286. *The Carbon Valency Angle and Dipole Induction in Benzyl Compounds.*

By Frederick Charles Frank.

When some preliminary results were obtained early in 1933 (*Trans. Faraday Soc.*, 1934, **30**, 860), the view that the dipole moments of the methyl halides should be different in gas and in solution ran counter to accepted views, though already supported by Horst Müller's first paper on the subject. With the subsequent establishment of this as a quite general phenomenon, all stereochemical calculations from dipole-moment data became suspect until a better understanding of the solvent effects could be reached. This being now achieved, the calculations appear to be justified, and, although the method of allowing for induction in the molecule is no longer novel, they form an interesting example of the method and demonstrate that dipole-moment data give quite consistent results in stereochemical calculations if due allowance is made for complicating influences.

The following effects of the solvent are now recognised :

(1) A solvation moment, due to dipoles induced in the solvent by primary dipoles in the solute (Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284; Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171). This depends on molecular geometry, but the solvation moment of a polar group in a molecule is unaltered by substitution in a fairly remote part of the molecule. The necessary limitation that the polar groups concerned should be remote was already laid down by Smyth before the discovery of solvent effects.

(2) A solvation polarisation, due to the change of solvation moment (1) when solute

molecules are displaced relative to solvent (Frank and Sutton, in the press). This is of uncertain magnitude and forms a part of the " atomic polarisation." Its recognition does not affect the position with regard to stereochemical calculations, but only the interpretation of ${}_{A}P$, which is known to be limited to a few c.c. and to produce only minor errors when applied to molecules of large or moderate moment.

(3) A negative solvation polarisation arising from dielectric " saturation " in polar solvents, which are rightly avoided.

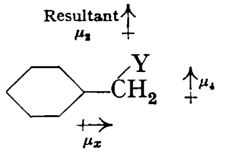
(4) Further corrections to the Clausius–Mosotti equations necessary in the case of anisotropically polarisable molecules, or when the volume refractivities of solvent and polar solute differ (Weigle, *Helv. Phys. Acta*, 1933, **6**, 68; Govinda Rau, *Proc. Indian Acad. Sci.*, 1935, **1**, 498; Guggenheim, *Nature*, 1936, **137**, 459). All the evidence indicates that only minor additional errors arise under these heads—in the last case the main difference between μ_G and μ_D is a uniform proportional lowering which will not change the results of stereochemical calculations.

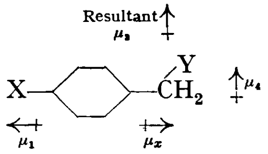
Solvent effects, therefore, do not invalidate stereochemical calculations based on dipole moments.

The possibility of estimating the configuration of molecules from dipole moments depends on the experimental fact that the moment of a molecule is approximately the vector sum of the moments possessed by its component groups when they are in simple molecules. The value of the moment assigned to a group X is the difference between the moment of ⁝C–X and ⁝C–H with appropriate sign, plus an inductive effect which is most completely eliminated in the methyl compound, plus solvent effects, and is thus only approximately the same as the moment of ⁝C–X. When two groups X and Y are attached to the same rigid hydrocarbon structure, vector addition is applicable so long as each is outside the sphere of induction of the other.

The paradoxical apparent absence of induced moments except in the very first members of hydrocarbon chains is now known to be an error due in part to opposing solvent effects, and it is clearly desirable to consider inductive effects when estimating the carbon valency angle from the moments of benzyl compounds and their *p*-substituted derivatives, as was done (without considering induction) by Smyth and Walls (*J. Amer. Chem. Soc.*, 1932, **54**, 1854). In the extended treatment now given, the only simplifying assumptions made are that the induced moment in the phenyl radical due to the C–Y primary moment in the compound $\mathrm{Ph{-}CH_2}{\diagup}^{\mathrm{Y}}$ is parallel to the Ph–C link, and that in the compound $C_6H_4X{\cdot}CH_2Y$, X and Y are outside each other's spheres of inductive influence. In support of the former assumption it should be noted that the direct field from the primary dipole acts upon the phenyl group roughly in the Ph–C direction, and that this direction is also favoured by the anisotropy of polarisability of phenyl.

