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BOND LENGTHS AND HYPERCONJUGATION

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AMONG the data first cited as supporting the concept of hyperconjugation were the observations on bond lengths reported by Pauling *et al.*[1] in 1939. Nineteen years have elapsed, so it is useful to review the evidence which this criterion provides.

According to standard theory, if hyperconjugation really occurs we should expect that:

(1) When a methyl group is hyperconjugated with a triple bond, a double bond or even another methyl group, the bond joining it to this system should be shorter than normal.

It is immediately apparent that we may have difficulty in detecting an anomaly in the last case, because such a bond would naturally be taken as a standard itself; but at least we could detect anomalies relative to it.

(2) Some effect on the bonds in the rest of the system should be apparent. We should expect some degree of lengthening.

(3) If the symmetry of the methyl group is destroyed by substituting a methyl group for a hydrogen atom, to make an ethyl group, or if all three hydrogens are thus substituted to make a *tert.*-butyl group, hyperconjugation should be destroyed or at least reduced. The length of a bond joining such a group to an unsaturated system should therefore be normal, or more normal, in length.

(4) A perfluoromethyl group should also hyperconjugate; and the bond joining it to the rest of the system should therefore show shortening. Since, however, it attracts electrons, instead of repelling them as a methyl group is often supposed to do, it may produce rather different changes in the other parts of the system.

(5) The longer the hyperconjugated system is, the more will be the anomalies, particularly at its ends. Cross hyperconjugation effects should diminish it, just as happens in ordinary, or first-order, conjugation.

(6) The methyl group, or the perfluoromethyl group, might itself show anomalous lengths and bond angles as a result of hyperconjugation.

These points have been clearly realised for a long time, and many investigations have been made to test them. The more obviously relevant results are collected in Tables 1 to 6 and are discussed *seriatim*.

It is not clear what one looks for in the saturated compounds. If theoretical estimates of C–C bond order could be made for the different compounds, the lengths might be compared on this basis. The most immediate conclusion, however, is that the distances are all the same to within 0·005 Å save in CF_3–CH_3, in which it is shortened by about 0·04 Å.

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[1] L. Pauling, H. D. Springall and K. J. Palmer *J. Amer. Chem. Soc.* 61, 927 (1939).

TABLE 1. SATURATED COMPOUNDS

C–C (average) = 1·541 ± 0·003 Å[2]

C–C (diamond) = 1·54451 ± 0·00014 Å[2]

Compound*	C–C (Å)	C–H (Å)	∠HCH	C–F (Å)	∠FCF	Method of measurement
CH_3–CH_3	1·543	1·102	109·3°	—	—	Infra-red spectrum[2]
	(1·536 ± 0·016)	—	—	—	—	Electron diffraction[2]
CF_3–CH_3	(1·512 ± 0·014)	—	—	—	—	Electron diffraction[3]
	1·492	1·078	109° 31′	1·348	106° 42′	Microwave spectrum[4]
CHF_3	—	1·098	—	1·332 ± 0·008	108·8° ± 0·75°	Microwave spectrum[5]

* The values for propane and for *n*-butane are not accurate enough to provide useful comparisons.

Brockway and his co-workers have shown[5,6,7] that a CF_3 group often causes the fourth bond formed by the carbon atom to be shorter than that formed by a CH_3 group by about this amount (e.g., for C–F, C–Cl, C–Br and C–I by 0·068, 0·033, 0·029 and 0·009 Å respectively). Hence there is nothing which need be ascribed particularly to hyperconjugation, save in so far as the shortening is more than would be expected from the electronegativity of carbon.

∠ FCF is probably less in CH_3CF_3 than it is in CHF_3 or in $CClF_3$ (108·6° ± 0·4). This may indicate something: but it is not an obvious electrostatic result of more negative charge on the fluorine atoms.

Duchesne has suggested[8] that this reduction of angle causes an increase of *s* character in the fourth (the C–C) bond, which may account for the shortening. This, however, leaves unexplained the reduction of angle: in an earlier communication[9] he concluded that increase of electronegativity of the halogen in the methyl halides causes a decrease in the degree of *p* character in the C-halogen bond. An increase of *p* character would seem to be required to explain the angle reduction by a change of hybridisation.

This observation might be attributed to hyperconjugation.

In the olefines, recent measurements have shown that the C–C = bond is distinctly shorter than the paraffinic bond, by about 0·05 Å. There appears to be a lesser contraction in the C–C_6H_5 bond, of about 0·02 Å; but there is a dearth of good measurements for it.

