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CONJUGATION, HYBRIDIZATION, AND STERIC HINDRANCE IN RELATION TO BOND LENGTHS*

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Abstract—Three theories which have been proposed to explain the observed shortening of a single bond when it is adjacent to a double bond are discussed. Possible predictions from these theories are examined, especially for comparison with various quantities measurable by microwave spectroscopy. It is concluded that the steric theory is probably untenable, that some conjugation appears necessary to explain observed barriers to internal rotation, and that it is difficult to find testable predictions from the hybridization theory.

IN theoretical chemistry various words have been introduced such as *conjugation*, *hybridization*, etc. which are used as the basis for explanations of certain empirical observations and generalizations. These explanations are sometimes only qualitative and sometimes semi-quantitative, but they never achieve anything approaching mathematical rigor and almost always have a heavy ingredient of parametric empiricism. This latter is often somewhat hidden from the casual observer.

It is therefore a fair question to ask about each of these words whether it represents a real physical concept or merely a psychologically consoling substitute therefore. In principle there is a simple test: does the concept lead with confidence to a substantial number of true predictions later successfully checked by experiment? The literature of chemistry is littered with the debris of discarded theories which provided satisfactory explanations of facts known at the time but which failed to predict correctly future facts—or just failed to predict.

Unfortunately, this test is simpler to state than it is to apply. Most of these concepts are sufficiently ill-defined so that their predictable consequences are usually subject to argument.

Recently various new experimental techniques, particularly microwave spectroscopy, have begun to yield data which are either of improved accuracy or of a qualitatively new type. These include more accurate bond lengths and bond angles, dipole moments and their components, change of dipole moment with vibrational state or isotopic substitution, barriers to internal rotation and some associated fine points, nuclear quadrupole coupling coefficients, molecular quadrupole moments, rotational magnetic moments, etc. It should be possible to use some of these to test the predictive power of some of our currently fashionable vocabulary.

THE ADJACENT BOND EFFECT

Rather than trying to cover all these items, this paper will concern itself primarily with a discussion of the observed fact[1] that a single bond adjacent to one or more multiple bonds is shorter than a single bond with only single bonds adjacent.

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[1] G. Herzberg and B. P. Stoicheff, *Nature, Lond.* 175, 79 (1955).

The object of the discussion will be to compare three current theories of this effect and to try to evaluate their respective power to predict other measurable quantities. Only qualitative arguments will be used.

It is perhaps first worthwhile to demonstrate the reality of the phenomena to be explained. Costain and Stoicheff[2] have reviewed the available data but several more recent examples can be added. Table 1 lists the lengths of some single bonds in various molecules whose structures have been determined by reasonably complete microwave studies with adequate isotopic substitution.

TABLE 1. LENGTHS OF SINGLE BONDS ADJACENT TO A DOUBLE BOND

Molecule	Bond	Length	Reduction
Propylene[a]	C—C	1.50$_1$	0.02$_5$*
Acetaldehyde[b]	C—C	1.50$_1$	0.02$_5$
Acetyl fluoride[c]	C—C	1.50$_3$	0.02$_3$
Acetyl chloride[d]	C—C	1.49$_9$	0.02$_7$
Acetyl cyanide[e]	C—C	1.49$_0$	0.03$_6$
Vinyl fluoride[f]	C—F	1.34$_7$	0.03$_7$†
Acetyl fluoride[c]	C—F	1.34$_8$	0.03$_6$
Vinyl chloride[g]	C—Cl	1.72$_6$	0.05$_5$‡
Acetyl chloride[d]	C—Cl	1.78$_9$	−0.00$_8$

* Compared with 1.52$_6$ in propane[h]

† Compared with 1.38$_4$ in CH_3F[i]

‡ Compared with 1.78$_1$ in CH_3Cl[i]

[a] D. R. Lide, Jr. and D. Christensen, to be published.

[b] R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.* 26, 1695 (1957).