The moment of CH_2PhY will be that of CH_3Y (designated μ_4) modified by the addition of a moment μ_x due to the phenyl at an angle θ (the valency angle we desire to measure), which moment is composed of a primary part, approximately that of toluene (0·4), and an induced part designated μ_i in the opposite direction. In $C_6H_4X{\cdot}CH_2Y$ we have also to reckon the moment of C_6H_5X (designated μ_1) in the C–Ph direction: or preferably we may take in place of this the difference between the moments of toluene and $C_6H_4Me{\cdot}X$, so making an allowance for the inductive effect due primarily to X, on the aliphatic carbon atom.





The moments of the various substances are

C_6H_5X	μ_1	CH_3Y	μ_4
$C_6H_5{\cdot}CH_2Y$	μ_2	$C_6H_4Me{\cdot}X$	μ_5
$C_6H_4X{\cdot}CH_2Y$	μ_3	C_6H_5Me	$\mu_6 = 0{\cdot}4$

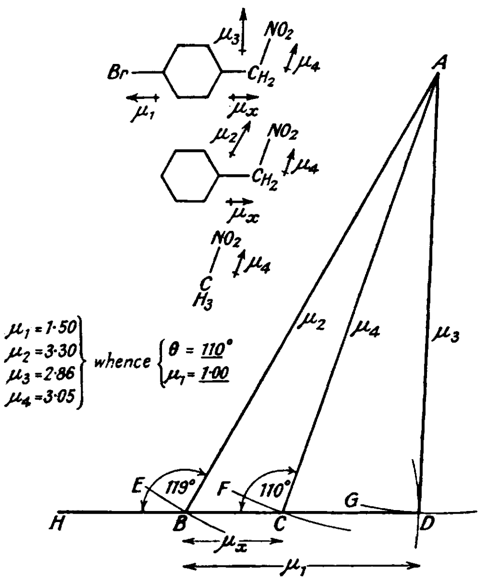
Induced moment along Ph–C $= \mu_i$

$$\mu_x = \mu_i - \mu_6$$

The equations for solution are

$$\mu_2^2 = \mu_4^2 + \mu_x^2 - 2\mu_4\mu_x \cos\theta$$
$$\mu_3^2 = \mu_4^2 + (\mu_x - \mu_1)^2 - 2\mu_4(\mu_x - \mu_2) \cos\theta$$

As explained above, it is preferable to use $(\mu_5 - \mu_6)$ in place of μ_1 when there is any difference between these two. The equations are most easily solved by a graphical method which provides as good an accuracy as the data warrant.

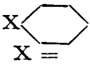


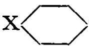
With centre *A* draw circles *EB*, *FC*, *GD*, with radii proportional to μ_2, μ_4, μ_3, respectively. With centre *B* and radius proportional to μ_1 draw a circle cutting *GD* in *D*. Join *BD*, cutting *FC* in *C*. The angle $\widehat{BCA}$ is the required valency angle θ; $\widehat{HBA}$ is the angle obtained by Smyth and Walls's method. The method is applied to *p*-bromophenylnitromethane in the figure.

Dipole moments measured in this research were: phenylnitromethane, 3·30; *p*-bromophenylnitromethane, 2·85. The moment of bromobenzene in benzene is taken as 1·50, and that of nitromethane in benzene as 3·05, from the following measurements: Höjendahl 3·05, Weissberger and Sängewald 3·13, Hunter and Partington 3·02 (see *Trans. Faraday Soc.*, 1934, **30**, Appendix). The above method can then be applied to measure the carbon valency angle and the induced moment in the phenyl in phenylnitromethane, yielding the results :

Valency angle of aliphatic carbon ($\widehat{BCA}$) . .	110°
Apparent angle by Smyth and Walls's method .	119°
Induced moment in the phenyl radical $= \mu_x + 0{\cdot}4 =$	1·00

Unfortunately, the results obtained by various workers for the dipole moments of acetonitrile and methyl halides in benzene are too discrepant for the direct application of this method to Smyth and Walls's measurements; but the reverse calculation has been made, assuming the angle 110° and predicting the true moments of these compounds in benzene, at the same time estimating the induction in the phenyl radical. It was found necessary to use in place of μ_1 for the *p*-nitro-compounds the difference between the moments of toluene and *p*-nitrotoluene, *i.e.*, 4·04 instead of 3·90; otherwise, higher values of μ_4, 1·79 and 1·80, inconsistent with the rest, or with values directly measured, and inconsistently low values of μ_1, 0·46 and 0·50 for the chloride and bromide respectively, are obtained. This gives another explanation for the lower angles found by Smyth for these compounds, which he explained on the grounds that atomic polarisation was less significant with the substances of higher moment. Treated thus, their data yield the results :

