112. *The Determination of the Angle between the Phenyl Groups in αα-Diphenylethylene, from Electric Dipole Moment Measurements.*

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From the electric dipole moments obtained for αα-diphenylethylene and several *p*-substituted derivatives thereof, the valency angle between the attached phenyl groups has been calculated by methods previously developed. The value obtained is 125° ± 3°.

This large value can hardly be explained except by "resonance" involving the two benzene rings and the ethylenic double bond, which would make the two rings tend to be coplanar and so, by creating steric repulsion, cause the angle between them to be greater than that found in diphenylmethane (115° ± 5°) or for the CH_2 angle in ethylene (118°). It therefore confirms a conclusion reached by other workers from measurements of bond distances in other phenylethylenes.

The valency angle observed is not large enough to allow of the rings being coplanar, and in order to give the distance of 2·4 A. believed to be the minimum permissible between unbonded hydrogen atoms it is necessary that the rings be twisted about 30° out of the common plane.

THE method of determining the valency angle of the linking atom in diphenyl compounds by means of dipole moment measurements is now well established, and, in particular, methods have been developed by which the errors common in earlier work have been overcome (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562; Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853; Sutton and Hampson, *ibid.*, 1935, **31**, 945; Coop and Sutton, J., 1938, 1869). The investigation of the angle in αα-diphenylethylene is of interest in connexion with the effect of resonance on the nature of carbon–carbon bonds in conjugated systems.

EXPERIMENTAL.

Preparation and Purification of Materials.—αα-Diphenylethylene. This was prepared by removal of the elements of water from diphenylmethylcarbinol (*Organic Syntheses*, **6**, 32). Special care was taken to ensure the absence of carbinol from the product, which was purified according to Anschütz (*Annalen*. 1886, **235**, 336), and fractionated three times in a vacuum in an all-glass apparatus. A final distillation was carried out just before the dipole moment was measured; b. p. 145—146° (corr.)/14 mm. [Klages and Heilmann, *Ber.*, 1904, **37**, 1449, give b. p. 147° (corr.)/16 mm.].

*a-Phenyl-a-*p*-chlorophenylethylene.* This, and the other derivatives, were prepared by dehydration of the carbinol formed by hydrolysis of the reaction product from methylmagnesium iodide and the corresponding derivative of benzophenone. The preparation of the *p*-chloro-derivative is described by Bergmann and Bondi (*Ber.*, 1931, **64**, 1468). The compound had b. p. 157° (corr.)/12 mm. (four distillations in a vacuum).

*a-Phenyl-a-*p*-bromophenylethylene.* After five vacuum distillations, this compound boiled at 185° (corr.)/10 mm. Stoermer and Simon (*Ber.*, 1904, **37**, 4168) described the substance as an oil, b. p. 199—201°/19 mm., but it was possible to crystallise it from ethyl alcohol by cooling the solution in ice–salt, and after four crystallisations it was obtained as white crystals, m. p. 25·5—26·0° (corr.).

*aa-Di-*p*-chlorophenylethylene.* This was prepared from *pp*′-dichlorobenzophenone as described by Bergmann and Bondi (*loc. cit.*), who gave m. p. 91°. After three crystallisations from methyl alcohol–benzene (7 : 1 by vol.), the m. p. became constant at 86·2—86·5° (corr.), unchanged after a crystallisation from purified light petroleum and after six crystallisations from methyl alcohol (Found : C, 67·2; H, 4·1. Calc. for $C_{14}H_{10}Cl_2$: C, 67·5; H, 4·1%).

*aa-Di-*p*-bromophenylethylene.* Prepared from *pp*′-dibromobenzophenone, this *substance* had m. p. 85·8—86·2 (corr.) (Found : C, 49·9; H, 3·0. $C_{14}H_{10}Br_2$ requires C, 49·7; H, 3·0%), depressed by 8—9° on admixture with di-*p*-chlorophenylethylene; it is slightly soluble in boiling methyl alcohol and very sparingly soluble in cold; it is very much more soluble in ethyl alcohol, benzene, and acetic acid. The solubility in light petroleum is very small.

*aa-Di-*p*-fluorophenylethylene.* When the diazonium borofluoride from *pp*′-diaminodiphenylmethane was heated, it afforded *pp′-difluorodiphenylmethane*, m. p. 27·0—27·4°, b. p. 263·5° (corr.)/754 mm. (Found : C, 76·2; H, 5·0. $C_{13}H_{10}F_2$ requires C, 76·5; H, 5·0%); this is easily soluble in all the usual organic solvents and has a characteristic smell similar to but a little sweeter than that of diphenylmethane. Oxidation with chromic acid gave the corresponding benzophenone, from which *aa-di-*p*-fluorophenylethylene* was prepared in the usual way. After four distillations in a vacuum the b. p. was 137·5—138·5° (corr.)/12 mm., and after four crystallisations from ethyl alcohol the m. p. was 46·5—47·0° (corr.) (Found: C, 77·7; H, 4·9. $C_{14}H_{10}F_2$ requires C, 77·8; H, 4·6%). The compound crystallises from ethyl alcohol in short thick prisms, and is easily soluble in all the usual solvents except cold ethyl alcohol and cold light petroleum.

