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STERIC ENHANCEMENT OF RESONANCE

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THOUGH steric inhibition of resonance is well-known, steric enhancement of resonance is almost unknown. We report in this communication the electric dipole moments of a number of compounds which indicate that there is steric enhancement of resonance in some substituted anisoles and thioanisoles. The data given in Table 1 reveal certain interesting points.

Table 1

Anisole	μ(D) in C_6H_6 at 30°C	Reference Compound	μ(D)
2-t-Butyl-4-fluoro	2.16	p-F.C_6H_4.OMe	2.04[1]
2-t-Butyl-4-chloro	2.64	p-Cl.C_6H_4.OMe	2.32[2]
4-Bromo-2-t-butyl	2.74	p-Br.C_6H_4.OMe	2.23[3]
4-Chloro-2-methyl	2.58	p-Cl.C_6H_4.OMe	2.32
4-Bromo-2-methyl	2.52	p-Br.C_6H_4.OMe	2.23
4-Bromo-2,6-dimethyl	2.27	p-Br.C_6H_4.OMe	2.23

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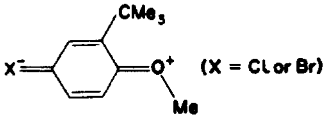
[1] N.J. Leonard and L.E. Sutton, J. Amer. Chem. Soc. **70**, 1564 (1948).

[2] C.S. Copel and M.W. Rigg, ibid. **73**, 3584 (1951).

[3] C.P. Smyth and W.S. Walls, ibid. **54**, 3230 (1932).

In p-halogenoanisoles the dipole moment acts towards the halogen. So an alkyl group such as t-butyl or methyl, when present ortho to the methoxyl group, should be expected to cause a slight increase in the moment. This is indeed the case with 2-t-butyl-4-fluoroanisole. There is, however, a much higher increase in the moments of 2-t-butyl-4-chloro- and 4-bromo-2-t-butyl-anisole. The moment of 4-bromo-2-t-butylanisole is even greater than the sum of the moments of p-bromoanisole and t-butylbenzene. 4-Chloro- and 4-bromo-2-methylanisole also have significantly higher moments than those of p-chloro- and p-bromo-anisole, respectively, though the differences for the t-butyl compounds are larger. It is also of interest to note that the moment of 4-bromo-2,6-dimethylanisole is almost the same as that of p-bromoanisole. The larger moments of 2-t-butyl-4-chloro- and 4-bromo-2-t-butyl-anisole seem to be due to the O-methyl occupying a position away from the alkyl group. Such a preferred orientation will restrict the rotation of -OMe and the probability of its attaining planarity with the benzene ring will increase. Then the following structure, in which the halogen expands its valence shell by utilising



one of its vacant d-orbitals, makes a greater contribution to the ground state of the molecule. When the halogen involved is fluorine, there can be no d-orbital resonance.[4]

If the above reasoning is correct, the dipole moments of 2-methyl-4-nitroanisole, 4-methoxy-3-methylacetophenone and methyl 2-methyl-4-nitrophenyl sulphide should also have moments higher than those expected. Furthermore, the dipole moments of 2,6-dimethyl-4-nitroanisole, 4-methoxy-3,5-dimethylacetophenone and methyl 2,6-dimethyl-4-nitrophenyl sulphide should almost be the same as or even lower than the moments of p-nitroanisole, p-methoxyacetophenone and methyl p-nitrophenyl sulphide, respectively, because in the former compounds there can be no preferred orientation of -OMe or -SMe to cause enhanced resonance. On the other hand the two ortho methyl groups will cause steric inhibition of resonance. With a view to testing these ideas the dipole moments of compounds listed in Table 2 have been experimentally determined and they have also been calculated for comparison.

The dipole moments of 2-methyl-4-nitroanisole, 4-methoxy-3-methylacetophenone and methyl 2-methyl-4-nitrophenyl sulphide are seen to support the concept of steric enhancement of resonance. The difference between the observed and

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[4] V. Baliah and (Miss) M. Uma, Naturwiss. 45, 512 (1958).

Table 2

Compound	Dipole moment (D)	
	Observed (in C_6H_6 at 30°C)	Calcd. for free rotation of -OMe or -SMe
p-Nitroanisole	4.74	4.51
2-Methyl-4-nitroanisole	5.29	4.71
2,6-Dimethyl-4-nitroanisole	4.77	4.89
p-Methoxyacetophenone	3.51	3.37
4-Methoxy-3-methylacetophenone	3.91	—
4-Methoxy-3,5-dimethylacetophenone	3.49	3.62
Methyl p-nitrophenyl sulphide	4.36[5]	3.78
Methyl 2-methyl-4-nitrophenyl sulphide	4.77	3.99
Methyl 2,6-dimethyl-4-nitrophenyl sulphide	4.12	4.17

calculated moments of p-nitroanisole is 0.23 D which is attributable to the resonance interaction of the -OMe and $-NO_2$ groups. But in the case of 2-methyl-4-nitroanisole the difference between the observed and calculated moments is 0.58 D, the observed value being higher. This can only be interpreted to mean that the resonance interaction of

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[5] H. Lumbroso and G. Dumas, Bull. soc. chim. France 651 (1955).

-OMe and -NO_2 in this compound is greater than in p-nitroanisole. The same may be said of 4-methoxy-3-methylacetophenone and methyl 2-methyl-4-nitrophenyl sulphide. The view that there is steric enhancement of resonance in the above compounds gains further support from the fact that the expected steric inhibition of resonance is revealed in 4-substituted 2,6-dimethylanisoles.