THE POLARITY OF THE C-H BOND

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Although the inertness of the paraffin hydrocarbons implies that the C–H bond in isolation has no spectacular properties, yet it is upon a medium of such bonds that more reactive associations exert their effects, giving to each organic molecule its peculiar properties. Our interest in this bond derives, therefore, from its quality of passivity [1] and it is the intention of this Review to consider the polar nature of the C–H linkage from this aspect.

The electrical dissymmetry of a molecule has its quantitative expression in the magnitude and direction of the electric moment vector, or dipole moment, which it is convenient to regard as the product of the distance separating the electrical " centres of gravity " and the magnitude of the charges at those points. The moment of a bond may be defined in the same way, but in neither case is one informed of the actual electron distributions; for this a knowledge of the wave functions concerned, and, consequently, of the electron density, is required. According to wave-mechanical principles the electron density at any one part of a molecule is not, in general, independent of that at any other part, so that we may expect, not only electrostatic interactions between atoms not directly bonded as implied by the concept of point charges, but also quantum-mechanical effects between linked atoms.

If we accept the fiction of a bond polarity determined by the isolated combination of the most usual orbitals of the atoms concerned, the pure sp^3 and s orbitals in the C–H bond, then from our present knowledge it appears that in any molecule the polarity of the bond may be modified by one or more of the following effects [2]: (1) Electrostatic induction by which the field generated by an indirectly bonded dipole polarises the bond. (2) Mesomeric electron-release of the Baker–Nathan type, or as it is otherwise called, π-hyperconjugation, in which a CH_3—, $>CH_2$, or $-\!\!>CH$ group behaves as a compound atom of high electron lability. (3) Change of hybridisation whereby the C–H bond takes more s character when one or more of the other carbon orbitals increases its p character as a result of their own bonding. The operation of these effects is considered in detail in a later section.

Historical Survey.—The earliest estimate of the C–H bond moment was made by J. W. Williams [3] and A. Eucken and L. Meyer.[4] It was demonstrated that in toluene the electric moment (0·4 D.) is directed from the

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[1] C. K. Ingold, *Chem. Reviews*, 1934, **15**, 238.

[2] J. W. Linnett, *Trans. Faraday, Soc.*, 1945, **41**, 223, uses the same classification to account for variations in the C–H bond force constant, but (1) assumes a classical model, (2) and (3) a quantum-mechanical model.

[3] *Physikal. Z.*, 1929, **30**, 391. [4] *Ibid.*, p. 397.

methyl group across the benzene ring, and by assuming no interactions, tetrahedral distribution of valencies in the methyl group, and an aromatic C–H bond moment of zero, it follows that the required moment is 0·4 D. $(\overset{-}{C} - \overset{+}{H})$. By taking into account the electrostatic interactions of methyl and phenyl groups K. B. McAlpine and C. P. Smyth [5] showed that both for the aliphatic and the aromatic C–H bonds in toluene the electric moment would be 0·4 D. $(\overset{-}{C} - \overset{+}{H})$. Using an estimate of the moment for hydrogen fluoride, and computing the O–H and N–H bond moments from the molecular moments of water and ammonia respectively, neglecting mutual interactions, H. M. Smallwood [6] made an extrapolation to find 0·5 D. $(\overset{-}{C} - \overset{+}{H})$. A calculation was made by L. E. Sutton,[7] using dipole-moment data and electron-diffraction results of C. L. Bewilogua [8] for methyl and methylene chlorides (later shown to be in error), which indicated 0·2 D. $(\overset{-}{C} - \overset{+}{H})$. The generally accepted opinion, therefore, during the early part of the last decade was that the C–H moment is small and that hydrogen is effectively positive. The contrary view was first expressed by A. E. Van Arkel and J. de Boer [9] and strongly supported by O. Fuchs and K. L. Wolf [10] on evidence from several sources. Most of this can now be neglected as it is indirect and qualitative but the keystone of their argument was at that time more difficult to bring down. As a generalisation of work by W. Heisenberg,[11] F. Hund [12] was able to show that by the use of classical electrostatics, later confirmed by quantum-mechanical methods,[13] that in molecules of the type AB_2, AB_3 or AB_4 the highest symmetry is obtained when the polarisability of the atoms B is greater than that of A. The term highest symmetry means linear, triangular, and tetrahedral, respectively, for the molecular types quoted. Wolf noted that in the examples for which data were available the more polarisable elements (relative to carbon) are also the more electronegative and argued that, since methane was known to be tetrahedral, then hydrogen must be more polarisable than carbon and hence more electronegative. Although the generalisation has a wide validity there are exceptions such as the angular structures of F_2O and Cl_2O,[14] molecules which should on Hund's theory be linear.