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[2] *Interatomic Distances in Molecules and Ions. Special Publication* No. 11, The Chemical Society, London (1958).
[3] L. O. Brockway and R. H. Schwendeman, personal communication.
[4] L. F. Thomas, J. S. Heeks and J. Sheridan, *Z. Electrochem.* **61**, 935 (1957).
[5] L. O. Brockway and R. Anderson, personal communication.
[6] L. O. Brockway and C. Thornton, personal communication.
[7] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.* **23**, 1860 (1955).
[8] J. Duchesne, *J. Chem. Phys.* **20**, 540 (1952).
[9] J. Duchesne, *Nature, Lond.* **159**, 62 (1947).

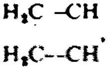
TABLE 2. OLEFINES*

Compound†	C–C (Å)	C=C (Å)	C–H methyl (Å)	∠HCH methyl	Method of measurement
$CH_2=CH_2$	—	(1·334)	[(1·085)]‡	[(116°)]‡	Electron diffraction[10]
	—	(1·337)	[(1·086)]‡	[(117° 22′)]‡	Infra-red spectrum[11]
CH_3–CH=CH_2	1·488	1·353	1·090 (ass.)	107° 11′	Microwave spectrum[12]
	(1·49)	—	—	—	Electron diffraction[13]
$(CH_3)_2CH=CH_2$	(1·50)	—	—	—	Electron diffraction[13]
CH_3–CH=CH–CH_3 (*cis*)	(1·51)	—	—	—	Electron diffraction[13]
CH_3–CH $C=CH_2$	1·48§	—	—	—	Microwave spectrum[14]

* Aromatic: C–C in C–Ph = $1{\cdot}52_8 \pm 0{\cdot}01$ (average).

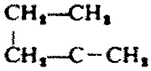
† Less accurate values are available also for:

CH_3–CH=CH–CH_3 (*trans.*),



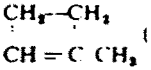
$$\begin{array}{l} H_2C-CH \\ H_2C-CH \end{array}$$

,



$$\begin{array}{l} CH_2-CH_2 \\ CH_2-C-CH_2 \end{array}$$

and



$$\begin{array}{l} CH_2-CH_2 \\ CH=C\ CH_3 \end{array}$$

(Ref. 2).

‡ Values for the CH_2 groups.

§ Consistent with the observations.

These anomalies could be due to hyperconjugation; but there are two other causes which must be considered. One is that the covalent radius of carbon is reduced when the hybridisation changes[15] from sp^3 to sp^2, and the other is that the difference of electronegativity, arising from the same cause, results in a contraction of bond length.[11] A difference of about 0·5 of Pauling's electronegativity units would be required to explain the whole of this contraction; this seems high.

Concerning the effect of hybridisation, it may be noted that very recent measurements on butadiene (CH_2=CH–CH=CH_2) by O. Bastiansen (personal communication) give a value of 1·483 ± 0·003 Å for the central bond; so if the *whole* of the contraction of 0·06 Å in this bond relative to the paraffinic standard be attributed to change of carbon radii, the change is 0·03 Å in each, leaving only 0·02 Å to be explained by electronegativity difference in the methyl–ethylene bond. From the C–H bond lengths in methane and in ethylene (r_0 = 1·091 and 1·07 Å respectively) the change of carbon radius appears to be −0·02 Å: so there is fair agreement between the two estimates.

∠ HCH in methyl seems to be smaller (107° 11′) than the tetrahedral value if the C–H bond length is assumed to be 1·090 Å.

It is not certain if the C=C bond length is increased relative to ethylene, for the

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

[11] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).

[12] D. R. Lide, Jr. and D. E. Mann, *J. Chem. Phys.* **27**, 868 (1957).

[13] See E. Goldish, K. Hedberg and V. Schomaker, *J. Amer. Chem. Soc.* **78**, 2714 (1956).

[14] D. R. Lide, Jr. and D. E. Mann, *J. Chem. Phys.* **27**, 874 (1957).

[15] C. A. Coulson, *Victor Henri Mem. Vol.* p. 15. Desoer, Liège (1948).

error in the propylene measurement is not given. The value tried therein was the older one[2] of 1·353 Å: a much shorter one appears not to have been tried.

In the related compound, acetaldehyde, the C–C bond is somewhat less shortened, by 0·04 instead of 0·05 Å. The opposite would be expected if difference of electronegativity were the cause, for this should be increased by the attachment of =O instead of $=CH_2$ to the middle carbon atom. Possibly, therefore, shortening by electronegativity difference is not important.

