N–H Bond Dissociation Energies, Reduction Potentials and pK_as of Multisubstituted Anilines and Aniline Radical Cations

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The one-electron reduction potential and the pK_a of 10 *ortho-*, *meta-* and *para*-substituted aniline radical cations have been determined by means of pulse radiolysis. The N–H bond dissociation energies of the corresponding anilines were also determined using a thermodynamic cycle. All three properties of the aniline radical cations and the corresponding anilines were shown to be linearly dependent on the sum of the Brown substituent constants, $\Sigma\sigma^+$. A conditional scale for *ortho* substituents was also derived ($\sigma_o^+ = 0.73\sigma_p^+$). The results from this work along with previously published results have been used to derive a linear free energy relationship between one-electron reduction potentials of benzene radical cations and the substituent pattern. In addition an equation for the calculation of X–Y bond dissociation energies of arbitrarily substituted molecules with the general formula Ph–X–Y is proposed.

Anilines are of both basic chemical and biological importance. The chemical activity of anilines is partly due to their hydrogen-donating (reducing) ability. Thus, anilines fulfil some important requirements for antioxidants and are used as such, *e.g.*, in polymer materials. Although the toxicity of a large number of substituted anilines limits their use, a basic understanding and quantification of the effects of ring substituents on the chemical activities is of great interest.

Recent studies of the redox properties of anilines have mainly been focused on the effects of 4-substituents.[1,2] In this work we have studied the effects of 2-, 3- and 4-substituents as well as their combined effect.

One-electron oxidation of anilines can easily be accomplished by radiation chemical methods, *e.g.*, pulse radiolysis. The reaction with a radiolytically formed oxidant, as exemplified by $N_3^\bullet$, results initially in the formation of aniline radical cations [reaction (1)]. The cations thus formed can be deprotonated

$$PhNH_2 + N_3^\bullet \rightleftharpoons PhNH_2^{\bullet +} + N_3^- \qquad (1)$$

[reaction (2)] to yield the corresponding anilinyl radical. These

$$PhNH_2^{\bullet +} \rightleftharpoons PhNH^\bullet + H^+ \qquad (2)$$

two equilibria are characterised by the one-electron reduction potential (E°) and the pK_a value of the aniline radical cation, respectively. In a recent study we measured these properties for 4-substituted anilines in aqueous solution by means of pulse radiolysis.[2] These quantities can also be used to calculate the N–H bond dissociation energy of the corresponding anilines [eqn. (3)].[3] The constant C in eqn. (3) is solvent dependent,

$$D(\text{X–H}) = 96.48\,E^\circ + 5.70\,\text{p}K_a + C\,(\text{kJ mol}^{-1}) \qquad (3)$$

but appears to be unaffected by the substituent. The same type of information can also be obtained from electrochemical measurements.

The increasing amount of experimentally determined one-electron reduction potentials of substituted benzene radical cations have enabled us to derive a linear free energy structure–activity relationship for 1,4-substituted benzene radical cations.[4] Similar relationships have also been shown to hold for the N–H bond dissociation energies of 4-substituted anilines and the pK_as of 4-substituted aniline radical cations.[2] In addition the reduction potentials of substituted phenoxyl radicals and the O–H bond dissociation energies of substituted phenols have been shown to follow linear free energy relationships of the same kind.[5]

In this work we have measured the one-electron reduction potential and pK_a of 10-substituted aniline radical cations in water. The results have been used to quantify the effect of arbitrary substitution on the one-electron reduction potential of benzene radical cations, N–H bond dissociation energies of anilines and pK_as of aniline radical cations. We also propose an equation to estimate X–Y bond dissociation energies of arbitrarily substituted molecules with the general formula Ph–X–Y.

Experimental

All chemicals of the purest grade available (Aldrich and Merck) were used as supplied. Millipore Milli-Q filtered water was used throughout. Radiolysis of water results in the formation of $OH^\bullet$, e^-_{aq}, H_2O_2, H_2 and H_3O^+, with $OH^\bullet$ and e^-_{aq} being the major radical species with primary radiation chemical yields of 0.28 μmol J^{-1} each[6] above pH 3. N_2O-saturated solutions were used in order to convert the reducing solvated electron into the oxidising hydroxyl radical[6] ($G_{OH} = 5.6 \times 10^{-7}$ mol J^{-1}) unless otherwise stated.