[c] L. Pierce and L. C. Krisher, *J. Chem. Phys.* 31, 875 (1959).

[d] K. M. Sinnott, *J. Chem. Phys.* 34, 851 (1961)

[e] L. C. Krisher and E. B. Wilson, *J. Chem. Phys.* 31, 882 (1959).

[f] B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *Spectrochim. Acta* 13, 120 (1958).

[g] D. Kivelson, E. B. Wilson and D. R. Lide, *J. Chem. Phys.* 32, 205 (1960).

[h] D. R. Lide, Jr., National Bureau of Standards Report 6802.

[i] C. C. Costain, *J. Chem. Phys.* 29, 864 (1958).

Examination of Table 1 does show that single bonds are shortened when they are adjacent to multiple bonds, C–Cl in acetyl chloride being an apparent exception.

The principal theories of this effect might be called the steric hindrance, the hybridization, and the conjugation theories, respectively. Very plausible arguments have been put forward in support of each and a certain amount of controversy has been engendered.

STERIC HINDRANCE THEORY

The simplest theory is that of steric hindrance.[3,4] It is claimed that when three atoms are attached to each carbon at the end of a single bond, there is sufficient repulsion between the two sets of atoms to lengthen the single carbon–carbon bond beyond its "normal" length. When one carbon forms also a double or triple bond, it of course has one or two fewer atoms attached to it, so the steric repulsion tending to lengthen the single bond is reduced. Hence the single bond shortens, as is observed.

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[2] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* 30, 777 (1959).

[3] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *J. Amer. Chem. Soc.* 61, 1868 (1939).

[4] Many others have supported this theory; e.g. L. S. Bartell, *J. Chem. Phys.* 32, 827 (1960). See also A. Burawoy, *Trans. Faraday Soc.* 40, 537 (1944).

This is an interesting picture which qualitatively explains the whole set of data on the shortening not only of single but also of double bonds as the number of attached atoms is diminished. However there are certain difficulties. In the first place it has to be said that extremely little is really known about the forces between non-bonded atoms within a given molecule. In many if not most cases there is at present no solid evidence as to whether the force is repulsive or attractive. However, the evidence from gas imperfections, compressibility of solids, and quantum mechanical theory all points to steric repulsion being a very steep function of distance. Consequently it would seem rather remarkable if different substituents did not have markedly different repulsions and hence a noticeably different effect on the C—C bond length.

The values of barriers to internal rotation about C—C bonds also do not appear to be compatible with the idea that there is strong repulsion between small atoms attached to the carbons. Table 2 gives some barrier values for ethane derivatives, all the simple ethane derivatives whose barriers have so far been reported by microwave frequency methods. The relatively small variations of these values is noteworthy, suggesting that these barriers are not mainly due to steric repulsion. On the other hand, if atoms such as chlorine are substituted at each end there is fairly general belief that they do repel, at least when they are opposite one another. Normally they occupy a staggered conformation and then may or may not repel one another.

TABLE 2 BARRIERS FOR ETHANE DERIVATIVES

Molecule	Barrier (kcal)
CH_3CH_3[a]	~2·8
CH_3CH_2F[b]	3·30
CH_3CHF_2[b]	3·18
CH_3CHCl[c]	3·56
CH_3CHBr[d]	3·57
CH_3CHI[d]	3·2
CH_3CHCN[e]	3·05

[a] K. S. Pitzer, *Disc. Faraday Soc.* **10**, 66 (1951).
[b] D. R. Herschbach, *J. Chem. Phys.* **25**, 358 (1956).
[c] D. R. Lide, Jr., *J. Chem. Phys.* **30**, 37 (1959).
[d] T. Kasuya, *J. Phys. Soc. Japan* **15**, 1273 (1960).
[e] V. W. Laurie, *J. Chem. Phys.* **31**, 1500 (1959).