Substance. X  CH_2Y. X =	Y =	Smyth's angle.	μ_4.	μ_i.
Br	Cl	119°	1·71	0·73
Cl	Br	119·5	$1{\cdot}72_5$	0·74
NO_2	Cl	113·5 (118)	1·73	0·70
NO_2	Br	114° (118)	1·73	0·70
NO_2	CN	114 (116)	3·29	0·85



(The angles in parentheses are those obtained when 4·04 is used in place of 3·90, as explained above.)

The μ_4 values are well within the range of direct measurements of the methyl compounds, and in agreement with the best of them; *e.g.*, the value 1·73 in benzene corresponds, according to Müller's empirical equation, to 1·85 in the gas, while Sänger's gas value for methyl chloride is 1·861 ± 0·008.

The mean induced dipoles estimated are:

In phenyl, by groups Y.	
Y = halogen	0·72
Y = cyano	0·85
Y = nitro	1·00

In *p*-methyl, by group X.	
X = nitro	0·14

From Hunter and Partington's values 3·02 for nitromethane and 3·19 for nitroethane, with an assumed angle of 110°, the induced dipole in the second methyl is found to be 0·41. These measured effective induced moments will be rather smaller than those of the actual induced dipoles in the molecules, because of solvent effects which work in the opposite direction (Frank, *loc. cit.*).

EXPERIMENTAL.

Materials.—Phenylnitromethane was prepared after Wislicenus and Endres (*Ber.*, 1902, **35**, 1755; Meisenheimer, *Annalen*, 1907, **355**, 284) by hydrolysis and spontaneous decarboxylation of the condensation product (the sodium salt of the *aci*-form of phenylnitroacetonitrile) from benzyl cyanide and ethyl nitrate. Samples were also prepared, less satisfactorily, from benzyl chloride or iodide and silver nitrite. The substance was purified by steam-distillation, solution in sodium hydroxide, ether washing, liberation by carbon dioxide (20 hours' passage), drying with sodium sulphate, and three fractional distillations under low pressure, finally with an oil-pump vacuum. It froze sharply by seeding at — 10·5° (corr.); it supercooled persistently, and could not be made to freeze at — 30°, though it did so readily at — 40°, or when the tube was touched with solid carbon dioxide.

p-Bromophenylnitromethane was prepared by a similar method (Wislicenus and Elvert, *Ber.*, 1908, **41**, 4121), the bromobenzyl bromide for preparation of the cyanide being made by photobromination in the cold (Schramm, *Ber.*, 1884, **17**, 2922; 1885, **18**, 350). The free *aci*-nitro-compound liberated by hydrochloric acid from the sodium salt at 0° was allowed to isomerise (in a desiccator it was still changing after a week) and was crystallised four times from alcohol and once from ligroin and ether; the m. p. remained constant at 55·5—56° (Hantzsch and Schultze 60°; Wislicenus and Elvert 56—57°).

The following measurements of dipole moment were made:

Phenylnitromethane in benzene at 25°.

f_2.	d, g./c.c.	ϵ.	n^2.	${}_{T}P_2$, c.c.	${}_{E}P_2$, c.c.
0	0·8738	2·2727	2·25713	263	36·5
0·0126904	0·87843 *	2·46929	2·25874	253·29	36·52
0·0046998	0·87509	2·34691	2·25784	263·14	36·83
0·0187931	0·88060	2·56321	2·25949	248·76	36·53
0·0287087	0·88420	2·71458	2·26070	241·60	36·47
0·0070852	0·87641 *	2·38181	—	255·82	—

${}_{O}P(+{}_{A}P)$ = 226·5 c.c.; μ = 3·30.

p-*Bromophenylnitromethane in benzene at* 25°.

0	0·8738	2·2727	2·25713	213·2	45·2
0·0082023	0·88289	2·37141	2·26028	213·17	45·08
0·0120536	0·88716	2·41671	2·26135	210·39	45·50
0·0224006	0·89835	2·54230	2·26518	207·98	45·01
0·0054867	0·87975 *	2·33998	—	209·55	—

${}_{O}P(+{}_{A}P)$ = 168·0 c.c.; μ = 2·85.

* = Interpolated values.

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