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ON THE NATURE OF BONDS BETWEEN CARBON ATOMS

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Abstract—The combined effect of conjugation and van der Waals' interaction has been calculated for carbon sp^2 sp^2 single bonds of different lengths and for different molecular conformations. The bond shortening effect of conjugation is found to be comparable to that of hybridization. The attractive van der Waals' interaction, on the other hand, is always found to be small. It seems thus most improbable that this interaction should be the cause of the planarity of butadiene.

It seems to be fairly generally recognized that the distance between bonded atoms is governed by several factors: electron delocalization, hybridization, electronegativity, steric effects, etc. Especially for bonds between carbon atoms, the electronegativity differences should be of minor importance. In a recent paper Bak and Hansen-Nygaard[1] (see this paper for references to other recent publications in this field) have discussed the combined effect of changes in hybridization status and electron delocalization on the length of bonds between carbon atoms. From experimental data for such molecules, where the bond distance is essentially determined by hybridization, atomic covalent radii can be derived. Bak *et al.*[1] suggest the following values of single bond, covalent radii of carbon: $r_C(sp^3) = 0{\cdot}7723$, $r_C(sp^2) = 0{\cdot}7587$, $r_C(sp) = 0{\cdot}7333$. In the present note a few data in support of this assignment will be discussed and the combined effect of electron delocalization, i.e. conjugation, and steric repulsion will be considered.

Table 1 gives the experimental values of the length of the sp^2-sp^2 single bond, connecting two π-electron systems, and of the twist angle around this bond.

TABLE 1

Substance	Bond length (Å)	Twist angle
1,3-Butadiene[2]	1·483	0°
Biphenyl[3]	1·490	42°
Hexaphenyl benzene[4]	1·515	90° ± 10°
$2 \cdot r_C(sp^2)$	1·517	

It has been suggested previously by Adrian[5] that experimental values of the twist angle in similar molecules depend on a minimum of the potential curve (energy vs. angle), obtained from the combined effect of conjugation and steric repulsion between the two parts of the molecule, connected by the single C—C bond. The present

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[1] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* **33**, 418 (1960).
[2] A. Almenningen, O. Bastiansen, and M. Trætteberg, *Acta Chem. Scand* **12**, 1221 (1958).
[3] A. Almenningen and O. Bastiansen, *Kgl. Norske Vid. Selsk. Skr.* No **4** (1958).
[4] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand* **12**, 1215 (1958); private communication by Skancke.
[5] F. J. Adrian, *J. Chem. Phys* **28**, 608 (1958)

author would like to modify this suggestion slightly by considering the combined effect of conjugation and a more general van der Waals' interaction. Moreover, it is suggested that a correlation could be found between the depth of this potential minimum and the length of the bond around which the molecule is twisted.

In order to find this correlation one must know the angular dependence of the van der Waals' interaction and of the energy of conjugation across the single bond. The van der Waals' interaction between molecules has been extensively investigated and can be computed according to different, more or less accurate formulae.[6] These formulae may be modified to be applicable to intra-molecular van der Waals' interaction, giving at least the correct order of magnitude. Hill[7] has, however, derived a special formula for the intra-molecular case, which seems to give the most accurate estimate of this effect. In the present study only the van der Waals' interaction between the hydrogen atoms of the two parts of the molecule has been investigated. In the cases of butadiene and biphenyl it is obvious from a study of steric models of these molecules that the H–H interactions are the only important ones. In the case of hexaphenyl benzene this is also true for the "antipropeller" model (*cf.*[4]) but not so for the "propeller" model, where steric interaction between the carbon rings is important. Because of the difficulty in obtaining parameter values for this kind of interaction, only the "antipropeller" model has been studied at present.

TABLE 2 COMBINED EFFECT OF CONJUGATION AND STERIC FORCES
ENERGIES IN kcal/mole

Substance	Twist angle (conformation)	van der Waals' interaction	Conjugation energy	Combined effect
Butadiene	0 (*trans*) (min)	0·10	9·0	9·1
	90	0·08	0	+ 0·1
	180° (*cis*)	+1·18	9·5	−8·3
Biphenyl	0	+1·49	3·9	2·4
	24 (min)	+0·23	−3·3	−3·0
	42	0·10	2·2	2·3
	90	0·04	0	0·0
Hexaphenyl benzene, antipropeller model	90	0·25	0	0·2
	80 (min)	0·32	0·7	−1·0
	70	+17·51	2·7	14·8

The estimate of the angular dependence of the conjugation energy is considerably more difficult. This question has been discussed in detail by Adrian,[5] who has developed a method for this estimate, based on the valence bond treatment. He has also applied his method to a number of molecules, including biphenyl. Furthermore, the general interaction of two conjugated systems has been investigated by Longuet-Higgins and Murrell[8] on the basis of the molecular orbital method. They have applied their method *inter alia* to butadiene and biphenyl, but only to the extreme

[6] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*. John Wiley, New York (1954).
[7] T. L. Hill, *J. Chem. Phys.* 16, 399 (1948).
[8] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.* **68**, 601 (1955).

cases of either coplanar or perpendicular conjugated systems. On the basis of their method the present author has made a rough estimate of the energy in intermediate cases. The details of this method and a comparison with Adrian's method will be published in a forthcoming paper, where all details of the present calculations will be given. The results of these calculations are listed in Table 2.

A few comments should be made on the values of Table 2. The values of conjugation energy are taken from theoretical calculations of electronic spectra.[8] These values are not always in accordance with conjugation energy values determined more directly from empirical data.[9] In the case of butadiene for instance, the "empirical" value is only half as large as the theoretical one. Hence, it is not advisable to try to find a correlation between bond length and potential minimum by aid of the values of Table 2 only. Nevertheless, these two quantities are listed together in Table 3.

TABLE 3

Substance	Bond length (Å)	Potential minimum (kcal/mole)
Butadiene	1·483	9·1
Biphenyl	1·490	−3·0
Hexaphenyl benzene	1·515	1·0

Table 2 shows unquestionably that the van der Waals' interaction cannot be the cause of the planarity of butadiene, since this interaction has almost the same value for the perpendicular conformation as for the *trans*-conformation. Moreover, Table 2 indicates that biphenyl is most likely non-planar, although the potential hill of the planar conformation is very low (0·6 kcal/mole). All conformations between 0° and 40° seem to be comparatively easy of access at room temperature. As for hexaphenyl benzene, finally, the most stable conformation should be close to the perpendicular one. These results agree reasonably well with the experimentally determined twist angles of Table 1.

The only comment that at present could be made on the values of Table 3 is that the deeper potential minima correspond to the shorter bond distances and that the bond shortening effect of conjugation seems to be of a magnitude comparable to that of hybridization.

[9] G. W. Wheland, *Resonance in Organic Chemistry* John Wiley, New York (1955)