B. Timm and R. Mecke,[15] by an analysis of the intensity of absorption bonds of the rotation-vibration harmonics of chloroform, and H. G. Trieschmann,[16] by combination of dipole-moment data and *X*-ray and electron-

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[5] *J. Amer. Chem. Soc.*, 1933, **55**, 453.

[6] *Z. physikal. Chem.*, 1932, *B*, **19**, 242 ; see also J. G. Malone, *J. Chem. Physics*, 1933, **1**, 197.

[7] *Proc. Roy. Soc.*, 1931, *A*, **133**, 668.

[8] *Physikal. Z.*, 1931, **32**, 265.

[9] " Chemische Bindung als Elektrostatische Erscheinung ", Leipzig, 1931 ; see also " La Valence et L'Electrostatique ", Paris, 1936.

[10] " Dielektrische Polarization ", Berlin, 1935, p. 356.

[11] *Z. Physik*, 1924, **26**, 196.

[12] *Ibid.*, 1925, **31**, 81 ; 1926, **32**, 1.

[13] F. Hund, " Handbuch d. Physik ", 2 Aufl., Bd. 24, 1, Berlin, 1933.

[14] L. Pauling, " Nature of the Chemical Bond ", 2nd ed., 1941, p. 79.

[15] *Z. physikal. Chem.*, 1935, **98**, 363.

[16] *Ber.*, 1936, **69**, 22.

diffraction results from methyl and methylene chlorides, also decided on a polarity $\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}$ with a magnitude of about 0·3 D. A complete re-examination by C. P. Smyth [17] of all existing data showed that none was wholly reliable and in the same paper it was decided to adopt $\mu = 0{\cdot}4$ D. $(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}})$ on the basis of evidence from two sources :

(1) Hirschfelder (reported by Smyth) treated methane wave-mechanically and found $\mu = 0{\cdot}3$ D. $(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}})$; this calculation was shown by C. A. Coulson [18] to be deficient and his objections are noted later.

(2) J. G. Malone [19] had demonstrated a rough parallelism between such bond moments as were then estimated and electronegativity differences as calculated by L. Pauling.[20] C. P. Smyth [21] elaborated the data but the relationship is only of limited validity and may be subjected to further criticism : (*a*) The bond moments are derived without allowance for inductive effects (this applies especially to H–X moments). (*b*) The C–X moments depend entirely on the magnitude and direction assigned to the C–H bond moment. (*c*) The contention that the bond moment μ(AB) is related to the electronegativity difference :

$$\mu(\mathrm{AB}) \propto (x_\mathrm{A} - x_\mathrm{B}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

is not consistent with Pauling's [22, 23] relation of percentage ionic character and electronegativity difference, *viz.*,

$$I = K_1(x_\mathrm{A} - x_\mathrm{B}) + K_2(x_\mathrm{A} - x_\mathrm{B})^2 \quad . \quad . \quad . \quad (2)$$

where $I = \mu(\mathrm{AB})/\mu(\mathrm{AB})^*$; $\mu(\mathrm{AB})^*$ is the moment of the fully ionic bond

$$\mu(\mathrm{AB})^* = e(r_\mathrm{A} + r_\mathrm{B}) \quad . \quad . \quad . \quad . \quad (3)$$

Combination of equations (2) and (3) leads to an impossible non-periodic function between $(r_\mathrm{A} + r_\mathrm{B})$ and $(x_\mathrm{A} + x_\mathrm{B})$.

The only permissible conclusion to be drawn from this earlier evidence is that the polarity of the C–H bond is small but of unknown direction.

Recent Theoretical Evidence.—It was not until 1942 that a complete quantum-mechanical treatment of the methane molecule was made with a view to establishing the polarity of its bonds. Coulson,[18] using wave functions calculated [24] by the molecular-orbital approximation, obtained normalised molecular orbitals. These are not localised but describe the movement of the electrons over the whole molecule. Taken in linear combination these orbitals may be transformed into four equivalent localised orbitals in which the electron density is concentrated along the tetrahedral directions. The displacement of the centroid of this type of orbit from the positive centre is calculated and the dipole moment is shown to be $\mu(\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}) = 0{\cdot}40$ D.