Benzene. Benzene was the solvent used for all measurements, special precautions being taken to ensure dryness (see Hampson and Sutton, *loc. cit.*).

Measurement of Dipole Moments.—The dielectric constant, refractive index, and density of dilute benzene solutions were measured at 25° by means of the apparatus and procedure described by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). The refractivities were measured at the frequency of the mercury line λ 5461 A. Auwers and Eisenlöhr (*J. pr. Chem.*, 1911, **84**, 49) measured the refractivity of aa-diphenylethylene at various frequencies in the visible region, and extrapolation to zero frequency indicates that the electron polarisation at 5461 A. exceeds that at zero frequency by 2—2·5 c.c. It was assumed that the same frequency variation occurred in the substituted compounds measured. The measured refractivities agreed well with those calculated from tables, if the same allowance for optical exaltation was made as was observed from aa-diphenylethylene.

The methods available for determination of atom polarisation, *viz.*, determination of refractive index in the far infra-red and well away from absorption bands, plotting total polarisation against $1/T$ and measuring from the graph the polarisation at $1/T = 0$, and determination of the dielectric constant of the solid substance, all in effect involve the atom polarisation as the small difference between two large numbers, and are experimentally difficult. The method adopted here was to take the atom polarisation of one compound (a-phenyl-a-*p*-chlorophenylethylene) to be 3 c.c., *i.e.*, approximately 5% of P_E (cf. Groves and Sugden, J., 1935, 971), and to make the values for the other compounds proportional to 3 c.c. according as their moments compare with that of a-phenyl-a-*p*-chlorophenylethylene, a procedure in general accordance with modern ideas about atom polarisation. The atom polarisations calculated in this way did not differ much from 3 c.c. It is most unlikely that the true values differ from 3 c.c. by more than ± 2 c.c., and this difference would cause a variation of calculated angle of only ± 1—1·5°.

Experimental Results.—The dipole moment data are given in the table, in which P represents the total polarisation, P_E the electron polarisation, P_A the atom polarisation, and μ the dipole moment in Debye units.

Compound.	P.	P_E.	P_A.	μ.
aa-Diphenylethylene	62·1	59·1 †	(see below)	0·0—0·38 ‡
a-Phenyl-a-*p*-chlorophenylethylene	113·6	64·1 †	3·0	1·49
aa-Di-*p*-chlorophenylethylene	115·0	69·3,† 69·0 *	3·3	1·43 §
a-Phenyl-a-*p*-bromophenylethylene	117·0	67·6,† 66·6 *	2·9	1·50
aa-Di-*p*-bromophenylethylene	120·9	74·8 *	3·3	1·43
aa-Di-*p*-fluorophenylethylene	110·0	59·1 *	3·1	1·52

* From refractivity tables. † From observed refractivities.

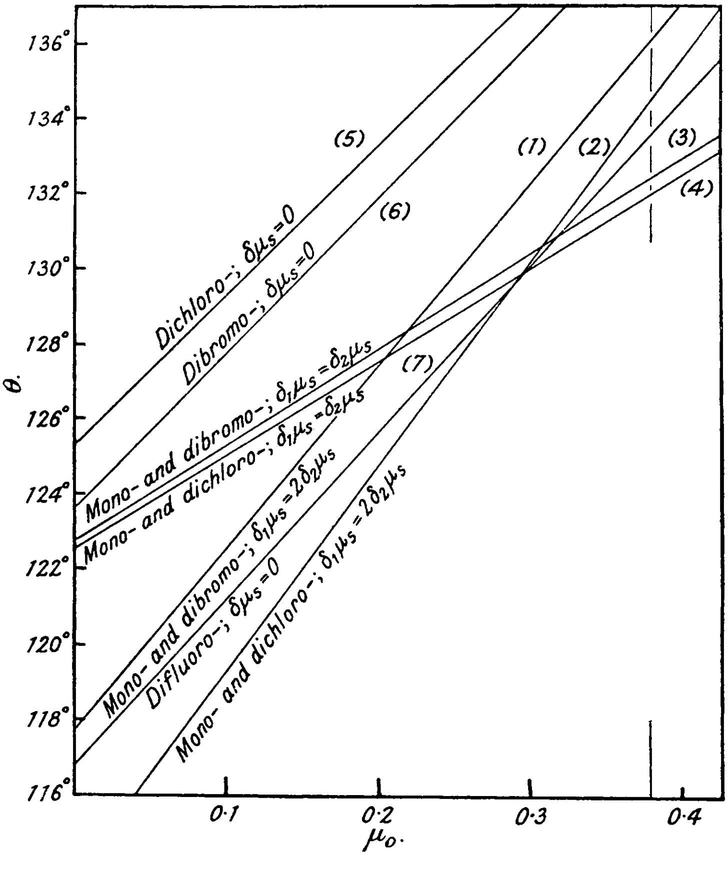
‡ Smyth and Dornte (*J. Amer. Chem. Soc.*, 1931, **53**, 1296) give μ = 0·58 D. at 70°, 0·35 D. at 10°.

