polystyrene, samples were prepared under conditions best suited to obtaining large amounts of fractions in various molecular weight ranges. These fractions of polystyrene then were studied under ideal conditions by equilibrium ultracentrifugation, light scattering and osmometry on the assumption that the ideal temperatures would be identical for all of the fractions when they were dissolved in cyclohexane. However, it was discovered that the