The crudest useful approximation for non-bonded repulsions is the rigid sphere model, e.g. Pauling's van der Waals radii,[5] such as form the basis for ordinary space-filling wooden ball atom models. In the bond directions these are of course flattened off at the appropriate covalent radius. This illustrates an important uncertainty of this approximation; namely the question of the way in which the radius should vary with the angle to the bond direction. There are probably numerous compounds in which two atoms attached to the same atom are closer together than the sum of their van der Waals radii but because of the angle, the area of overlap is small. One example is CH_2CCl_2, in which the Cl atoms are separated[6] by 2·90 Å whereas twice the van der Waals radius of Cl is 3·60 Å.

Bartell[4] has proposed that bond angles, at least about trigonal carbon, are largely determined by steric interference between pairs of attached atoms. He lists twenty-two

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[5] L. Pauling, *Nature of the Chemical Bond* (3rd Ed.) p. 257. Cornell University Press, New York (1960).
[6] S. Sekino and T. Nishikawa, *J. Phys. Soc. Japan* **12**, 43 (1957).

molecules in which the angles are said to be predictable by this model. However, in evaluating this evidence it has to be remembered that the radii for X=C, H, F, and Cl were obtained from the compounds $H_2C=CX_2$, so these four do not provide a check. Similarly formic acid and urea were employed to give the oxygen and nitrogen radii. Further, the corresponding double ended molecules, such as F_2CCF_2, Cl_2CCCl_2 are not really independent. Some of the other molecules listed have not yet been adequately studied experimentally.

TABLE 3. PREDICTIONS OF BOND ANGLES

Molecule	Angle	Obs *	Calc †	Δ ‡	Δ §
CH_3CHO[a]	CCO	123° 55′	123° 10′	0° 45′	0° 30′
	OCH	118° 36′	124° 24′	5° 48′	4° 44′
	CCH	117° 29′	122° 27′	5° 2′	4° 19′
CH_3CFO[b]	CCO	128° 21′	125° 53′	2° 28′	4° 56′
	OCF	121° 21′	123° 14′	1° 53′	2° 4′
	CCF	110° 18′	110° 54′	0° 36′	2° 52′
CH_3CClO[c]	CCO	127° 5′	126° 47′	0° 18′	3° 40′
	OCCl	120° 16′	120° 42′	0° 26′	3° 9′
	CCCl	112° 39′	112° 32′	0° 7′	0° 31′
CH_3CCNO[d]	H_3CCO	124° 3′	121° 37′	1° 86′	0° 38′
	OCCN	120° 58′	123° 23′	2° 34′	2° 27′
	CCCN	114° 59′	115° 0′	0° 1′	1° 49′
CH_2CHCl[g]	CCCl	122° 18′	121° 42′	0° 36′	1° 7′
	CCH	123° 49′	127° 2′	3° 3′	0° 24′
	HCCl	113° 53′	111° 15′	2° 38′	0° 43′
HFCO[f]	FCO	122° 7′	122° 40′	0° 33′	1° 18′
	HCO	129°	122° 50′	6° 10′	5° 35′
	HCF	108°	114° 30′	6° 30′	5° 10′
H_2CCHCH_3[e]	CCC	124° 18′	122° 52′	1° 26′	0° 53′
	CCH	119° 0′	124° 58′	5° 58′	4° 25′
	HCC	116° 42′	112° 10′	4° 32′	3° 32′
H_2CCCl_2[h]	CCCl	123° 10′	(123° 21′)	0° 7′	0° 15′
	ClCCl	113° 40′	(113° 29′)	0° 11′	0° 30′
Root-mean-square				3·2°	3·3°

* Precision perhaps ± 30′
† Calculated with Bartell model
‡ Obs.–calc.
§ Obs.–123° 25′ or obs.–113° 10′