The pulse radiolysis equipment consisted of a linear accelerator delivering 3 MeV electrons and a computerised optical detection system.[7] The pulses were of 5–10 ns duration giving doses of 3–6 Gy. For dosimetry an N_2O-saturated 10^{-2} mol dm^{-3} KSCN solution was used.[8] The $G\varepsilon$ value of $(SCN)_2^{\bullet -}$ was taken to be 4.78×10^{-4} m^2 J^{-1} at 500 nm.

Primary oxidation of the substituted anilines was carried out by $N_3^\bullet$ in solutions at pH values above the pK_a of HN_3 (pK_a = 4.7). In solutions with pH near or below 4.7, $SO_4^{\bullet -}$ (reduction potential measurements) or $Br_2^{\bullet -}$ (pK_a measurements) was used for the primary oxidation of the substituted anilines. These three primary oxidants were produced in the following way upon irradiation.

$$^\bullet OH + N_3^- \longrightarrow OH^- + N_3^\bullet \qquad (4)$$

$$e^-_{aq} + S_2O_8^{2-} \longrightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad (5)$$

$$^\bullet OH + Br^- \longrightarrow OH^- + Br^\bullet \qquad (6a)$$

$$Br^\bullet + Br^- \longrightarrow Br_2^{\bullet -} \qquad (6b)$$

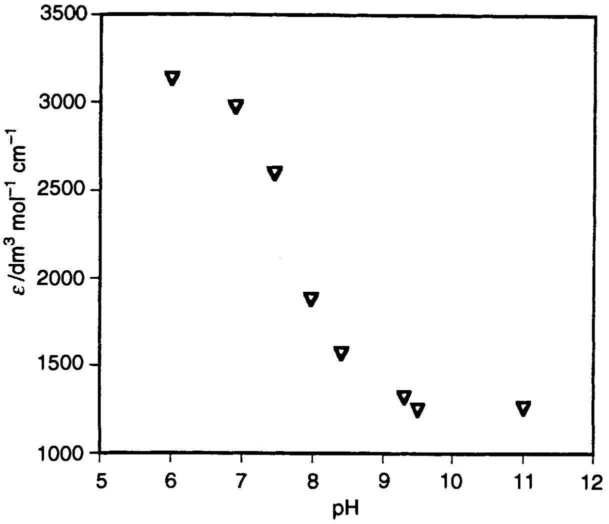

Fig. 1 pH titration curve for the 2-methylaniline radical cation (430 nm)

The above reactions have the following rate constants (dm^3 mol^{-1} s^{-1}): $k_4 = 1.2 \times 10^{10}$,[9] $k_5 = 1.1 \times 10^{10}$,[9] $k_{6a} = 1.1 \times 10^{10}$,[9] and $k_{6b} = 1.2 \times 10^{10}$,[10] respectively. The concentrations of N_3^-, $S_2O_8^{2-}$ and Br^- were 10^{-2}, 10^{-2} and 0.1 mol dm^{-3}, respectively. When $SO_4^{\bullet -}$ was used as the primary oxidant, 2×10^{-2} mol dm^{-3} 2-methylpropan-2-ol was added to the Ar-purged solution to scavenge the hydroxyl radicals. The use of OH$^\bullet$ for oxidation of the anilines was avoided, OH$^\bullet$ being known to participate in reactions other than one-electron oxidation. The reduction potential measurements were performed at pH values lying between the pK_a of the substituted anilinium cation and that of its corresponding radical cation. Phosphate buffers, borate buffers, carbonate buffers, sulfuric acid and NaOH were used to adjust the pH.

Methods.—The optical spectra of substituted aniline radical cations and the corresponding substituted aniline radicals differ markedly, making determination of radical cation pK_a values possible. The pK_a curve is obtained simply by measuring the absorbance at a suitable wavelength for a number of different pH values (see Fig. 1) and allowing for differences in the dose.