TABLE 3. ALDEHYDES

Compound	C–C (Å)	C=O (Å)	∠CCO	CH (Å)	∠HCH	CH (Å)	∠CCH	Method of measurement
$CH_3{\cdot}CH{=}O$	$1{\cdot}500_6$ ± 0·005	$1{\cdot}215_6$ ± 0·0021	123° 55′ ± 6′	1·086 ± 0·005	108° 16′ ± 15′	1·114 ± 0·015	117° 29′ ± 45′	Microwave spectrum[16]
	(1·504)	(1·208)	(123° 36′ ± 90′)					Electron diffraction[16]
C–C=O (various)	1·516 ± 0·005 (average)							Reference 2
CF_3–CH=O	(1·54 ± 0·02)							Electron diffraction[3]

The bond length in trifluoroacetaldehyde is equal to the paraffinic standard, i.e., the fourth bond formed by the perfluoromethyl carbon atom is now longer than that formed under the same conditions by the methyl carbon atom. This, as Brockway has pointed out (personal communication), is the opposite of what is normally found (see above); so it can hardly be explained by a normal change of atomic radius due to fluorine substitution. It could indicate an absence of hyperconjugation caused by the unwillingness of the CF_3 group to part with electrons as required by the –CH=O group, i.e., to mutual incompatibility.

The C–H bond length in the methyl group (1·086 Å) is very slightly shorter than that in methane (r_0 = 1·091 Å), and ∠HCH (108° 16′) is slightly less than tetrahedral.

There are therefore some anomalies which do not agree with ideas of fixed radii or with shortening by electronegativity difference. Another point to note is that ∠CCC in propylene is 124° 45′ and ∠CCO is 123° 16′ in acetaldehyde compared with 121° 19′ for ∠CCH in ethylene: these might indicate a tendency to an allene-like structure.

In the several acetylenes which have been measured, the striking feature is the essential constancy of the C–C bond length, at 1·456 ± 0·002 Å. This is 0·087 Å shorter than the paraffinic standard.

Unfortunately, errors are not usually ascribed in microwave measurements; so the real significance of this observation is not quite clear. Fluorine substitution in methyl may possibly cause a small increase, but substitution by bromine or chlorine of the acetylenic hydrogen causes no change, although there is evidence from electric dipole moment measurements that a considerable degree of conjugation or other disturbance results. It is a striking fact that the mean of the C–C paraffinic standard (1·543) and of the C–C bond between two triple bonds

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[16] R. W. Kilb, Chun Chia Lin and E. B. Wilson, Jr., *J. Chem. Phys.* **26**, 1695 (1957).

TABLE 4. ACETYLENES

Compound	C–C (Å)	$C\equiv C$ (Å)	C–H methyl (Å)	∠HCH	C–H -yne (Å)	Method of measurement
$H-C\equiv C-H$	—	1·201	—	—	1·064	Infra-red spectrum[2]
$CH_3-C\equiv C-H$	1·458	1·207	1·112 (D)1·108	108·4°	1·060	Microwave spectrum[2]
$CH_3{\cdot}C\equiv C{\cdot}CH_3$	1·457	1·211	-	—	—	X-ray crystallography[17]
$CF_3{\cdot}C\equiv C{\cdot}H$	1·464 ±0·02	1·201 ±0·002	(F)1·33$_5$ ±0·01	(F)107·5° ±1°	1·056 ±0·005	Electron diffraction + microwave spectrum[2]
$CF_3{\cdot}C\equiv C-CH_3$	1·455	1·189	1·097 (F)1·340	108° 30′ (F)106° 8′	. .	Microwave spectrum[18]
$CH_3-C\equiv C{\cdot}Br$	(1·458)	—	—		—	Microwave spectrum[19]
$CH_3-C\equiv C{\cdot}Cl$	1·458	—	1·117	108° 8′	—	Microwave spectrum[20]
$(H-C\equiv C-)_2$	—	1·205 (ass.)	C–C = 1·379		1·064 (ass.)	Infra-red spectrum[2]
1·456 1·375 1·059 $CH_3-C\equiv C-C\equiv C-H$ 1·208 1·209			1·111 (D)1·103	108·6°	1·059	Microwave spectrum[19]
$(CH_3-C\equiv C-)_2$	1·450	1·205	C–C = 1·377			Electron diffraction[21]
$(CH_3-C\equiv C-C\equiv)_2$	1·466	1·199		1·375		X-ray crystallography[17]
	1·47 ±0·02	1·20		1·38		X-ray crystallography[2]

(D) Deuterium substituted. (F) Fluorine substituted.

