ability assigned to the bond under consideration. The polarisabilities assigned to the C—Hal bonds include those of all the unshared halogen electrons. The polarisabilities assigned to the carbonyl double bond include those of all the unshared electrons of the oxygen atom. And if these, in analogy with most bond electrons, are much more polarisable along the orbital axes than transversely, that would account for the large difference between the two transverse polarisabilities assigned to the carbonyl double bond. The NH and NC bond polarisability values each include a one-third share of the polarisabilities of the unshared nitrogen electrons. And if these electrons are anisotropic, as suggested for oxygen unshared electron pairs, this would explain why the transverse polarisabilities, assigned to the NH and NC bond, are so large, relatively to the longitudinal polarisabilities.

(10f) **Directed Polarisabilities of Conjugated and Hyperconjugated Systems.**—As we have seen already (Section 7g), the excited electronic states which are important as prescribing the pathways of electromeric polarisability in the ground states of conjugated systems of double bonds can in first approximation be regarded as resonance hybrids of pairs of polar structures with reversed charges, the charges being concentrated towards the ends of the system. This picture requires that the observed exaltations of polarisability should be directed essentially in one way, namely, along the path of conjugation.

R. J. W. LeFèvre and C. G. LeFèvre have carried through a series of studies of the electrical double refraction and light-scattering depolarisation of comparable aromatic and aliphatic compounds, containing substituents which can conjugate with the benzene ring. Thus they compared PhX and MeX, with an identical substituent X of $+E$ type having unshared electrons; and PhY and MeY with the same substituent Y of $-E$ type, having an electronegative unsaturated group capable of conjugation. This has enabled them to determine, as a function of direction, the exaltations of polarisability, due to conjugation of the substituents with the aromatic ring, by a subtractive method, analogous to that used for developing Table 10-6 for such exaltations of spherical-average polarisabilities, as given by molecular refraction. Their data[38] are in Table 10-13.

The LeFèvres found generally, as should be expected, positive exaltations $\Delta a$ of polarisability along the dipole axis, which is the axis of conjugation in all cases. The substituent fluorine exceptionally gave a small negative exaltation $\Delta a$; but as explained in connexion with spherical average polarisabilities, (Section 10c), the effect of the electronegativity of fluorine on the polarisability of the groups attached

[38] C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, **1954**, 1577; R. J. W. LeFèvre and B. P. Rao, *ibid.*, **1958**, 1465.

TABLE 11-2.—PAULING'S COVALENT RADII OF ATOMS (IN A).

|             | C     | N     | O     | F    |
|-------------|-------|-------|-------|------|
| Single bond | 0.772 | 0.70  | 0.66  | 0.64 |
| Double bond | 0.667 | 0.60  | 0.55  |      |
| Triple bond | 0.603 | 0.55  |       |      |
|             | Si    | P     | S     | Cl   |
| Single bond | 1.17  | 1.10  | 1.04  | 0.99 |
| Double bond |       |       | 0.94  |      |
| Triple bond |       | 0.93  |       |      |
|             | Ge    | As    | Se    | Br   |
| Single bond | 1.22  | 1.21  | 1.17  | 1.14 |
|             | Sn    | Sb    | Te    | I    |
| Single bond | 1.40  | 1.41  | 1.37  | 1.33 |

traction (Fig. 11-1). The term "bond order" is not used here, because different definitions of it derive from different approximate quantal treatments. The term "bond multiplicity" derives only from the common expression "multiple bond," and means one-half of the electron content of the bond.

When mesomerism introduces symmetry into a molecule, we can assign to the bonds a proper-fractional multiplicity, such as $\frac{3}{2}$ and $\frac{4}{3}$ for the CC bonds of benzene and graphite, respectively, or for the CO
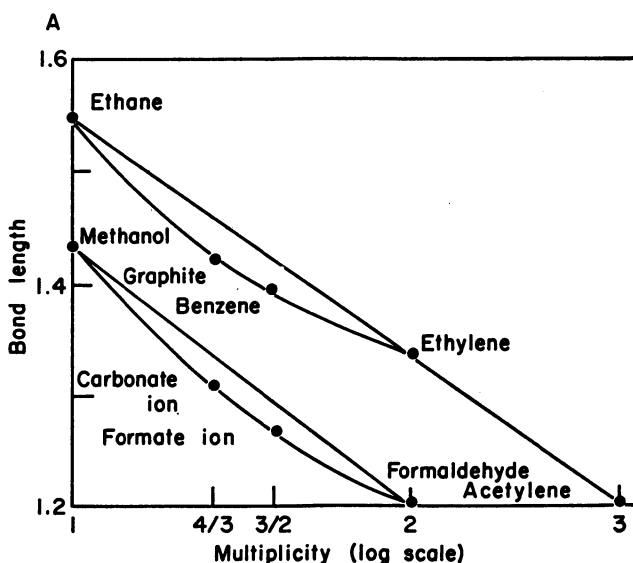