The one-electron reduction potentials of the substituted aniline radical cations were determined by measuring the equilibrium concentrations of radical cations or the radicals formed upon oxidation of the reference substance, with varying concentrations of substituted aniline and reference substance [reaction (7)].[11] The resulting equilibrium concentrations yield

$$\mathrm{PhNH_2} + \mathrm{Ref}^{\bullet(n)} \rightleftharpoons \mathrm{PhNH_2}^{\bullet+} + \mathrm{Ref}^{(n-1)} \qquad (7)$$

the equilibrium constant which can be inserted into the Nernst equation to calculate the one-electron reduction potential. The redox partners employed undergo the same charge change as the $\mathrm{PhNH_2}^{\bullet+}/\mathrm{PhNH_2}$ couples, *i.e.* the charge changes from 0 to +1 during oxidation.[12] Consequently the equilibrium constant K_7 can, to a good approximation, be regarded as independent of the ionic strength. The rates of equilibration can also be measured and used to obtain a kinetically determined equilibrium constant.

Equilibrium constants are best determined by plotting $1/A$ (A = absorbance at equilibrium) or k_{obs} against the ratio between the concentrations of substituted aniline and reference substance. The equilibrium constant is obtained from eqn. (8) which can be shown to hold for the equilibrium

$$1/A = \left\{1 + \frac{[\text{reference substance}]}{K[\text{substituted aniline}]}\right\}\frac{1}{A^\circ} \qquad (8)$$

[reaction (7)]. A° is the maximum signal obtainable. The forward and reverse rate constants used to calculate the 'kinetic' equilibrium constant were determined using eqn. (9).

$$\mathrm{k_{obs}} = k_f[\text{substituted aniline}] + k_r[\text{reference substance}] \qquad (9)$$

The experimental conditions for the reduction potential and the pK_a measurements are given in Tables 1 and 2. The reference substances (reduced form given) employed were 1,4-$(CH_3O)_2$–C_6H_4, 1,2,4-$(CH_3O)_3$–C_6H_3, 4-NH_2–PhNH_2 and promethazine [10-(2-dimethylaminopropyl)phenothiazine],* their one-electron reduction potentials *vs.* NHE being 1.30 V,[4] 1.13 V,[4] 0.59 V[2] and 0.91 V,[2] respectively.

Results and Discussion

Table 3 contains the redox equilibrium constants, K_A and K_{kin} (derived using the two methods previously described), the one-electron reduction potentials, E° ($\mathrm{PhNH_2}^{\bullet+}/\mathrm{PhNH_2}$) and the p$K_a$ values determined in this work.

Since there is no established σ- or σ^+-scale for *ortho* substituents we have derived a conditional scale for anilines by plotting the change in one-electron reduction potential and the change in pK_a upon *ortho* substitution of aniline radical cations against the Hammett σ_p and the Brown σ_p^+ constants, respectively. The resulting linear least-squares fit was better for the Brown σ_p^+-scale[13] than for the Hammett σ_p-scale.[13] The conditional σ_o^+-scale is given by eqn. (10). The

$$\sigma_o^+ = 0.73\sigma_p^+ \qquad (10)$$

corresponding scale for phenoxyl radicals has been found to be $0.66\sigma_p^+$ thus an *ortho* scale could roughly be estimated as $0.7\sigma_p^+$.[5]

One-electron Reduction Potentials.—The one-electron reduction potentials determined in this work and some previously published[2] reduction potentials are plotted against the sum of the substituent constants ($\Sigma\sigma^+$) (see Fig. 2). As may be expected, electron-donating substituents in *ortho* and *para* positions lower the reduction potential. Similarly, electron-withdrawing substituents raise the potentials. Eqn. (11)

$$E^\circ = 1.05 + 0.31\sum_{i=2}^{6}\sigma_i^+ (\text{V } vs. \text{ NHE}) \quad R^2 = 0.92 \qquad (11)$$

describes the substituent dependence on one-electron reduction potentials of aniline radical cations (the line drawn in Fig. 2). σ_i^+ in eqn. (11) denotes σ_o^+ for substituents in positions 2 and 6, σ_m^+ for substituents in positions 3 and 5 and σ_p^+ for the substituents in position 4. The slope of the straight line in Fig. 2 (0.31) is close to 0.28, given by a previously derived relationship for 1,4-disubstituted benzene radical cations[4] [eqn. (12)] where σ_{p1}^+ is −1.30 for anilines.

$$E^\circ = 2.2 + 0.8(\sigma_{p1}^+ + \sigma_{p4}^+) + 0.4\sigma_{p1}^+\sigma_{p4}^+ \qquad (12)$$
$$(\text{V } vs. \text{ NHE})$$

The last term in eqn. (12) is a 'cross-interaction constant'[14] accounting for the non-additivity of the substituent constants.

