623. *Polarisation in Conjugated Systems. Part II. Steric Hindrance in Derivatives of 4-Dimethylaminostilbene.*

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The exaltations and dipole moments of the following derivatives of 4-dimethylaminostilbene are discussed: 2′-chloro-, 2′-methyl-, 2′ : 5′-dimethyl-, 2 : 2′-dimethyl-, 2′-ethyl-, and 2′ : 4′ : 6′-trimethyl-. The conjugation is found to decrease in this order. This is attributed to steric hindrance.

Hampson and his co-workers (*J.*, 1937, 10; 1939, 981) were the first to show that the anomalous dipole moments of mesitylene and durene derivatives were due to the steric inhibition of resonance in the molecules, and their work has been extended by Kadesch and Weller (*J. Amer. Chem. Soc.*, 1941, **63**, 1310) and by Bentley, Everard, Marsden, and Sutton (*J.*, 1949, 2957).

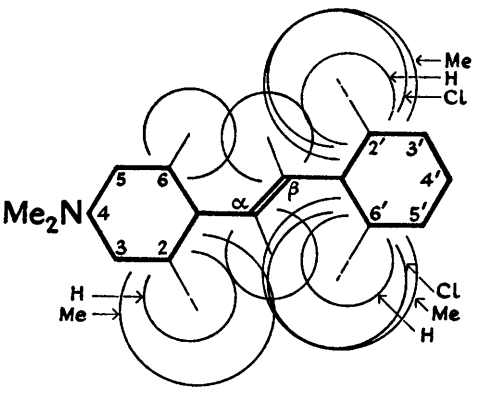
The moments of some alkyl derivatives of 4-dimethylaminostilbene have now been measured, together with their molar refractions (Part I); and both show anomalies attributable to steric inhibition of resonance. The results are collected in the table.

Exaltations and dipole moments of 4-dimethylaminostilbene derivatives.

	E[*R*]D.*	μ (obs.).	μ (expected).
4-Dimethylaminostilbene	7·5	2·41	—
2′-Chloro-4-dimethylaminostilbene	7·8	—	—
4-Dimethylamino-2′-methylstilbene	—	2·51	2·60
4-Dimethylamino-2′ : 5′-dimethylstilbene	—	2·31	2·41
4-Dimethylamino-2 : 2′-dimethylstilbene	3·3	2·25	⩾2·41
4-Dimethylamino-2′-ethylstilbene	—	2·45	2·73
4-Dimethylamino-2′ : 4′ : 6′-trimethylstilbene	1·6	2·11	2·41

* Exaltations are expressed relative to that of stilbene, taken as 0 c.c. (see Part I, Discussion, p. 2812).

The molar exaltations of 4-dimethylaminostilbene and of both its 2′- and its 4′-chloro-derivatives are much the same (the last is 8·1), whereas those of the 2 : 2′-dimethyl and 2′ : 4′ : 6′-trimethyl derivatives are markedly less. These figures indicate (i) that there is negligible inhibition of conjugation in the chloro-compounds, but appreciable inhibition in the



Dimensions are taken from Pauling, "Nature of the Chemical Bond," Cornell, 1945, *and from Robertson and Woodward,* Proc. Roy. Soc., 1937, *A*, **162**, 568.

methyl compounds, and (ii) that two *o*-methyl groups on the same ring are more effective than one on each ring. This is in accordance with expectation. Pauling gives the van der Waals radius of a chlorine atom as 1·8 A., and that of a methyl group as 2·0 A.; and examination of scale models demonstrates the greater effectiveness of the former combination of two methyl groups than of the latter (see figure).

The dipole moments give the same indications. The "expected" values are calculated vectorially without allowing for inhibition of resonance; it is assumed that a methyl group

substitution moment is the same as that of toluene (0·35), and that an ethyl group moment is the same as that of ethylbenzene (0·58; Baker and Groves, *J.*, 1939, 1144). The direction of the moment of the parent compound, 4-dimethylaminostilbene, is considered in Part IV; and that of the 2′-chloro-derivative in Part VI.

It is seen that the steric effect of the several substitutions appears to increase in the order of arrangement in Table I. Conclusions drawn by Haddow, Harris, Kon, and Roe (*Phil. Trans.*, 1948, *A*, **241**, 147) from a study of the ultra-violet absorption spectra of some of the substances are similar to ours, except that the effect of a single *o*-methyl group could not be positively established. The present results support the hypothesis put forward in that paper, that such compounds show growth-inhibitory activity only when the stilbene system is coplanar.

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