FIG. 11-1.—Bond length versus bond multiplicity.

with doubly bound carbon is easily understood. We could hot confidently expect the electron depletion concurrent with delocalisation in the flanking bonds to have any observable effects on these lengths; and no such effect is observed.

Again a case has been pressed for interpreting these bond shortenings by changes in the hybrid constitution of the carbon atomic orbitals, without hyperconjugation, that is, without electron redistribution and delocalisation. But the previous answer applies, *viz.*, that, if this were true, the shortenings from —C—A to =C—A and to ≡C—A should be independent of A; whereas the observed shortenings are more than twice as great as those which would be deduced on these principles. Once again, the conclusion is, not that atomic orbital hybridisation makes no difference to the bond lengths, but that the shortenings owe much of their magnitude to hyperconjugation.[44]

TABLE 11-7.—SINGLE BOND LENGTHS (IN A) IN MOLECULES ALLOWING BOTH CH AND CHal HYPERCONJUGATION (+M AND −M)[1].

| Example | CC Length | Shortening[2] | CHal Length | Lengthening[2] |
|---------|-----------|---------------|-------------|----------------|
| $ClCH_2 \cdot C:CH$ | $1.47 \pm 0.02$ | ∼0.07 | $1.82 \pm 0.02$ | ∼0.06 |
| $BrCH_2 \cdot C:CH$ | $1.47 \pm 0.02$ | ∼0.07 | $1.95 \pm 0.02$ | ∼0.04 |
| $ICH_2 \cdot C:CH$ | $1.47 \pm 0.02$ | ∼0.07 | $2.13 \pm 0.03$ | ∼0.03 |

[1] Electron-diffraction data by L. Pauling, W. Gordy, and J. H. Saylor (*J. Am. Chem. Soc.*, 1942, **64**, 1733).

[2] The deviations of bond length are relative to the summed covalent radii from Table 11-2.

The results of Pauling, Gordy, and Saylor's electron-diffraction measurements on propargyl chloride, bromide, and iodide are summarised in Table 11-7. The CC single bonds in these compounds had the uniform length $1.47 \pm 0.02$ A. They are therefore significantly shortened. Having regard to the authors' estimate of error, the shortenings are not significantly different from what would be expected from CH hyperconjugation, $+M$, involving the two hydrogen atoms available for such in these examples. But neither are they distinguishably different from what might result from the combined effect of this CH hyperconjugation, $+M$, and a CHal hyperconjugation, $-M$. Both forms of hyperconjugation should contribute to the shortening:

[44] This was D. P. Craig's view in 1951, before the micro-wave precision data on bond lengths had become available (*cf.* the first edition of this book, p. 148, footnote).

rivatives. It soon became clear that the additional symmetry introduced by the oscillation hypothesis was demanded by the observed extent of isomerism.

Subsequently to the original theory, but before its emendation, two other attempts were made to represent the symmetry that seemed to be indicated by the observed isomerism. One is expressed in the prism formula for benzene (below), first seriously advocated in 1869 by Ladenburg.[6] This formula requires the correct numbers of all the different kinds of substitution products. But the symmetry properties of the combining positions are such that these positions have to be correlated with those of a simple ring formula as indicated by the numbering:



Ortho-positions (6 pairs) are at the ends of face-diagonals, meta-positions (2 trios) at the corners of triangular faces, and para-positions (3 pairs) at the ends of longitudinal edges. Thus, in the prism structure, ortho-positions are not directly bound, while meta- and also para-positions are directly bound, in contrast to the bonding arrangements in the simple ring structure. One result of this was an exceedingly awkward formula for naphthalene.