[17] *J. Physical Chem.*, 1937, **41**, 209.
[18] *Trans. Faraday Soc.*, 1942, **38**, 433.
[19] *J. Chem. Physics*, 1933, **1**, 197.
[20] *J. Amer. Chem. Soc.*, 1932, **54**, 3570.
[21] *Ibid.*, 1938, **60**, 183.
[22] Ref. (14), p. 69.
[23] The original equation was revised by C. P. Smyth and J. Hannay, *J. Amer. Chem. Soc.*, 1946, **68**, 171, after their determination of the electric moment of HF.
[24] *Trans. Faraday Soc.*, 1937, **33**, 388.

Expansion of the localised orbital in terms shows that the net formal charge on the carbon atom is greater than that on the hydrogen atoms, from which it is clear that the dipole moment of the bond is not simply determined by these qualities. In demonstrating the reason for this, Coulson is able to show where Hirschfelder's calculation[17] fails. An extension of an analysis made by R. S. Mulliken[25] of the electric moment of a bond A–B in terms of the wave-mechanical properties of the atoms shows that the moment may be represented as the sum of four terms: (1) A term dependent on the relative electronegativities of the atoms A and B. (2) A homopolar dipole term expressing the properties of the bonding electron pair. (3) An atomic dipole term composed of the moments generated by the electrons in their atomic orbits which in combination give the molecular orbit. (4) A moment term resulting from induction in the unbonded electrons (if any) of one of the atoms.

Mulliken's original equation did not contain the third term which, although not of importance for either pure p or s bonding, becomes of considerable magnitude in hybrid orbitals. Coulson shows that, using Hirschfelder's wave functions, this term is of the order of 1 D., and that its inclusion in the complete equation changes the moment from $\mu(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}}) \approx 0{\cdot}3$ D. to $\mu(\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}) \approx 0{\cdot}7$ D.

The electron-pair method is then used to consider $\Psi(\mathrm{C{-}H})$ as the combination of covalent and ionic wave functions; $\psi(\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}})$ is not included as it has greater energy than either ψ (covalent) or $\psi(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}})$. The covalent function alone leads to a value $\mu(\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}) \approx 2$ D. and the ionic term alone to $\mu(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}}) \approx 1{\cdot}5$ D. By mixing to give to the moment the magnitude and direction found by the molecular-orbital method it is shown that $\psi(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}})$ is nearly as important as ψ (covalent). Although this seems remarkable, it is calculated that for a moment of the same magnitude (0·4 D.) but of opposite direction $(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}})$ an impossibly large contribution by the ionic state is required.

More recently, Coulson[26] in an investigation of the size of the carbon atom has concluded that an electron in a $2s$ orbit more closely approaches the nucleus than does an electron in a $2p$ orbit. It follows from this that, in hybrid orbitals the average position of an electron will depend upon the precise composition of the orbital. Although in the original treatment[18] of the methane molecule it was shown that the moment of the C–H bond is unlikely to vary with the usual hybrid compositions (tetrahedral, trigonal, and diagonal) the newer work introduces a fresh factor, and A. D. Walsh[27] has interpreted this to mean that the more s character a C–H bond has the more negative will the carbon atom be. As a corollary to this Walsh postulates that the more electronegative an atom bonded to carbon the

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[25] *J. Chem. Physics*, 1935, **3**, 573.

[26] V. Henri Memorial Vol., Liége, 1948.

[27] Faraday Soc. Discussion, 1947, **2**, 18.

more p character will the bond have. In support of his extension of Coulson's results, Walsh [28] has correlated internuclear C–H distance, force constant, and bond strength with hybrid composition, as shown in Table I.

TABLE I

Correlation of hybrid composition and bond properties

Molecule.	Hybridisation of σ bond.	K(CH), dynes/cm. × 10^5.	r(CH), A.	E(CH), kcals./mole.	Polarity.
CH . . .	p	4·1	1·12	80	C+
CH_4 . . .	sp^3	5·0	1·094	104	↓
C_2H_4 . . .	sp^2	5·1	1·087	106	
C_2H_2 . . .	sp	5·9	1·059	121	C−

Very recently, H. Hartman,[29] using a different type of model for the methane molecule from that of Coulson, has calculated that the moment is $\mu(\overset{+}{C} - \overset{-}{H}) = 0{\cdot}4$ D. On the basis of as yet unpublished work, R. S. Mulliken [30] considers it likely that there is a polarity reversal from methane to acetylene as envisaged by Walsh.