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* Even though the reference substance promethazine formerly undergoes a charge change from +1 to +2 (due to a charged side chain), the reactive centre changes its charge from 0 to +1 during oxidation.

Table 1 Experimental conditions for reduction potential measurements

Substituted aniline (conc./mol dm^{-3})	Primary oxidant	pH	Ref. substance (conc./mol dm^{-3})	λ/nm
2-CF_3-$PhNH_2$ (5×10^{-4}–9×10^{-4})	$SO_4^{\bullet -}$	3	1,2,4-$(CH_3O)_3$-C_6H_3 (10^{-4}–10^{-3})	460
3-CF_3-$PhNH_2$ (1×10^{-4}–6×10^{-4})	$SO_4^{\bullet -}$	3	1,4-$(CH_3O)_2$-C_6H_4 (10^{-4}–10^{-3})	460
2-CH_3-$PhNH_2$ (5×10^{-4}–10^{-3})	$N_3^{\bullet}$	7	Promethazine (1×10^{-5}–5×10^{-4})	525
2,4-$(CH_3)_2$-$PhNH_2$ (1×10^{-4}–8×10^{-4})	$N_3^{\bullet}$	5.5	Promethazine (2×10^{-4}–9×10^{-4})	525
3,4-$(CH_3)_2$-$PhNH_2$ (1×10^{-4}–8×10^{-4})	$N_3^{\bullet}$	6	Promethazine (2×10^{-4}–9×10^{-4})	525
3,5-$(CH_3)_2$-$PhNH_2$ (5×10^{-4}–10^{-3})	$N_3^{\bullet}$	5.5	Promethazine (1×10^{-5}–5×10^{-4})	525
2-CH_3O-$PhNH_2$ (3×10^{-4}–9×10^{-4})	$N_3^{\bullet}$	7	Promethazine (1×10^{-4}–7×10^{-4})	525
2,4-$(CH_3O)_2$-$PhNH_2$ (5×10^{-4}–10^{-3})	$N_3^{\bullet}$	9.2	4-NH_2-$PhNH_2$ (1×10^{-5}–5×10^{-4})	480
3,4-$(CH_3O)_2$-$PhNH_2$ (5×10^{-6}–10^{-4})	$N_3^{\bullet}$	6	Promethazine (9×10^{-4}–10^{-3})	525
3,5-$(CH_3O)_2$-$PhNH_2$ (5×10^{-4}–9×10^{-4})	$N_3^{\bullet}$	5.7	3,5-$(CH_3)_2$-$PhNH_2$ (1×10^{-4}–5×10^{-4})	570

Table 2 Measuring wavelengths for pK_a measurements

Substituted aniline radical cation	λ/nm
2-CF_3-$C_6H_4NH_2^{\bullet +}$	410
3-CF_3-$C_6H_4NH_2^{\bullet +}$	420
2-CH_3-$C_6H_4NH_2^{\bullet +}$	430
2,4-$(CH_3)_2$-$C_6H_3NH_2^{\bullet +}$	440
3,4-$(CH_3)_2$-$C_6H_3NH_2^{\bullet +}$	460
3,5-$(CH_3)_2$-$C_6H_3NH_2^{\bullet +}$	470
2-CH_3O-$C_6H_4NH_2^{\bullet +}$	410
2,4-$(CH_3O)_2$-$C_6H_3NH_2^{\bullet +}$	445
3,4-$(CH_3O)_2$-$C_6H_3NH_2^{\bullet +}$	480
3,5-$(CH_3O)_2$-$C_6H_3NH_2^{\bullet +}$	570