In 1886 Baeyer commenced a series of experimental researches designed to determine the arrangement of the valencies of benzene, his method being to reduce benzene derivatives to *cyclo*hexadiene, *cyclo*hexene, or *cyclo*hexane compounds, and to determine the constitutions of the reduction products by the standard methods of aliphatic chemistry.[7] This work disproved the prism structure. For ortho-, meta-, and para-benzene compounds gave *cyclo*hexane-1,2-, -1,3-, and -1,4-derivatives, respectively; and one compound, ethyl 2,5-dihydroxyterephthalate, in which all three pairs of para-positions are labelled, gave a reduction product, ethyl succinosuccinate, having all substituents where they would be expected if benzene had the simple ring structure.

The other early formula of the requisite symmetry was the diagonal formula, first advanced in 1867 by Claus:[8]

[6] A. Ladenburg, *Ber.*, 1869, **2**, 141, 272.

[7] A. v. Baeyer, *et al.*, *Ann.*, 1887, **245**, 103; *Ber.*, 1888, **19**, 1797; *Ann.*, 1889, **251**, 257; *Ber.*, 1890, **23**, 1277; *Ann.*, 1890, **256**, 1; 1892, **266**, 169; 1893, **276**, 259.

[8] A. Claus, "Theoretische Betrachtungen und deren Anwendung zur Systematik der organischen Chemie," Freiburg, 1867, p. 207.
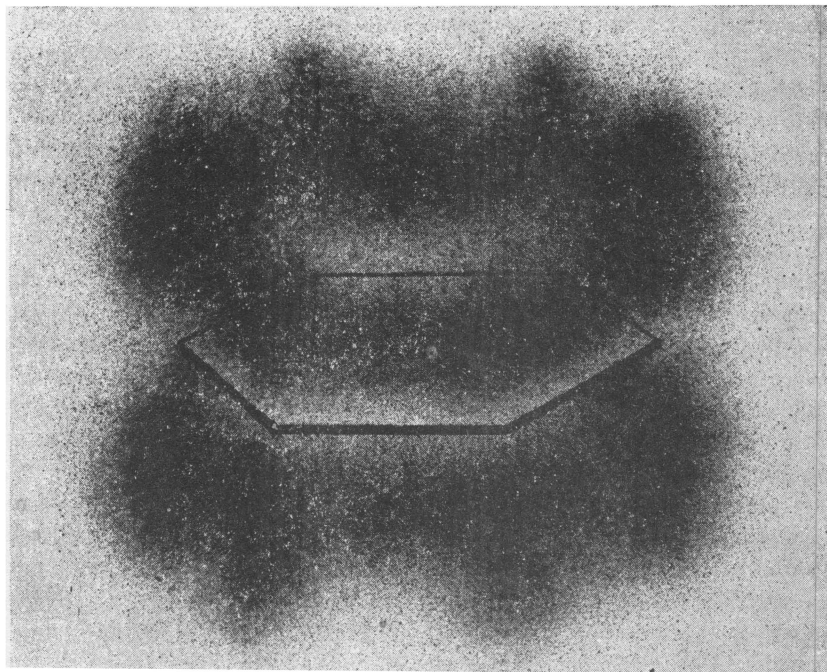
Fig. 13-1.—Illustrating the charge distribution of the $\pi$ electron shell in benzene.

valency concepts. The second method, which Hückel himself invented, is known as the valency-bond treatment. It goes to the other extreme, over-emphasizing the covalent character of the binding; and, for that very reason, it appears particularly easily in the role of an interpretation of valency concepts. The technique of this method was simplified by Pauling and Wheland, who applied it to benzene and other aromatic hydrocarbons.[17]

In setting up the problem, Hückel, and likewise Pauling and Wheland, assumed that each carbon atom of benzene supplies one electron in an atomic $p$ orbital, having its symmetry axis at right angles to the molecular plane, to form a molecular group of six $\pi$ electrons. The remaining electrons are left to hold, with single $\sigma$ bonds, the regular hexagonal frame of six CH carbonium-ionic centres. Each $\pi$ electron is then considered as moving in the combined potential field of the framework and the smoothed-out field of the remaining $\pi$ electrons. It is easily shown that the plane of the atomic nuclei is a nodal plane for all the $\pi$ electrons, which together must produce a charge-density

[17] L. Pauling and G. W. Wheland, *J. Chem. Phys.*, 1933, **1**, 362; J. Sherman, *ibid.*, 1934, **2**, 488; G. W. Wheland, *ibid.*, 1935, **3**, 356.