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[17] E. Pignataro and B. Post, *Acta Cryst.* **8**, 672 (1955).
[18] B. Bak, D. Christensen, L. Hansen-Nygaard and E. Tannenbaum, *J. Chem. Phys.* **26**, 241 (1957).
[19] J. Sheridan, personal communication.
[20] C. C. Costain, *J. Chem. Phys.* **23**, 2037 (1955).
[21] A. Almenningen, O. Bastiansen and J. Munthe-Kaas, *Acta Chem. Scand.* **10**, 261 (1956).

(1·377) is 1·460 Å. If the 1·377 Å is a distance which includes the effect of conjugation, or increase of bond order, the 1·460 Å also includes some such increase: this is tantamount to saying that the effects of increase of bond order due to conjugation or to hyperconjugation are additive; but that might be the case. Were this so, resonance could not be demonstrated by departure from additivity; and a decision as to whether or not there is an increase of bond order would have to depend upon theoretical calculations, e.g., of overlap, or on some other experimental means of diagnosis. Alternatively, the results could be explained by fixed radii resulting from *sp* hybridisation. However, from the difference between the C–H lengths in methane and in acetylene (1·091 and 1·064 Å) the decrease in radius due to *sp* bonding would appear to be only 0·027 Å; so the apparent decrease of 0·087 Å shown in the C–C bond is not obviously due to this alone.

If the whole contraction were a Schomaker–Stevenson contraction,[22] the electronegativity difference would have to be 1 Pauling unit.

The C–H methyl bond lengths (1·109 Å average) are about 0·02 Å longer than in methane, but a similar effect is also produced by electronegative substitution, e.g., by halogens (CH_3X, has C–H = 1·11, 1·11, 1·109 and 1·11 for Br, Cl, F and I), but ∠HCH (108·5°) is somewhat smaller than tetrahedral. The C–F bond lengths are much the same as in CHF_3, but ∠FCF (106·5°) is distinctly less than tetrahedral, and is more anomalous than it is in CHF_3 (108·8°).

Duchesne has suggested[8] that the shortening of the C–C bond can be correlated with the decreases in ∠HCH in methyl and of ∠FCF in perfluoromethyl: but this still leaves the need of an explanation for these reductions in angle (cf. p. 119).

The C≡C bond length in the substituted acetylenes shows no perceptible lengthening (average 1·203 Å) relative to that in acetylene itself.

For the cyanides there is a particularly interesting series of measurements. For methyl cyanide and for methylcyanoacetylene the C–C length is 1·456 Å, i.e., exactly the same as for the acetylenes. This suggests, again, that electronegativity difference is not the cause of the contraction. The C–H length in hydrogen cyanide (1·068 ± 0·003 Å) is essentially the same as that in acetylene 1·064 Å, also indicating that the carbon radius is unchanged by substitution of ≡N for ≡CH. As was remarked for the acetylenes, the radius change shown by this bond length is far too small to explain the observed C–C contraction. Fluorine substitution in the methyl group again may, possibly, cause an increase of length, but values are not concordant.

When the trigonal symmetry of the methyl group is broken, as in ethyl cyanide the bond length appears to increase by about 0·017 Å. According to standard theory therefore, this is all that is attributable to hyperconjugation. The remaining 0·070 Å may be due to other causes. Two preliminary results for *tert.*-butyl cyanide indicate no increase at all.

In all these compounds, the C–H bond length in the methyl group (1·104 Å) is longer than the paraffinic standard, and much the same as that in the acetylenes (1·109 Å). ∠HCH is tetrahedral. The C–F length is the same as in CHF_3, but ∠FCF is only 107·5°.

There is no perceptible lengthening of the C≡N bond in the cyanides, compared with that in hydrogen cyanide itself.

The silicon compounds shown in Table 6 indicate a contraction of the C–Si bond

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[22] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.* 63, 37 (1941).