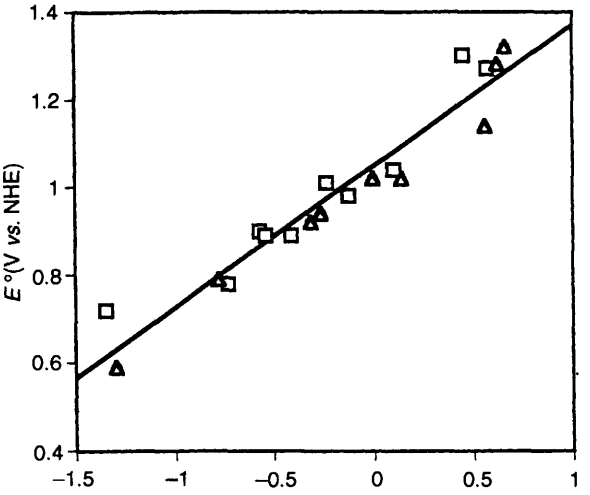

Fig. 2 One-electron reduction potentials of the aniline radical cations studied in this work (□) and some previously studied aniline radical cations (△)[2] as a function of the sum of the substituent constants, $\Sigma\sigma^+$

Since the slope for multisubstituted aniline radical cations does not differ significantly from that of 4-substituted aniline radical cations, we feel confident that no additional 'cross-interaction constant' needs to be included in a general equation for one-electron reduction potentials of multisubstituted benzene radical cations. We propose the following relationship between reduction potential and substituent pattern. σ_{p1}^+ in eqn. (13)

$$E^\circ = 2.2 + 0.8\left(\sigma_{p1}^+ + \sum_{i=2}^{6}\sigma_i^+\right) + 0.4\sigma_{p1}^+\sum_{i=2}^{6}\sigma_i^+ \quad (13)$$

(V *vs.* NHE)

corresponds to the substituent with the lowest substituent constant (NH_2 for anilines) and σ_i^+ is σ_o^+, σ_m^+ and σ_p^+ for the substituents in positions 2–6.

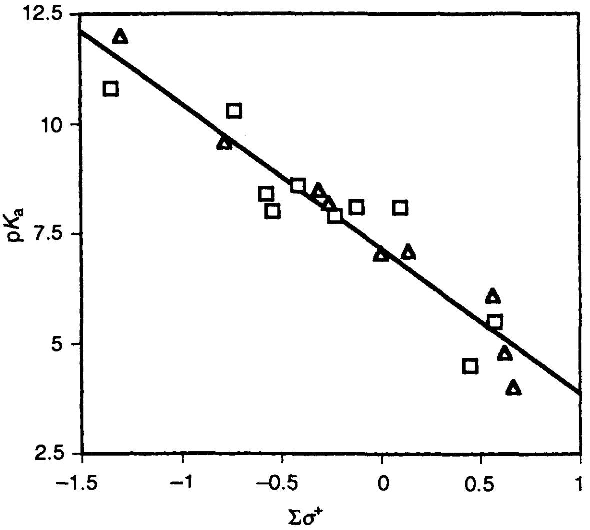

Fig. 3 pK_a values of the aniline radical cations studied in this work (□) and some previously studied aniline radical cations (△)[2] as a function of the sum of the substituent constants, $\Sigma\sigma^+$

A problem arises when considering, for instance, 1,2,3-$(CH_3O)_3$–$C_6H_3^{\bullet +}$. Should it be treated as a 2,6- or 2,3-dimethoxyanisole radical cation? Judging from experimental data, the latter seems to be the case.[4] Similar problems can also occur for other symmetrical radical cations, even though eqn. (13) is expected to hold for the majority of structures.

pK_a *Values.*—In Fig. 3 the pK_as of the aniline radical cations studied in this work and some previously published[2] pK_as are plotted against the sum of the substituent constants ($\Sigma\sigma^+$). The corresponding linear least-squares fit is given by eqn. (14).

$$pK_a = 7.09 - 3.17\sum_{i=2}^{6}\sigma_i^+ \quad (R^2 = 0.89) \quad (14)$$

Electron-donating substituents increase the pK_a while electron-withdrawing substituents lower it. Experimental difficulties occur for aniline radical cations with weak absorbances. This makes the spectral distinction between the aniline radical cation and the corresponding anilinyl radical harder. Also, between 3 and 5 the pH is difficult to adjust accurately.

N–H Bond Dissociation Energies.—The one-electron reduction potentials and the pK_as presented in Table 3 have been used to calculate the corresponding N–H bond dissociation energies using eqn. (3). The derivation of the constant *C*, 236.2 kJ mol^{-1} for anilines, has previously been described in detail.[2] In Table 4 the resulting bond dissociation energies are given along with some previously published[2] data for 4-substituted anilines.

