624. *Polarisation in Conjugated Systems. Part III. The Dipole Moments of Positional Isomers of Some Stilbene and Diphenyl Derivatives.*

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The effect on the dipole moment of the position of substitution of a polar group in stilbene or diphenyl is examined. *para*-Substitution by the Cl, NO_2, NH_2, NMe_2, and CN groups gives a moment larger than that of the corresponding derivative of benzene; *meta*-substitution gives a moment about the same; and *ortho*-substitution gives one which is lower. This is explained in terms of resonance. The moment of 2-dimethylaminostilbene is exceptionally small, because the dimethylamino-group is sterically prevented from conjugating with the aromatic system.

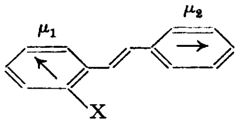
Sufficient dipole moments are now known of positional isomers of derivatives of the two hydrocarbons, stilbene and diphenyl, to allow a general statement to be made about the effect on polarity of the position of substitution. The available data are given in the table, and the dipole moments of the corresponding benzene derivatives are given also for comparison in the last column. Those relating to chlorodiphenyl have been treated in detail by Hampson and Weissberger, who take into account the effect of induction in the unsubstituted benzene ring (*J. Amer. Chem. Soc.*, 1936, **58**, 2111).

	Position of substitution:			
	4.	3.	2.	Ph.[a]
Chlorodiphenyl	1·64 [b, c]	1·64 [b]	1·45 [b, d]	1·60
Nitrodiphenyl	4·41 [e]	3·90 [f]	3·81 [g]	4·01
Aminodiphenyl	1·83 [h]	—	1·42 [i]	1·52
Aminostilbene	2·07 [e]	1·51 [e]	1·49 [e]	1·52
Dimethylaminostilbene	2·41 [e]	1·67 [e]	1·07 [e]	1·61
Cyanodiphenyl	4·33 [e]	—	3·81 [j]	4·05
Cyanostilbene	4·42 [e]	4·12 [e]	—	4·05

[a] All values in this column are taken from Table VIII, Part I. [b] Weissberger's second value (Hampson and Weissberger, *loc. cit.*) is assumed to supersede his first one (Weissberger and Sängewald, *Z. physikal. Chem.*, 1933, *B*, **20**, 145). [c] Literature values are: 1·5$_3$ (*idem, ibid.*), 1·63 (Næshagen, *ibid.*, 1934, *B*, **25**, 157), 1·63 (Hampson and Weissberger, *loc. cit.*), and 1·56 (Le Fèvre and Le Fèvre, *J.*, 1936, 1130). The last authors omit details of purity: ω–ε plots of their measurements differ markedly from those of Hampson and Weissberger, from which a moment of 1·64 has been recalculated. [d] Næshagen gives 1·44 (*loc. cit.*). Measured in present work (Part I). [f] Næshagen, *loc. cit.* The value of 3·40 given by Syrkin and Dyatkina ("Structure of Molecules," Butterworth, 1950, p. 222) is presumably a misprint. [g] Næshagen (*loc. cit.*) gives 3·79, Le Fèvre and Le Fèvre (*loc. cit.*) 3·80 (recalculated), and Lumbroso (*Bull. Soc. chim.*, 1949, **16**, D387) 3·82. [h] Literature values are: 1·73 (Næshagen, *loc. cit.*), 1·76 (Le Fèvre and Le Fèvre, *loc. cit.*), 1·74 (Kumler and Halverstadt, *J. Amer. Chem. Soc.*, 1941, **63**, 2182), and 1·71 (Bergmann and Weizmann, *Chem. Rev.*, 1941, **29**, 553). Kumler and Halverstadt's measurements are considered the most reliable; recalculation of them gives 1·83. [i] Næshagen, *loc. cit.* [j] Bergmann, *J.*, 1936, 402.

If the conjugated hydrocarbon radical is attached *para* to the other substituent in the first benzene ring, the moment in all cases is increased; if in the *meta*-position, it is hardly changed (differences ≯0·1); and if in the *ortho*-position, it is decreased. These facts can readily be explained on current theory. Resonance between the radical and the substituent can take place only when they are *ortho* or *para* to one another; and when it occurs, it should lead to an increase in moment of the *p*-substituted compounds (the case of 4-chlorodiphenyl receives separate consideration in Part V). The only effect of *m*-substitution of a conjugated system into a benzene derivative should be an inductive one, and it would be expected to be small.

The decreases brought about by *o*-substitution are, reading down the table, 0·15, 0·20, 0·10, 0·03, 0·54, and 0·24. These are probably partly due to induced moments (Hampson and Weissberger, *loc. cit.*). For the groups considered (except chlorine, which is considered later), the additional resonance involving the *o*-substituted conjugated system will decrease the moment relative to that of the parent benzene derivative because, as it involves a shift of charge from the benzene ring to the *o*-substituted system, the moment to which it gives rise will be partly opposed to the original one. This is indicated in the diagram, where μ_2 clearly has a component antiparallel to the original moment μ_1.



2-Aminostilbene shows an insignificant reduction relatively to aniline, whereas 2-dimethylaminostilbene shows a very large one relatively to dimethylaniline. The difference is too large to attribute to the slight difference in mesomeric effects of the two groups (Table II, Part V, p. 2824); it must be ascribed to the steric inhibition of resonance, such as is found in dimethylmesidine (Ingham and Hampson, *J.*, 1939, 981). Scale models show that this should not occur in 2-aminostilbene, on the other hand.

Twisting of either the dimethylamino-group or the styryl group about the bonds joining them to the benzene ring would relieve the interference, though only incompletely in the latter case. If the styryl group alone twisted through 90°, 2-dimethylaminostilbene would be expected to have much the same moment as dimethylaniline, 1·61. If, on the other hand, the dimethylamino-group twisted, a moment similar to that of the sterically-hindered dimethylmesidine (1·03 : Ingham and Hampson, *loc. cit.*) or 2 : 4 : 6-tribromodimethylaniline (1·05 : Few and Smith, *J.*, 1949, 2663) would be expected. The experimental result, 1·07, shows that the latter process occurs. A similar conclusion has been drawn from the ultra-violet absorption spectrum of the substance (Roe, personal communication).

It is particularly important to establish the coplanarity of the stilbene fragment in this compound for, if it were not coplanar, it would be an exception to the rule (Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, *A*, **241**, 147) that an essential feature of growth-inhibitory properties in stilbene derivatives is the unbroken conjugation of the stilbene system. This compound is active, though less so than the 4-substituted isomer.

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