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MOLECULAR POLARIZABILITIES OF SOME HALOGENOANILINES AND N,N-DIMETHYLANILINES

RECENTLY Lippincott and Stutman[1] have proposed the use of a semi-empirical δ-function model for the calculation of molecular polarizabilities. The δ-function model has been applied by several workers[2–8] for different systems. The molecular polarizability can also be obtained from the experimentally obtained molar refraction of the system by the Lorentz–Lorenz equation In this note, we have calculated the polarizabilities of some halogenoanilines and N,N-dimethylanilines with a view to testing the applicability of the δ-function model and compare the results with those obtained from the measured molar refractions[9].

The mean molecular polarizability is given by the expression

$$\alpha_M = \tfrac{1}{3} [\Sigma \alpha_{\|p} + \Sigma \alpha_{\|n} + \Sigma 2\alpha_\perp] \qquad (1)$$

where $\Sigma\alpha_{\|p}$ and $\Sigma\alpha_{\|n}$ are the contributions from bond region electrons and non-bond region electrons res-

pectively to the bond parallel polarizability and $\Sigma 2\alpha_\perp$ is the sum of the bond perpendicular contribution.

The bond region electron contribution to parallel polarizability after introducing the polarity correction is calculated using linear combination of atomic δ-function wavefunction[1] and is given by

$$\alpha_{\|p} = \frac{4n A_{12}}{a_0} \left[\frac{R^2}{4} + \frac{1}{2 C_{R12}^2} \right]$$
$$\times \exp\left[-\tfrac{1}{4}(X_1 - X_2)^2 \right] \qquad (2)$$

where $A_{12} = (A_1 A_2)^{1/2}$, A being the δ-function strength determined from reduced electronegativity of the atom, a_0 is the radius of the first Bohr orbit and n is the bond order. R is the internuclear distance at equilibrium configuration and

$$C_{R12} = (n_1 n_2 N_1 N_2)^{1/4} (A_1 A_2)^{1/2}$$

where n_i ($i = 1, 2$) is the principal quantum number of the valence shell and N_i is twice the column number in the periodic table. X_1 and X_2 are the electronegativities of the atoms 1 and 2 respectively on the Pauling scale.

The non-bond region electron contribution is taken from Linnett[10] as

$$\Sigma \alpha_{\|n} = \Sigma f_i a_i \qquad (3)$$

where f_i is the fraction of valence electrons in the ith atom not involved in bonding and a_i is the atomic polarizability of the atom.

The perpendicular component as given by Lippincott and Stutman[1] is

$$\Sigma 2\alpha_\perp = n_{df} \frac{\Sigma x_j^2 a_j}{\Sigma x_j^2} \qquad (4)$$

where $n_{df} = (3N - 2nb)$ is called the residual atomic polarizability degrees of freedom.

For the calculation of molecular polarizabilities of halogenoanilines and N,N-dimethylanilines the equations (1)–(4) have been employed. The atomic polarizabilities and δ-function strengths are taken from Ref. 1 and the structural data from Refs. 11 and 12. The electronegativity values are taken from Durrant and Durrant[13]. The calculated A values and C_{R12} values for various bonds are given in Table I. The n_{df} values for anilines and N,N-dimethylanilines are taken as 20 and 26 respectively.

TABLE I

Delta function strengths A's (in 10^3 cm^{-1}) and C_R's (in 10^3 cm^{-1}) of bonds

	Bond						
	C–C	C–H	C–N	C–F	C–Cl	C–Br	C–I
A	1·5989	1·7384	1·6737	1·7940	1·5086	1·3831	1·3285
C_{R12}	3·3958	4·1346	7·0790	8·2536	7·6805	7·5670	7·6852

TABLE II

Observed and calculated mean molecular polarizabilities (in 10^{-25} cm^3)

Molecule	$\Sigma a_{\parallel_p}$	$\Sigma a_{\parallel_n}$	$\Sigma 2 a_\perp$	a_M(calcd.)	a_M(obsd.)	
					para	meta
Anilines						
Aniline	204·180	2·927	159·330	121·170	120·899	
Fluoroaniline	217·479	7·172	150·329	122·903	118·910	120·099
Chloroaniline	253·331	14·869	174·520	142·617	145·467	142·296
Bromoaniline	268·166	19·564	183·772	150·646	153·701	155·951
Iodoaniline	295·678	28·446	193·458	163·045	177·600	179·951
Dimethylanilines						
Dimethylaniline	286·110	2·972	203·881	163·327	160·925	
Fluorodimethylaniline	291·005	7·172	195·457	162·154	163·304	163·304
Chlorodimethylaniline	321·349	14·869	218·451	179·934	182·726	197·788
Bromodimethylaniline	336·183	19·564	227·123	187·769	193·428	196·202
Iododimethylaniline	370·067	28·446	236·004	199·900	..	218·399

The calculated values of $\Sigma a_{\parallel_p}$, $\Sigma a_{\parallel_n}$, $\Sigma 2a_\perp$ and a_M (calcd.) are the same for para and meta derivatives. These values and the a_M (obsd.) are tabulated (Table II). The data in Table II clearly show that there is a good agreement between the theoretical and experimental values indicating the validity of the application of the δ-function model for calculating the polarizabilities of these bases. It may also be noted here that as the electronegativity of the substituent group decreases the difference between the observed and calculated values increases. The marked lower value of $\Sigma 2a_\perp$ in the fluoro compounds is due to the fact that a (*cf.* eq. 4) is small for fluorine in comparison with the a values for other halogens and hydrogen.

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