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IONIZATION POTENTIALS OF PRIMARY AROMATIC AMINES AND AZA-HYDROCARBONS

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The recent publication of some calculations of molecular parameters, including ionization potentials, for some amino- and hydroxy-aromatic compounds[1] prompts us to report some further work on the estimation of ionization potentials from charge-transfer spectra. Although amino compounds are of interest to the molecular biologist, only a few measurements of their ionization potentials by any method have been reported (see table).

In a previous paper[2] we obtained the relationship between the ionization potential of a donor, (I_D), and the energy of the long wavelength charge-transfer band of its complex with tetracyanoethylene measured in chloroform solution, ($h\nu_{CT}$), shown in equation (1):

$$h\nu_{CT} = 0.82\ I_D - 4.28 \text{ e.v.} \tag{1}$$

We then used this to determine I_D values for a number of N-substituted anilines and ring substituted N,N-dimethyl- and N,N-diethylanilines, the rate of ring tricyanovinylation being fairly slow. We have extended this study to primary aromatic amines which can undergo either ring- or N-tricyanovinylation, and the results are shown in the table, experimental details being as in ref. 2. Also included in the table are some results obtained from other workers' data for aromatic amine and aza-aromatic hydrocarbon-tetracyanoethylene complexes. Although (1) was obtained empirically from studies of substituted benzenes, there seems to be no reason in principle why this expression should not be used to predict ionization potentials for heterocyclic molecules, and it is of interest to note that the agreement between values obtained using (1) and Nishimoto and Forster's calculated values[1] is extremely good. I_D values obtained from charge-transfer data with various acceptors are always higher than electron-impact values, but are generally in good agreement with photoionization data.

Values for the ionization potentials of the primary amines follow a similar pattern to that for the tertiary amines. The introduction of an electron-releasing methyl group decreases the I_D value in accordance with the position of substitution, i.e. para < ortho < meta, and varying the para-alkyl group results in an increase in the ionization potential as the bulk of the substituent increases. Substitution of a second methyl group into the ring lowers the I_D value further in the order expected from consideration of their combined electron-releasing inductive effects, i.e. 3,5- > 2,3- > 2,5- > 2,6- > 2,4- aniline. The ionization potentials of the para-halogen substituted compounds decrease with decreasing electro-negativity of the halogen. Para-phenyl and para-alkoxyl groups decrease the value of I_D relative to aniline, as does an amino group substituted at any position in the ring (I_D meta- > ortho- > para-phenylene diamine). The I_D values obtained using equation (1) above, are almost identical with those interpolated from Nepras and Zahradnik's spectroscopic data[3] and with those obtained from charge-transfer spectra, using p-bromanil as acceptor[4], although our value for p-chloroaniline is lower (see table). The mass spectroscopically obtained values of Crable and Kearns also reproduce the same pattern of results, but the values obtained are 0.5 - 0.6 e.v. higher. (c.f. Streitwieser's values calculated using the ω-technique[6].)

The effect of annellation upon the charge-transfer spectrum and hence upon the ionization potential, has been studied by Nepras and Zahradnik[3] who showed that the charge-transfer transition energy decreased in accordance with the decreasing charge density on the exocyclic amino group. I_D's interpolated from their data are shown in the table, as are values for some aza-aromatic hydrocarbons also interpolated from similar data[3]. The agreement between these interpolated values and the few calculated values for these compounds is remarkably good. In the aza-hydrocarbon series addition of one benzene ring to quinoline lowers the I_D value in all cases, linear annellation being the more effective, whereas angular addition of a benzene ring to acridine increases I_D slightly. A similar effect is observed in the hydrocarbon series and is in accord with the calculated increase in energy of the highest occupied molecular orbitals of these annellated hydrocarbons[7]. Of the two ~~sets~~ of values calculated by Nishimoto and Forster[1] by a self consistent field method neglecting penetration integrals, the one derived using two-centre integrals obtained from theoretical integrals with "adjusted exponents" gives better agreement with these spectroscopically derived I_D values.

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TABLE

Compound	$h\nu_{CT}^{a}$ e.v.	I_D^b e.v.	I_D^c e.v.
o-toluidine	1.940	7.59	$8.38^d, 7.75^e, 7.69^f$
m-toluidine	2.019	7.68	$7.5^g, 8.27^d, 7.75^e$
p-toluidine	1.925	7.57	$8.14^d, 8.2^h, 7.65^e, 7.58^f$
o-ethylaniline	1.925	7.57	
p-ethylaniline	1.971	7.62	
p-cumidine	2.019	7.68	
p-tertbutylaniline	2.052	7.72	
p-fluoroaniline	2.178	7.87	
p-chloroaniline	2.087	7.77	8.00^f
p-bromoaniline	2.069	7.74	
p-iodoaniline	2.003	7.66	
2-amino-1,3-dimethylbenzene	1.839	7.46	
3-amino-1,2-dimethylbenzene	1.881	7.51	

Compound	$h\nu^{a}_{CT}$, e.v.	I^{b}_{D}, e.v.	I^{c}_{D}, e.v.
2-amino-1,4-dimethylbenzene	1.867	7.50	
4-amino-1,3-dimethylbenzene	1.786	7.40	
3-amino-1,5-dimethylbenzene	1.961	7.61	
o-anisidine	1.839	7.46	
p-anisidine	1.799	7.41	7.82^{d}
p-phenetidine	1.774	7.38	
4-aminobiphenyl	$1.867, 1.862^{j}$	7.50, 7.49	
1-naphthylamine	$1.701, 1.676^{j}$	7.29, 7.26	$7.39^{f}, 7.4^{e}, 7.31^{k}, 7.46^{k}$
2-naphthylamine	$1.774, 1.763^{j}$	7.38, 7.37	$7.5^{e}, 7.48^{k}, 7.61^{k}$
o-phenylenediamine	1.749	7.35	$8.00^{d}, 7.45^{e}, 7.36^{f}$
m-phenylenediamine	1.853	7.48	7.96^{d}
p-phenylenediamine	1.495	7.04	$7.58^{d}, 7.15^{e}, 6.59^{k}, 6.73^{k}$
2-aminophenanthrene	1.912^{j}	7.55	
9-aminophenanthrene	1.614^{j}	7.19	
2-aminopyrene	1.813^{j}	7.43	
1-aminopyrene	1.316^{j}	6.82	
6-aminochrysene	1.453^{j}	6.99	
2-aminodiphenyl	1.912^{j}	7.55	
2-aminostilbene	1.775^{j}	7.39	
quinoline	2.731^{j}	8.55	$8.55^{k}, 8.62^{k}, 8.59^{l}$
acridine	2.260^{j}	7.98	$7.98^{k}, 8.15^{k}, 8.04^{f}$
benzo[f]quinoline	2.595^{j}	8.38	
benzo[f]isoquinoline	2.545^{j}	8.32	

Compound	$h\nu^{a}_{CT}$, e.v.	I_D^b e.v.	I_D^c.e.v.
benzo[h]quinoline	2.558[j]	8.34	8.35[l]
benzo[g]quinoline	1.937[j]	7.58	7.68[k],7.91[k]
Phenanthridine	2.595[j]	8.38	8.54[l]
benz[a]acridine	2.334[j]	8.07	
benz[c]acridine	2.334[j]	8.07	

a. Energy of charge-transfer transition with TCNE

b. Calculated using equation (1); ± 0.1 e.v.

c. Values obtained by other workers

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