§ Bergmann, Engel, and Meyer (*Ber.*, 1932, **65**, 446) give μ = 1·39 D.

Until the atom polarisation of aa-diphenylethylene is evaluated, we can only say that the moment, μ_O, of the substance lies between 0 and 0·38 D., and we shall take these as the initial limits.

The values of the valency angle, θ, of the quaternary linking carbon atom were calculated according to the method described by Hampson and Sutton (*loc. cit.*), whereby allowance is made for interaction of the $>C=CH_2$ and substituent groups, for values of the moment of aa-diphenylethylene over the above range. Two sets of corrected values for the valency angle were obtained, one based on the assumption that the interaction in each substituted ring is the same in the mono- as it is in the di-substituted compound ($\delta_1\mu_S = \delta_2\mu_S$), and the other on the assumption that the interaction in the former is twice that in the latter ($\delta_1\mu_S = 2\delta_2\mu_S$), these being the extremes between which the true state of affairs probably lies. The relevant values for the moments of halogenated benzenes, μ_S, were obtained from the measurements in benzene solution recorded in " A Table of Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**, Appendix), *viz.*, fluorobenzene, 1·45; chlorobenzene, 1·56; bromobenzene, 1·52 D. None of the moments is corrected for solvent effect; but in this particular application solvent effect produces only a minor error (Coop and Sutton, J., 1938, 1869).

In the figure these values of θ are plotted as a function of μ_O (curves 1—4). Some derived from the disubstituted compounds without any correction for interaction are also shown (curves 5 and 6). It will be seen that the above limits of μ_O give the extreme limits for the angle θ as 114—136°—more probable limits being *ca.* 120—134°. The atom polarisation is certainly not zero, however, so μ_O must be less than 0·38 and the real upper limit for θ must be lower. Sugden (*Trans. Faraday Soc.*, 1934, **30**, 734) reports P_A = 1·7 c.c. for triphenylmethane, so that P_A for aa-diphenylethylene is probably not less than 1·1 c.c., corresponding to μ_O = 0·30 D. and $\theta \ngtr 131°$. The sum of twice the atom polarisability for benzene (1·1 c.c.; Groves and Sugden, J., 1934, 1097) and for ethylene (0·39 c.c.; Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144) is 2·6 c.c. If the source of the atom polarisation is the effect of the field on the slightly polar bonds, additivity would be expected (Audsley and Goss, J., 1941, 864). This would correspond to a value of 0·14 D. for μ_0 and an upper limit of 126·5° for θ. From unpublished work in this Laboratory by Mr. N. J. Leonard, and from the fact that the electric polarisations of aromatic compounds are unaltered by the substitution of hydrogen by fluorine, it appears that the interaction moments in *p*-substituted fluoro-compounds are small or zero; θ values have therefore been calculated from the moment of αα-di-*p*-fluorophenylethylene without any correction for interaction. They are shown by curve 7 which obviously is quite different from curves 5 and 6 and agrees well with curves 1 and 2. It will be noticed, however, that the two curves for the values derived from the chloro- and bromo-compounds agree much better when it is assumed that $\delta_1\mu_S = \delta_2\mu_S$ (curves 3 and 4) than when it is assumed that $\delta_1\mu_S = 2\delta_2\mu_S$ (curves 1 and 2). It may therefore be concluded that more weight can be attached to the former two curves than to the others, so the lower limit for θ now appears to be *ca.* 122°. The true value of the angle therefore probably lies between 122° and 128°. There is little point in trying to fix closer limits from the available data.

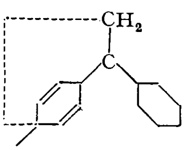


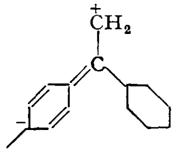
DISCUSSION.

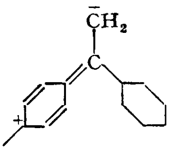
The valency angle of the quaternary carbon atom linking the two phenyl groups in αα-diphenylethylene was found to be 125° ± 3°; this is an unusually large value for an angle between single carbon valencies. The valency angles of the linking carbon atoms in diphenyl compounds are probably decided by the following three factors: (1) The natural valency angle of the atom for its particular valency state. (2) Repulsion between hydrogen atoms in the *o*-positions of the benzene rings. (3) Resonance leading to partial double-bond formation between the linking atom and the benzene rings; this promotes a coplanar configuration in which effect (2) is very strong, causing a widening of the angle.