[a] R. W. Kilb, C. C. Lin and R. B. Wilson, *J. Chem. Phys.* 26, 1695 (1957).
[b] L. Pierce and L. C. Krisher, *J. Chem. Phys.* 31, 875 (1959).
[c] K. M. Sinnott, *J. Chem. Phys.* 34, 851 (1961)
[d] L. C. Krisher and E. B. Wilson, Jr., *J. Chem. Phys.* 31, 882 (1959).
[e] D. Kivelson, E. B. Wilson and D. R. Lide, *J. Chem. Phys.* 32, 205 (1960).
[f] O. H. LeBlank, Jr., V. W. Laurie, and W. D. Gwinn, *J. Chem. Phys.*, 33, 598 (1960)
[g] Private communication, D. R. Lide and D. Christensen, to be published.
[h] S. Sekino and T. Nishikawa, *J. Phys. Soc. Japan* 12, 43 (1957).

Table 3 shows the results of applying this theory to some molecules with trigonal carbon whose structures have been determined by microwave spectroscopy using an adequate number of isotopes. Column 5 shows the deviations between the observed angles and those calculated with Bartell's method, using his radii. The root-mean-square deviation is 3·2° (calculated using the two independent angles for each molecule). However, examination of the data shows that angles between a double bond and a single bond tend to be somewhat larger than 120° and those between two single bonds somewhere around 113°. The last column of Table 3 shows the deviations between observations and prediction when it is predicted that all angles between a single and a double bond (to carbon) are the same, namely 123° 25′ while all single-single bond angles are therefore predicted to be $360° - 2 \times 123° 25' = 113° 10'$. The standard deviation here is 3·3° (on the same basis as above). So it seems that one can predict angles essentially as well with this simple theory with one empirical adjustable parameter as with the more elaborate one with six empirical radii. (Note that the six parameters were not, however, evaluated from these molecules.) The fact is that this steric model accomplishes nothing more than dividing the angles into the two classes, which it does because of the shortness of a double bond compared with a single bond. It does not successfully predict even the rank order within each class.

If steric repulsions do not appear to be important in determining variations in bond angles, they are even less likely to cause variations in bond lengths, for which the force constants are much larger than for angles. Consequently, the theory that bond shortening is due to the relief of steric repulsion seems not very likely, even though our ignorance of these forces is so great that it perhaps cannot be completely ruled out.

HYBRIDIZATION THEORY

The hybridization theory[7] is based on a particular picture of the nature of the orbitals used in forming single, double and triple bonds. If carbon forms four single bonds, Pauling's picture calls for each to be a hybrid of s and p and all alike, so each is a so-called sp^3 type. For double bonds there is an apparent choice. One picture has the double bond formed from two single bonds, as in the sharing of edges of a tetrahedron.

Here all bonds might still be tetrahedral and, incidentally, if the orbital angles remained at the tetrahedral value 109° 28′, the single–double bond angle would be 125° 16′, not far from the average value observed for such angles in Table 3. On the other hand, the more usual picture is that the s and two of the three p orbitals are hybridized to form three equivalent bonds in a plane, so-called sp^2 or trigonal bonds, making an angle of 120° with one another. The third p orbital is perpendicular to the plane of the other orbitals. The double bond is then formed by the overlap of a trigonal orbital from each carbon, directed toward the other carbon, and by the interaction of the two p (here called π) orbitals.

This picture will change the hybridization and, it is agreed, therefore the length of the single bonds on the same carbon as the double bond.

This picture would seem to require that other single bonds to carbon suffer a similar shortening. It is true that C—H bonds seem to diminish in length from ethane through ethylene to acetylene. However, it has to be pointed out that bond lengths involving hydrogen are the most uncertain experimentally because of the low scattering power of hydrogen for electrons and X-rays, the small contribution to moments of inertia, and the large amplitude of motion. Further, the shortening is only about 0·03 Å from ethane to acetylene whereas the carbon–carbon bond diminishes by nearly 0·07 Å from propane to methyl acetylene. Consequently, the idea of a carbon *radius* dependent only on hybridization is qualitatively but not quantitatively acceptable.

