The Lengths of the Links of Unsaturated Hydrocarbon Molecules

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The lengths of the links in conjugated chain molecules $C_{2n}H_{2n+2}$ and in condensed aromatic hydrocarbons such as benzene, naphthalene and diphenyl are calculated on the assumption that there is a simple interaction energy between all contiguous carbon-carbon bonds. The lengths thus deduced are in excellent agreement with those determined by the use of quantum-mechanical ideas of resonance.

IT is known that the links in many unsaturated hydrocarbons (e.g. benzene C_6H_6 or butadiene C_4H_6) have lengths which are neither those of a pure single bond nor of a pure double bond, but which are, in general, intermediate between the two. The author has recently shown[1] how these lengths may be calculated if we assume that certain of the electrons (the π- or mobile electrons) are able to move through the molecule in a manner similar to the conduction electrons of a metal. Alternatively[2] the calculations may be made, with similar results, using the valence-bond method of Pauling.

These calculations, however, are extremely cumbersome, and in this note we shall show how the various lengths may be obtained without much difficulty, using an empirical expression for the energy of interaction between each pair of consecutive links.

In the unsaturated hydrocarbons, the three bond directions are inclined at angles of approximately 120° and lie in a plane; they are the trigonal bonds of Pauling.[3] We may regard the

process of building up one of these molecules as consisting of two stages; first we "excite" the individual carbon atoms into the trigonal state, and second we allow these excited atoms to interact among themselves. We shall, as usual, neglect the effect of the $C-H$ bonds in this discussion; this does not mean that their presence has no effect upon the rest of the molecule, but we do, in fact, here assume that they merely add a constant amount to the energy. The second stage, therefore, consists solely in discussing the mutual interactions of a number of such trigonal, or aromatic, carbon atoms.

The natural length of a trigonal bond, when no other similar bonds are present (e.g. ethylene), is 1.330A.[4] Thus, if we write $a = 1.330A$, and choose our zero and unit of energy suitably, then the energy of such a bond, when its length is x, may be written

$$E = (x-a)^2. \qquad (1)$$

A more complete analysis, especially in those cases where the lengths differ greatly from the value a, would demand the use of a Morse func-

[1] (a) Coulson, Proc. Roy. Soc. **A169**, 413 (1939); (b) Lennard-Jones and Coulson, Trans. Faraday Soc. **35**, 811 (1939).

[2] Penney, Proc. Roy. Soc. **A158**, 306 (1937).

[3] Pauling, J. Am. Chem. Soc. **53**, 1367, 3225 (1931).

[4] Recent work of Thompson, Trans. Faraday Soc. **35**, 697 (1939), suggests 1.331A for the $C=C$ bond in ethylene. But 1.330 is within his probable error, and this value facilitates comparison with the results of reference 1.

TABLE I. *Lengths of links in conjugated chains $C_{2n}H_{2n+2}$.*

MOLECULE	n	LINK 1		LINK 2		LINK 3		LINK 4	
		PRES. PAPER	RESON.	PRES. PAPER	RESON.	PRES. PAPER	RESON.	PRES. PAPER	RESON.
Ethylene	1	1.330	1.330	—	—	—	—	—	—
Butadiene	2	1.347	1.347	1.432	1.432	—	—	—	—
Hexatriene	3	1.352	1.351	1.419	1.424	1.375	1.366	—	—
Octatetraene	4	1.349	1.353	1.425	1.422	1.376	1.371	1.400	1.415

tion instead of (1), but since we are chiefly interested in qualitative values, we shall adhere to the simpler expression.

When there are several trigonal bonds present, there will be an interaction between them (one way of describing this interaction is to say that there is "resonance"), and we shall have an interaction energy. To the same accuracy that the parabolic law (1) is valid, we may expect the contribution to this energy arising from a pair of contiguous links x_1 and x_2, to be expressible[5] in the form

$$2bx_1x_2 + 2c(x_1 + x_2). \qquad (2)$$

The total energy $E(x_1x_2 \cdots x_n)$ of these links in a molecule is then the sum of terms (1) from each trigonal bond, and terms (2) from each pair of links with a common carbon atom. The equilibrium values of x_1, x_2, $\cdots$ are those which minimize E and hence satisfy the "defining equations"

$$\partial E/\partial x_1 = \partial E/\partial x_2 = \cdots = \partial E/\partial x_n = 0. \qquad (3)$$

The values of b and c are so far unknown; they may be obtained by correlation with butadiene ($CH_2 \cdot CH \cdot CH \cdot CH_2$). Here, if x_1, x_2 and x_3 are the lengths of the three C—C links

$$E(x_1x_2x_3) = (x_1-a)^2 + (x_2-a)^2 + (x_3-a)^2$$
$$+ [2bx_1x_2 + 2c(x_1+x_2)] + [2bx_2x_3 + 2c(x_2+x_3)].$$

The first three terms are compression energies and the second two are interaction energies. The defining equations are

$$x_1 - a + bx_2 + c = 0$$
$$x_2 - a + b(x_1 + x_3) + 2c = 0$$
$$x_3 - a + bx_2 + c = 0.$$

If we put $x_1 = x_3 = 1.347$A, $x_2 = 1.432$A, as pre-

dicted by the writer[1] from resonance calculations, we find that

$$b = 0.400, \quad c = -0.590. \qquad (4)$$

We can now use our general formulae to predict the lengths of the links in other molecules, both of chain and ring type. The reasonableness of our fundamental assumptions with regard to bond interaction will be verified by our ability to predict proper values for these other links; we shall find almost complete agreement between the lengths calculated according to the methods of this paper and of quantum-mechanical resonance.