Evidence from Dipole-moment Data.—If, as the theoretical evidence indicates, the polarity of the bond is $\overset{+}{C} - \overset{-}{H}$ in methane, then it is to be expected that in simple aliphatic compounds the C–H bonds in methylene groups will be of similar polarity. Evidence that this may be so has been obtained from an analysis [31, 32] of the dipole moments of dimethyl ether and cyclic ethers, the molecular moments of which are shown in Table II.

TABLE II

Moments of various ethers

Molecule.	Electric moment, D.	Oxygen valencies angle.
Dimethyl ether	1·28	111°
Diethyl ether	1·15	111
Ethylene oxide	1·88	65
Trimethylene oxide	2·01	94
Tetramethylene oxide . . .	1·71	111
Pentamethylene oxide . . .	1·87	111

Although the higher moments of ethylene and trimethylene oxides relative to the open-chain ethers may be ascribed partly to the diminished valency angle, yet this is not the case in tetra- and penta-methylene oxides. Since the contributions of the C–H moments (irrespective of direction) are about the same in the two types of compound, clearly the inductive effect of the C–O dipoles on the rest of the molecules must be responsible.

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[28] *J.*, 1948, 400.

[29] *Naturforsch.*, 1948, **3**, 47.

[30] Private communication.

[31] W. L. G. Gent, *Nature*, 1946, **158**, 27.

[32] Unpublished work.

In considering the mutual interactions of solute and solvent from the point of view of the dielectric constant of solutions, F. C. Frank [33] had suggested a method for computing induction effects using a molecular model in which the individual atoms are regarded as dielectric spheres of uniform polarisability. A rather different approach is that of C. P. Smyth and K. B. McAlpine,[34] in which the whole polarisability of a bond is considered to be located at the " point of contact " of the atoms concerned. Although there are objections to both models, it is considered that they are reasonably good approximations on the basis of classical electrostatics and that although they should not yield identical results, because of the very different ways in which the electron distribution is regarded, the mean value should be a good approximation to the true. Using either of these models, it is possible to express the observed molecular moment as

$$\mu\,(\text{observed}) = a\mu(\text{CO}) + b\mu(\text{CH}) \quad . \quad . \quad . \quad (4)$$

where a and b depend on the geometry of the molecule concerned. Combination of such equations for the different ethers allows an evaluation of both μ(CO) and μ(CH). It is found that in every case * the value of μ(CH) is about 0·4 D. ($\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}$). From less complete and reliable data on the corresponding sulphides a similar result is obtained.[32] The effective polarity will be slightly less as a result of induced moments.

Spectroscopic Evidence.—It has been known for some time that the intensities of vibrational infra-red absorption bands depend on the change of dipole moment during bending or stretching movements. Very little is known quantitatively of the stretching moment but there have been several determinations of the C–H bending moment in various environments (Table III) although only in one case has it been possible to determine the sign of the vector.

TABLE III

Bending moments of C–H *bonds*

Molecule.	C–H Bending moment, D.	Molecule.	C–H Bending moment, D.
Chloroform . .	0·3[15]	Ethylene † . . .	0·37,[37] 0·52, 0·77
Methane . . .	0·307[35]	Benzene . . .	0·4[38]
Hydrogen cyanide	0·57[36]		

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[33] *Proc. Roy. Soc.*, 1935, *A*, **152**, 171 ; cf. L. G. Groves and S. Sugden, *J.*, 1937, 1992.

[34] *J. Chem. Physics*, 1933, **1**, 190.

[35] R. Rollefson and R. Havens, *Physical Rev.*, 1940, **57**, 710.

[36] R. T. Foley, *ibid.*, 1946, **69**, 628.

[37] A. Thorndike, A. J. Well, and E. B. Wilson, *J. Chem. Physics*, 1947, **15**, 157.

[38] R. P. Bell, H. W. Thompson, and (Miss) E. E. Vago, *Proc. Roy. Soc.*, in the press.

* Originally,[31] it appeared that ethylene oxide is anomalous, but assuming a more trigonal arrangement of C–H bonds in the models, a good agreement of μ (CO) and μ (CH) with the other molecules is obtained.

† The three values refer to the three different bending modes.