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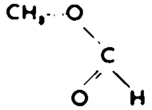
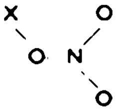
[7] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 5, 166 (1959)

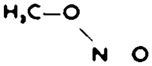
When the single bond from carbon connects an atom with one or more unshared pairs and also one or more additional bonds, such as can be the case with oxygen or nitrogen, the single bond again is reduced in length when adjacent to a double bond, but in this case it is possible to demonstrate that the shortening cannot be due to a change in hybridization alone. Consider for example the case of methyl formate



whose structure was carefully studied by Curl[8]. The single bond O—C= is 1·334 Å compared with $1{\cdot}43_7$ Å for O—C$\lessgtr$ so considerable shortening has occurred. However, all the atoms except CH_3 hydrogens are held in a plane, apparently rather firmly despite the real possibility of steric repulsion between the H's on CH_3 and the carbonyl oxygen. A similar result, which however involves nitrogen and not carbon, occurs with nitric acid[9] and with methyl nitrate.[10]



Here it is now well proven, contrary to earlier electron diffraction results,[11] that X = H or CH_3 lies in the plane of ONO_2 with a considerable barrier of the order of 9 kcal[12,13] interfering with rotation about the XO—N bond. Likewise NMR[14] data on methyl nitrite



give a considerable barrier for rotation about the middle bond. Acoustic absorption data[15] in the liquid phase also yields a barrier exceeding 5 kcal for single bonds adjacent to double bonds in the following molecules: acrolein, crotonaldehyde, cinnamaldehyde, methacrolein and furacrolein.

CONJUGATION AND HYPERCONJUGATION

These considerable barriers are not simply predictable from the change in hybridization alone. On the other hand, the conjugation theory[16] accounts for them nicely. According to this theory, there is resonance between the structures

In the latter, charge has migrated to the extreme carbon from an orbital on oxygen formerly filled with an unshared pair. The C—O bond then takes on a partial double

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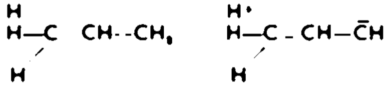
[8] R. F. Curl, Jr., *J. Chem. Phys.* **30**, 1529 (1959).
[9] D. J. Millen and J. R. Morton, *J. Chem. Soc.* 1523 (1960).
[10] W. Dixon and E. B. Wilson, Jr., *J. Chem. Phys.* **35**, 191 (1961).
[11] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 13 (1947).
[12] H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Phys.* **24**, 162 (1956).
[13] A. Palm and M. Kilpatrick, *J. Chem. Phys.* **23**, 1562 (1955).
[14] L. H. Piette and W. A. Anderson, *J. Chem. Phys.* **30**, 899 (1959).
[15] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.* A **242**, 36 (1957).
[16] See ref. 5, esp. Chap. 8.

bond character and is accordingly both shortened and endowed with considerable resistance to twisting.

Another type of evidence is available in case the attached atom has a nuclear electrical quadrupole moment. For example, in vinyl chloride[17,18] it is possible to measure a fine structure in the microwave spectrum due to the interaction of the chlorine nuclear quadrupole moment with the gradient of the electric field at the chlorine nucleus arising from the electrons and especially the outer shell electrons. The results show that the field gradients are not the same in the two directions perpendicular to the C—Cl bond, whereas a pure single bond would be expected to be cylindrically symmetrical. Orbital arguments[19] lead to a double bond character of about 6 per cent. The C—Cl bond is also shorter than in CH_3Cl, for example.