TABLE 5. CYANIDES

Compound	C–C (Å)	C≡N (Å)	C–H methyl (Å)	∠HCH	Method of measurement
H–C≡N	—	1·156 ± 0·001	—	—	Microwave spectrum[2]
CH_3·C≡N	1·458	1·157	1·112 (D)1·107	109·27°	Microwave spectrum[2]
CF_3–C≡N	(1·46 ± 0·01)	—	—	—	Electron diffraction[5]
	1·46	1·153	(F)1·335	(F)107·5°	Microwave spectrum[4]
	(1·495 ± 0·014)	—	—	—	Electron diffraction[6]
CH_3·CH_2·C≡N	1·4735 1·5479 both ± 0·0015	1·1566 ± 0·0015	1·0914 ± 0·0015	109° 19′ ∠CCC ± 10′ 110° 32′ ± 2′	Microwave spectrum[23]
$(CH_3)_3C$·C≡N	(1·460) (Bu) (1·540)	(1·158)	(1·110)	(109·5°) (109·5°)	Microwave spectrum[24]
	(1·46 ± 0·02) (Bu) (1·54 ± 0·01)	(1·16 ± 0·07)	—	(∠CCC) (109·5°)	Electron diffraction[25]
$\mathrm{CH_3{-}}\overset{1\cdot 208}{\mathrm{C{\equiv}C}}\underset{1\cdot 374}{\mathrm{{-}C}}\mathrm{{\equiv}N}$	1·454	1·159	—	—	Microwave spectrum[19]

(D) = Deuterium substituted. (F) = Fluorine substituted. (Bu) = C–C in the *tert*-butyl group.

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[23] R. G. Lerner and B. P. Dailey, *J. Chem. Phys.* **26**, 678 (1957).
[24] J. Sparstad and E. Amble, *J. Chem. Phys.* **27**, 317 (1957).
[25] R. L. Livingston and C. N. R. Rao, personal communication.

TABLE 6. SILICON COMPOUNDS

Compound	C–Si (Å)	Si–H (Å)	∠HSiH	C–H (Å)	∠HCH	Method of measurement
CH_3–SiH_3	1·8668 ±0·0005	1·485 ±0·005	108° 15′ ±30′	1·093 ±0·005	107° 40′ ±30′	Microwave spectrum[28]
C_6H_5–SiH_3	1·84 ±0·01	—	—	—	—	Electron diffraction[3]

by about 0·027 Å in the aromatic compound, which is about the same as that at present reported in methylated aromatics. This could be due to a change in carbon covalent radius.

Considering these results as a whole, it is difficult to avoid concluding that no consistent explanation can be given on the current hypotheses that atoms have constant covalent radii subject only to corrections for changes of hybridisation, differences of electronegativity and changes of bond order. It is generally appreciated that the hydrogen covalent radius is variable: thus *l*(C–H) in methane is 0·051 Å shorter than the mean of *l*(C–C) and *l*(H–H). Therefore, caution is necessary in predicting lengths of C–C bonds from observed changes in C–H bond lengths. Nevertheless, such a procedure is only to be discarded completely for our present purpose if there is reason to think that, from the C–H changes, too small contractions are predicted for the C–C bonds in olefines, acetylenes and related compounds. In fact, contractions of H–X bonds seem to be at least as large as those of C–X bonds, e.g., when X is a halogen, the anomalies relative to the mean of *l*(H–H) and *l*(X–X) are −0·162, 0·090, −0·099 and −0·096 Å for fluoride, chloride, bromide and iodide, while those relative to the mean of *l*(C–C) and *l*(X–X) in the methyl halides are,[2] respectively, −0·095, +0·021, +0·026 and +0·035 Å. Thus if the observed contraction in a C–C bond is considerably greater than that so predicted, it probably signifies something more than a general change of carbon radius due to change of hybridisation.

Electronegativity differences do not provide any consistent explanation of the remaining differences, as was seen for the aldehydes and the cyanides.

It is not satisfactory to ascribe the residual anomalies to changes of bond order arising from hyperconjugation unless they can be shown to conform to all the predictions made on this hypothesis. In the case of ethyl cyanide and *tert.*-butyl cyanide, one such is not satisfied. The increases of angle in propylene and in aldehyde do, however, satisfy qualitatively another prediction. The increases in C–H bond length in the CH_3 groups, and the changes of angle in these and in the CF_3 groups could be but do not have to be ascribed to hyperconjugation.

The general conclusion from this qualitative discussion is that hyperconjugation is not clearly and unambiguously proved by bond length anomalies to exist in the ground states of molecules, although on the other hand its existence is not certainly disproved. A more quantitative discussion would require comparisons of fact with predictions of bond length made essentially from independent data, e.g., from thermal data. Other explanations may prove possible: it can be safely said that there are indications

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[28] R. W. Kilb and L. Pierce, *J. Chem. Phys.* **27**, 108 (1957).

that the effective radius of an atom in a bond depends upon the nature of the other atom in ways which have not yet been defined.*

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* See Duchesne[27] for another suggestion for a cause of variation in bond length.

[27] J. Duchesne, *J. Chem. Phys.* **19**, 246 (1957).