Although the physical picture of the model used is clear since the bond moment is assumed to be constant and the intensities are calculated from this and the displacement of the atoms, it is not at present obvious what relation this calculated moment bears to that found by any other method. The energy associated with bending of H–C–H is only about one-tenth of the stretching energy for the same displacement,[39] which suggests that during bending the H– nucleus and bonding electrons move as an undisplaced unit. This is also suggested by the fact that the bending force constants $\mathrm{C{-}C{\diagup}^{H}} = 0{\cdot}66$; $\mathrm{C{=}C{\diagup}^{H}} = 0{\cdot}60$; $\mathrm{C{\equiv}C{\diagup}^{H}} = 0{\cdot}24 \times 10^{-11}$ dyne-cm./radian are more or less inversely proportional to the amount of space in which the vibration may take place. It seems reasonable to assume, therefore, that the character of the bond is not much altered on bending and hence that the moment is a constant. Nevertheless, since there are three different values of the bending moment in ethylene corresponding to the three bending modes, it does appear that the moment may depend on the character of the restoring-force fields. Clearly, the moment of a bond obtained by dipole-moment analysis (were this possible) would correspond to a weighted mean of the various bending moments but the moment calculated quantum-mechanically would be of an unperturbed bond.

Bell, Thompson, and Vago[38] have studied the absolute intensities resulting from vibrations in planes perpendicular to the ring plane of various alkyl- and halogen-substituted benzenes. They show that the extinction coefficient at a particular frequency may be expressed as :

$$\varepsilon = A\nu[\Sigma(a_{\mathrm{H}} - a_{\mathrm{C}})\mu(\mathrm{CH}) + \Sigma(a_{\mathrm{X}} - a_{\mathrm{C}})\mu(\mathrm{CX})]^2$$

where A is a constant, ν the vibration frequency, the a's represent amplitudes of classical vibrations of energy $h\nu$, the summation being taken over all bonds, and $\mu(\mathrm{CX})$ is a bond moment derived from the molecular moment of C_6H_5X. Insertion of observed extinction coefficients together with calculated or observed frequencies shows that $\mu(\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}}) = 0{\cdot}4$ D. Lacking knowledge of the other possible bending moments in these compounds, it seems best, at the moment, to accept this as a true value of the C–H electric moment in benzene and take it as evidence in favour of Walsh's contention that sp^2 bonds have a basic polarity $\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}}$.

Qualitative Evidence.—The most recent extensive collection of evidence concerning polarity of C–H bonds is that of Walsh[27, 28, 40] favouring $\overset{+}{\mathrm{C}} - \overset{-}{\mathrm{H}}$ in aliphatic compounds. He argues that if, in fact, this is the polarity, then the properties of the bond in various molecules should run parallel to those of C–Hal., and in support of this quotes evidence based on thermochemical data, force constants, and bond lengths. His interpretation of Coulson's work has already been noted (p. 386) and in support of his contention that the acetylenic carbon is negative relative to hydrogen he

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[39] J. W. Linnett, *Quart. Reviews*, 1947, **1**, 84.

[40] *Trans. Faraday Soc.*, 1947, **43**, 68.

has cited the well-known " acidic " properties of acetylene and the electrophilic behaviour of the —C≡C— group in certain organic compounds.

The Baker–Nathan Effect.—In considering the polarity of the methyl C–H bonds in toluene, W. L. G. Gent[41] remarked that if, in fact, these have the same magnitude and direction of moment as in methane then, making some allowance for induction and considering the phenyl group as an electronegative atom, a mesomeric moment of about 0·7 D. is indicated. Accepting the spectroscopic value $\mu(\overset{-}{C} - \overset{+}{H}) \approx 0{\cdot}4$ D., then an effective resonance moment of *ca.* 1 D. (see Fig. 1) is obtained, comparable with that of the halogens,[42] which have the same directive effect.

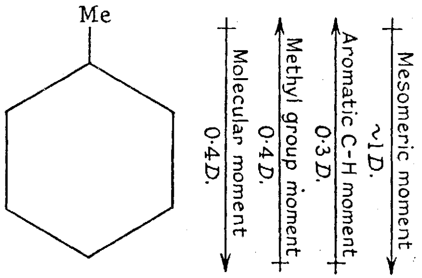
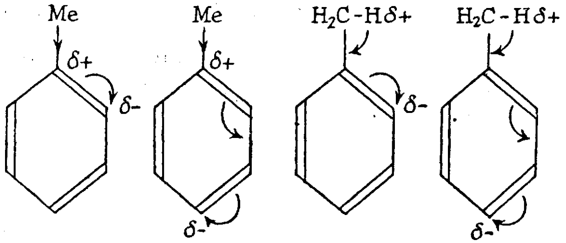


FIG. 1

J. W. Baker,[43] considering the dipole moments of alkylbenzenes, concluded that the order (toluene < ethylbenzene < *iso*propylbenzene < *tert.*-butylbenzene) depended primarily on the inductive effects of the alkyl groups, the action of which has been symbolised[41, 44] as in (I) of Fig. 2. In the unexcited state Baker considered that the forms (II) (Fig. 2) are of minor importance, but he was able to show convincingly that in a variety of reactions in which the molecules are capable of exhibiting this type of electron-release it undoubtedly is the determining factor, resulting in an inversion, sometimes only partial, of the inductive order of the alkyl groups.