In case the single bond connects an atom without unshared pairs, e.g. carbon, the question is somewhat more open (unless of course the bonds are part of a fully conjugated system such as in benzene). Without lone pairs it is necessary to invoke *hyperconjugation*,[20] a concept rather less esthetically appealing to many. Thus in propylene $CH_3HC{=}CH_2$ it is assumed that structures such as



contribute, in addition to the normal structure. It is difficult to obtain the same kind of evidence. Carbon does not have any nuclear electrical quadrupole moment. Further, hyperconjugation with a methyl group will not influence the three fold barrier to internal rotation ordinarily measured. However, it should contribute to the sixfold part of the barrier, but the amount to be expected would probably be very difficult to estimate because it would depend on the sixth order term in the Fourier expansion of the twofold components and that would depend in turn rather delicately on the barrier shape.

All these forms of conjugation imply a transfer of charge in the molecule which is the greater the more important is the conjugation. Consequently, if a distortion of the molecule is made which favors one or the other of the resonating forms, the dipole moment should be changed in a predictable direction by an amount depending on the amount of conjugation. This should appear as especially strong contributions to the intensity of certain infrared absorption bands. It may be possible to detect an effect of this kind in another way. In certain cases the average dipole moment should change with vibrational state. An example which has been partially examined is methyl nitrate in which one might expect the conjugation to be diminished by twisting the NO_2 group out of the plane. Since this effect should cause a charge to be transferred along the axis of twist, it should not average out over a cycle of the twisting motion but should change the dipole moment as the torsional state is changed. To about 1 per cent no change is experimentally observed up through the second excited state but crude calculations suggest that no effect larger than 1 per cent should be observed until a higher excited state is reached. It should be possible to look for this effect

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[17] J. H. Goldstein and J. K. Bragg, *Phys. Rev.* 75, 1453 (1949).

[18] D. Kivelson, L. B. Wilson and D. R. Lide, *J. Chem. Phys.* 32, 205 (1960).

[19] J. H. Goldstein, *J. Chem. Phys.* 24, 106 (1956).

[20] See for example R. S. Mulliken, *Tetrahedron* 5, 253 (1959).

with some refinements in technique.[*] It has been pointed out[21] that conjugation should also make a large positive contribution to the interaction force constant between the stretching of the two bonds with double bond character. However, such constants are difficult to determine.

It is more difficult to find possible experimental indicators of hybridization. One which is often invoked is the value of the bond angle. Unfortunately it is easy to find examples which show that this is not a simple indicator. Thus in tetrahedral carbon if the angle between one pair of bonds is opened up the opposite angle should close down,[22] if hybridization is the sole determinant of bond angle and only *s,p* orbitals are used. Instead, in CH_2Cl_2 both angles[23] open up. This is of course explanable in terms of "bent bonds" but once this additional concept is added to that of hybridization, the whole picture hardly satisfies Platt's requirement that "a theory must be capable of being disproved".

CONCLUSION

Despite the additional information provided by microwave spectroscopy it does not seem possible as yet to decide for certain whether a single bond next to a double bond is shortened because of relief of steric repulsion, change of hybridization, or conjugation. Nevertheless arguments are presented which make the steric theory seem the least important contributor whereas the data seem to indicate that some appreciable contribution from conjugation is required. A change in hybridization cannot be ruled out but seems unlikely to be the sole phenomena responsible, a conclusion in agreement with that of others.[24,25]

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[*] D. R. Lide, Jr., *J. Chem. Phys.* 33, 1879 (1960) points out also that a knowledge of the *components* of the dipole moment, determinable from microwave spectroscopy, seems to support a hyperconjugation rather than a hybridisation basis for the dipole in propylene.

[21] C. A. Coulson, J. Duchesne and C. Manneback, *Victor Henri Memorial Volume*. Desoir, Liege (1948).

[22] C. A. Coulson, *Valence*. Clarendon Press, Oxford (1952)

[23] R. J. Myers and W. D. Gwinn, *J. Chem. Phys.* 20, 1420 (1952).

[24] R. S. Mulliken, *Tetrahedron* 6, 68 (1959).

[25] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* 33, 418 (1960).