The angle between the phenyl groups in *p*-substituted diphenylmethane has been found from electric dipole moment measurements to be 115° ± 5° (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). This is rather larger than the tetrahedral angle, 109·5°, but a slight increase in the angle may be expected from the operation of effect (2), which should be increased by thermal agitation. In this connection, measurements on diphenylmethane derivatives at high temperatures would be of interest.

In αα-diphenylethylene the linking carbon atom is part of a group containing a double bond $CH_2{=}C{<}$ and is in the trigonal sp^2 state, in which the natural valency angle is 120° (Penney, "The Quantum Theory of Valency," Methuen, 1935, Chap. IV)—compare the CH_2 angle of 118° in ethylene (Badger, *Physical Rev.*, 1934, **45**, 648; Penney, *Proc. Roy. Soc.*, 1937, *A*, **158**, 317). The observed angle is some 5° or more greater than the natural angle; this suggests that effects (2) and (3) are operative. Resonance leading to the formation of partial double bonds between the linking atom and the benzene rings is to be expected, because many Lewis–Langmuir structures can be drawn for the substance, in which there is a double bond between the quaternary carbon atom and the benzene ring, *e.g.*,







Calculations of the resonance energies in phenyl-substituted ethylenes have been made by Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 679) and by Wheland (*ibid.*, 1934, **2**, 474). The heats of formation derived from heats of combustion are consistent with the results of these calculations; but, in direct conflict with theory, the heat of hydrogenation of styrene (Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831) indicates almost no resonance at all. The available thermal evidence must therefore be considered inconclusive for the purpose of showing whether resonance of this type is important in these compounds.

Calculations of its effects on the length of the carbon–phenyl bond in styrene and stilbene have been made by Penney and Kynch (*Proc. Roy. Soc.*, 1938, *A*, **164**, 409), also by Lennard-Jones and Coulson (*Trans. Faraday Soc.*, 1939, **35**, 811); and these agree exactly with the values found experimentally by Robertson and Woodward (*Proc. Roy. Soc.*, 1937, *A*, **162**, 568), who found, from *X*-ray analysis of the stilbene crystal, a length of 1·44 A., corresponding to a bond order [on the Penney length/order scale (*loc. cit.*)] of 1·31. These facts are in harmony with the conclusions from our results, *viz.*, that conjugation between the benzene rings and the ethylenic double bond occurs to a very marked degree.

If there were the maximum possible degree of double-bonding between the linking carbon atom and the phenyl groups, the two latter should be coplanar. The van der Waals radius of hydrogen being taken as 1·2 A. (Pauling, " The Nature of the Chemical Bond," Cornell, 1940, p. 189) and the interatomic distances (Pauling, *op. cit.*, pp. 168, 172, 218) as: $C_{ar.}$–H = 1·09, $C_{ar.}$–$C_{ar.}$ = 1·39, $C_{ar.}$–$C_{qu.}$ = 1·45 A., it can easily be shown that for the phenyl groups to be coplanar with the ortho-hydrogen atom nuclei 2·4 A. apart, the angle between them must be 160°. Now, according to our calculations, the upper limit for this angle must be about 130°, and if the phenyl groups were coplanar the H–H internuclear distance would then be only 1·08 A. It is therefore probable that the phenyl groups are twisted out of a common plane. If θ is 130° the angle of twist, ψ, must be 28°; if θ is 125°, ψ must be 29·5°; and if θ is 120°, ψ must be 31°; so, to make the H–H distance the 2·4 A. which is believed to be necessary, the phenyl groups must be twisted about 30° out of the common plane.

A similar twisting is observed in *cis*-azobenzene (Robertson, J., 1939, 232) where it is as much as 50° and results in a notable diminution of the conjugation of the phenyl groups with the $^-N{=}N^-$ group as shown by the increase in length of the Ph–N= bonds. From the dimensions supplied by the author and some of the bond lengths previously quoted, it is easy to calculate that the H–H distance in this configuration is 2·26 A., which is very close to what has been taken above as the distance of minimum approach.

The final configuration may be regarded as attained through the contest between the steric repulsion of the hydrogen atoms and the resistance of the valency angle to enlargement, on the one hand, and resonance in favouring a coplanar configuration, on the other.

This work adds to the already large body of evidence that resonance can have marked effects upon spatial configurations of molecules. The converse has also been demonstrated by Birtles and Hampson (J., 1937, 10) and Ingham and Hampson (J., 1939, 981), who showed that spatial configuration affects resonance. The reality of a connection between the two can therefore be taken as established.

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