(I.) (II.)

FIG. 2

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[41] Faraday Soc. Discussion, 1947, **2**.

[42] L. G. Groves and S. Sugden, *J.*, 1937, 1922.

[43] *J.*, 1939, 1156.

[44] H. B. Watson, " Modern Theories of Organic Chemistry ", 2nd ed., 1941, p. 94.

The effect naturally decreases from methyl to *tert.*-butyl since the number of hydrogen atoms available to provide resonance forms decreases in this order. That this mechanism is quantum-mechanically feasible was confirmed by R. S. Mulliken, (Mrs.) C. A. Rieke, and W. G. Brown [45] and termed π-hyperconjugation. It has been interpreted on the molecular-orbital theory as due to the interaction between the group orbital of a methyl group and the M.O. of the phenyl group in such a way as to allow electrons to flow into the ring, thus diminishing the negative charges on the methyl group. The idea has been extensively employed in interpreting other phenomena in molecules where the alkyl groups are adjacent to suitable atomic systems.[46] There has been, however, a tendency to overemphasise the importance of this phenomenon.

The ultra-violet spectra [47] of alkylbenzenes show clearly that the hyperconjugation effect does in fact diminish from methyl to *tert.*-butyl, and the chemical evidence indicates that the same order is observed in reactions in which there is a powerful electron-demand, as in the hydrolysis of *p*-alkylbenzhydryl chlorides [48] : $R\cdot Cl \rightarrow R^+ + Cl^-$. In these two types of process it is probable that ionisation is involved, that is, an excited state is reached, when, as W. C. Price [49] has recently suggested and as Baker postulated originally, a much greater hyperconjugation effect is possible. It is necessary, therefore, to regard the C–H bond polarity in the methyl group of toluene as having a polarity ($\overset{+}{C} - \overset{-}{H}$) but of reduced magnitude relative to that of the same bond in methane. In the excited state, however, this polarity is certainly reversed. The same conclusion may well apply to other systems, such as methylacetylene, in which hyperconjugation occurs.

Conclusions

We may summarise our present knowledge of the polarity of C–H bonds as follows :

(1) In methane and in aliphatic compounds, when not subjected to influences as detailed under (2) and (3), the polarity of the bond is $\overset{+}{C} - \overset{-}{H}$, the electric moment being about 0·40 D. A somewhat smaller moment is probable when the bond comes under the electrostatic influence of powerful fields generated by adjacent strongly polar groups.

(2) By what is believed to be an effect of the different electronegativities of a carbon atom towards its different bonding electrons, the polarity of a hydrogen atom, attached to a carbon atom whose other valencies are involved in an ethylenic or acetylenic bond, is more positive than in methane. In an acetylene this polarity is likely to be definitely $\overset{-}{C} - \overset{+}{H}$, whilst in an ethylene the moment is likely to approach zero.

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[45] *J. Amer. Chem. Soc.*, 1941, **63,** 41.

[46] C. L. Deasy, *Chem. Reviews*, 1945, **36,** 145.

[47] F. A. Matsen, W. W. Robertson, and R. L. Chuoke, *ibid.*, 1947, **41,** 273.

[48] E. D. Hughes, C. K. Ingold, and R. Taher, *J.*, 1940, 949.

[49] *Chem. Reviews*, 1947, **41,** 257.

(3) Where hyperconjugation is possible the polarity $\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}}$ of the bonds of the alkyl group involved will be reduced from that operative in methane, provided that the molecule is in the ground state. On excitation of the molecule it is likely that a much larger charge transfer is possible and the polarity is certainly reversed.

Quantitative knowledge of the polarity of the C–H bond in various situations is still small, but it is probable that under the stimulus of the newer hypotheses briefly noted here, experimental methods will be devised for better quantitative inference. This is of importance not only for the light which will be thrown on intermolecular interactions but also, since changes of polarity are likely to be paralleled in changes of binding energy, for a better understanding of reaction mechanism involving the C–H bond.

The Reviewer wishes to express his thanks for the benefit of discussion with Professor C. A. Coulson and Dr. A. D. Walsh, and of communication with Professor R. S. Mulliken.