Table 3 Equilibrium constants, one-electron reduction potentials and pK_a values

Radical cation	K_A	K_{kin}	E° ($PhNH_2^{\cdot+}/PhNH_2$) (V *vs.* NHE)	pK_a
$2\text{-}CF_3\text{-}PhNH_2^{\cdot+}$	450	900	1.30 ± 0.02	4.5 ± 0.3
$3\text{-}CF_3\text{-}PhNH_2^{\cdot+}$	0.26	0.55	1.27 ± 0.02	5.5 ± 0.3
$2\text{-}CH_3\text{-}PhNH_2^{\cdot+}$	50	58	1.01 ± 0.02	7.9 ± 0.2
$2,4\text{-}(CH_3)_2\text{-}PhNH_2^{\cdot+}$	0.43	0.21	0.89 ± 0.02	8.0 ± 0.2
$3,4\text{-}(CH_3)_2\text{-}PhNH_2^{\cdot+}$	2.2	2.9	0.89 ± 0.02	8.6 ± 0.2
$3,5\text{-}(CH_3)_2\text{-}PhNH_2^{\cdot+}$	15	73	0.98 ± 0.02	8.1 ± 0.2
$2\text{-}CH_3O\text{-}PhNH_2^{\cdot+}$	0.74	—	0.90 ± 0.02	8.4 ± 0.2
$2,4\text{-}(CH_3O)_2\text{-}PhNH_2^{\cdot+}$	297	131	0.72 ± 0.02	10.8 ± 0.2
$3,4\text{-}(CH_3O)_2\text{-}PhNH_2^{\cdot+}$	190	70	0.78 ± 0.02	10.3 ± 0.2
$3,5\text{-}(CH_3O)_2\text{-}PhNH_2^{\cdot+}$	10	3.6	1.04 ± 0.02	8.1 ± 0.2

Table 4 N–H bond dissociation energies

Aniline	D(N–H)/kJ mol^{-1}
$PhNH_2$	373[2]
$4\text{-}NH_2\text{-}C_6H_4NH_2$	360[2]
$4\text{-}(CH_3)_3C\text{-}C_6H_4NH_2$	372[2]
$4\text{-}CH_3CO\text{-}C_6H_4NH_2$	379[2]
$4\text{-}I\text{-}C_6H_4NH_2$	373[2]
$4\text{-}CN\text{-}C_6H_4NH_2$	384[2]
$2\text{-}CF_3\text{-}C_6H_4NH_2$	387
$3\text{-}CF_3\text{-}C_6H_4NH_2$	390
$4\text{-}CF_3\text{-}C_6H_4NH_2$	385[2]
$2\text{-}CH_3\text{-}C_6H_4NH_2$	379
$4\text{-}CH_3\text{-}C_6H_4NH_2$	371[2]
$2,4\text{-}(CH_3)_2\text{-}C_6H_3NH_2$	368
$3,4\text{-}(CH_3)_2\text{-}C_6H_3NH_2$	371
$3,5\text{-}(CH_3)_2\text{-}C_6H_3NH_2$	378
$2\text{-}CH_3O\text{-}C_6H_4NH_2$	371
$4\text{-}CH_3O\text{-}C_6H_4NH_2$	365[2]
$2,4\text{-}(CH_3O)_2\text{-}C_6H_3NH_2$	367
$3,4\text{-}(CH_3O)_2\text{-}C_6H_3NH_2$	370
$3,5\text{-}(CH_3O)_2\text{-}C_6H_3NH_2$	383

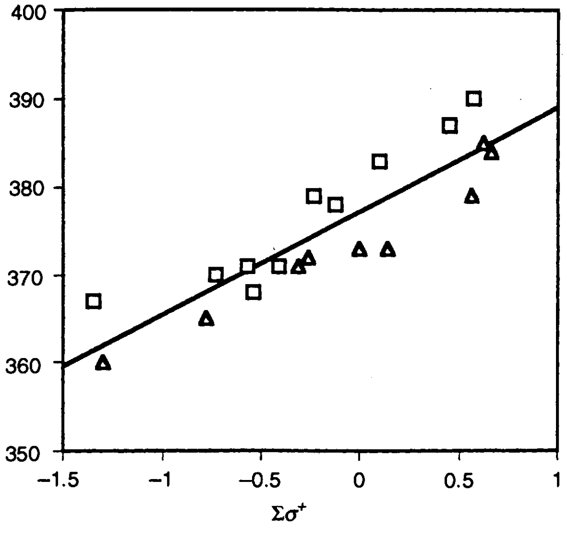

Fig. 4 N–H bond dissociation energies for the anilines studied in this work (□) and some previously studied anilines (△)[2] as a function of the sum of the substituent constants, $\Sigma\sigma^+$