Let us first apply our method to the allyl radical $CH_2 \cdot CH \cdot CH_2$. It appears that the links are of equal length 1.372A, in excellent agreement with the value 1.366A predicted quantum-mechanically by the writer.[6]

Next let us consider the conjugated chain molecules $C_{2n}H_{2n+2}$; we find precisely the same general properties which have been found before; thus, if we number the links in order from one end, the odd links are all shorter than the even links, but both tend to the same limiting value, sufficiently far from the end. Table I shows the results thus obtained, and in Table II we show the predictions for the infinite conjugated chain; in this latter case it appears that the length of

TABLE II. *Lengths in the infinite conjugated chain.*

LINK No.	1	2	3	4	5	6	7	ASYMP-TOTIC VALUE
Length, resonance*	1.355	1.419	1.377	1.407	1.383	1.403	1.386	1.394
Length, present paper	1.354	1.414	1.384	1.399	1.391	1.395	1.393	1.395

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[5] Terms in $x_1^2 + x_2^2$ appear to be unnecessary; their presence is partly allowed for by the compression energy $(x_1-a)^2 + (x_2-a)^2$.

* See reference 1.

[6] Coulson, Proc. Roy. Soc. A164, 383 (1938).

the jth link is given by the simple formula

$$x_j = 1.395 + 0.0805(-0.5)^j. \qquad (5)$$

The agreement is remarkably good; the differences nowhere exceed 0.008A.

When the calculations are applied to the ring compounds $C_{2n}H_{2n}$ $(n>1)$, it is found that all the links should have the length 1.395A. Quantum calculations, except for cyclobutadiene[1b] give lengths between 1.388 and 1.400A. Cyclobuta-
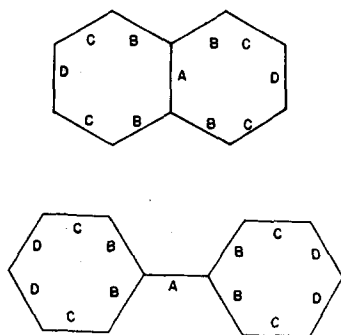

FIG. 1. The links of naphthalene and diphenyl.

diene, however, is unstable, and Wheland[7] has shown that in this case the quantum calculations are liable to serious errors.

Calculations have also been made for some more complicated structures, such as naphthalene and diphenyl. Using the notation of Fig. 1 the predicted lengths for the links are as shown in Table III; again there is excellent agreement. The lengths for naphthalene, using resonance methods are taken from a paper by the author shortly to be published, and those for diphenyl from some of the author's unpublished work. In the case of diphenyl, the difference between the two methods never exceeds 0.008A, and in particular the length of the interesting link A which connects the two closed rings, is almost the same in both treatments, being about halfway between a pure double and a pure single bond. In both molecules the relative order of the links is the same by both calculations, though there is a slightly more serious difference, amounting to

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[7] Wheland, Proc. Roy. Soc. **A164**, 397 (1938).

TABLE III. *Lengths of links in naphthalene and diphenyl.*

LINK		A	B	C	D	MEAN LENGTH
Naphthalene	resonance present	1.418	1.410	1.378	1.401	1.397
	paper	1.444	1.404	1.390	1.399	1.402
Diphenyl	resonance present	1.449	1.397	1.387	1.389	1.396
	paper	1.443	1.405	1.390	1.396	1.400

about one-fortieth of an angstrom, in the lengths of the central link A in naphthalene.

Similar calculations could be made for other molecules; but we do not make them because our object is chiefly to show, as the above tables have done, that lengths calculated in this way agree quite closely with those calculated on the basis of resonance; we could, also, with the inclusion of more parameters in Eqs. (1) and (2) have obtained even closer agreement between the methods. There is no point, however, in doing so at present, while it remains impossible to check the finer points of the bond lengths experimentally.

The empirical interaction term represented by Eq. (2) is one way of expressing the mutual influence of trigonal bonds; resonance is another way (in a sense artificial since it results from a forced separation of variables) of doing the same thing; before it can be used numerically, various unknown parameters have to be obtained by correlation with certain observed quantities. Our method is also empirical and again unknown parameters have to be obtained in the same way. Both treatments are essentially simplifications of the full quantum-mechanical analysis, which is evidently much too complicated to permit accurate calculations.

In conclusion we do not suggest that the present calculations should displace the resonance ones, since these latter are able to take account of other properties, such as excitation, fine structure, electrical and magnetic polarizabilities, etc., which our simple model is unable to include. But on the other hand, our calculations are very simple and provide excellent checks upon the other more laborious work.