In Fig. 4 the N–H bond dissociation energies in Table 4 are plotted against the sum of the substituent constants ($\Sigma\sigma^+$). The resulting linear least-squares fit is given by eqn. (15).

$$D(\text{N–H}) = 377 + 11.8\sum_{i=2}^{6}\sigma_i^+ \quad (R^2 = 0.79) \qquad (15)$$

Compared with a previously derived relationship for 4-substituted anilines the accuracy of eqn. (15) is rather poor ($R^2 = 0.97$ for 4-substituted anilines).[2] However, eqn. (15) is based on the bond dissociation energies of 19 different anilines including the nine 4-substituted anilines used to derive the former relationship.

Similarly to the previously mentioned relationship between substituent pattern and phenolic O–H bond dissociation energy[5] the slope of the equation does not change upon going from 4-substituted to multisubstituted compounds. Thus, no 'cross-interaction constant' needs to be invoked in these kinds of relationship. This extends the applicability of linear free energy relationships for bond dissociation energies.

X–Y Bond Dissociation Energies.—The slopes of linear free energy relationships describing the 4-substituent dependence on X–Y bond dissociation energies of aromatic compounds with the general formula $4\text{-}R\text{-}C_6H_4\text{-}X\text{-}Y$ have been shown to depend linearly on the difference in electronegativity between the bonded atoms of X and Y.[15] This means that the substituent not only affects the stability of the radicals formed upon homolysis, but also the parent molecules. This experimental finding has previously been discussed in more detail.[16] However, this relation enables us to predict the substituent dependence on an arbitrarily chosen X–Y bond, given the substituent pattern. Assuming the absence of 'cross-interaction constants' to hold also for molecules other than phenols and anilines we propose the following equation for the X–Y bond dissociation energy of multisubstituted molecules with the general formula Ph–X–Y [eqn. (16)]. $\rho^{+(\text{X–Y})}$ is the slope of the linear free energy

$$D(\text{X–Y}) = D_0^{\text{X–Y}} + \rho^{+(\text{X–Y})}\sum_{i=2}^{6}\sigma_i^+ \qquad (16)$$

relationship and is given by the empirically derived eqn. (17).[2] χ_X and χ_Y in eqn. (17) denote the electronegativity of the bonded

$$\rho^{+(\text{X–Y})} = -11.3 + 30.3(\chi_X - \chi_Y)\,(\text{kJ mol}^{-1}) \qquad (17)$$

atoms of X and Y, respectively. Eqn. (17) is based on the Pauling electronegativity scale (other electronegativity scales can also be used). $\Sigma\sigma_i^+$ in eqn. (16) is the sum of the substituent constants σ_o^+, σ_m^+ and σ_p^+ in positions 2–6 applying the conditional *ortho* scale $\sigma_o^+ = 0.7\sigma_p^+$. $D_0^{\text{X–Y}}$ in eqn. (16) is the X–Y bond dissociation energy of the unsubstituted parent compound ($\sigma_p^+ = 0$). An interesting finding is that eqn. (17) can also be derived from relationships between electronegativity and bond dissociation energy.[16]

The main drawback of eqn. (16) is the lack of methods to calculate $D_0^{\text{X–Y}}$. In order to remedy this problem, experimental data must become available for at least one member of a specific family of molecules. Methods based on electronegativity and hardness could possibly find future use for the determination of D_0^{X-Y}.*

Acknowledgements

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[*] Ghanty and Ghosh[17] have derived an equation for calculations of bond dissociation energies of diatomic molecules based on the absolute hardness[18] and the absolute electronegativity[18] scales. This equation could probably be extended to hold for polyatomic molecules.

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