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Gas-phase basicity and site of protonation of 4-nitroaniline and other substituted anilines[†]

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Summary – Contrary to previous statements, 4-nitroaniline can be protonated on the nitro group in the gas phase. This finding follows from the Hammett correlations of gas-phase basicities (GBs) of substituted anilines and nitrobenzenes. It can also be anticipated from AM1 calculations. By the same token, 4-cyanoaniline appears to be protonated on the cyano group, and methyl 4-aminobenzoate on the ester group. On the contrary, 3-nitroaniline, 3-cyanoaniline, 3-nitro-*N*,*N*-dimethylaniline, 3- and 4-cyano-*N*,*N*-dimethylaniline, and methyl 3- and 4-(dimethylamino)benzoate are protonated at the amino nitrogen. The site of protonation of 4-nitro-*N*,*N*-dimethylaniline and methyl 3-aminobenzoate cannot be deduced. The Hammett correlation for protonated nitrobenzenes, requiring the σ^+ constants, draws attention to the structure of these protonated forms. Their enthalpies of formation were estimated from gas-phase basicity measurements and are discussed with respect to the resonance structures.

protonation equilibrium / gas-phase basicity / Hammett correlation / site of protonation / AM1 calculation

Studies of protonation equilibria in the gas phase [1-5] are of utmost importance to correlation analysis and the theory of substituent effects. Their evident merits are the absence of any solvent effects, a great sensitivity to substitution, and a possible extension to very weak acids or bases. On the other hand, new problems may arise, in comparison with solution chemistry, with the site of protonation in basicity studies or the site of deprotonation in acidity studies. Aromatic bifunctional derivatives were investigated in extended series [1] and the equilibrium constants were correlated with the substituent constants. A fundamental assumption is that the reaction site remains unchanged. However, a benzene bis-derivative can be protonated on one of the two functional groups or even on the benzene ring. The last case was observed [2, 3] with derivatives bearing two donor groups in the *meta* position; the ring protonated cation is stabilized by conjugation with the substituents.

In this paper, we shall focus attention on derivatives with one donor and one acceptor group. The donor group is usually more basic as in substituted anilines, which represent a typical family. The mutual interaction then causes the basicity of the donor to decrease, and that of the acceptor to increase. In certain cases, the order of basicity may switch over. For instance, in nitro-substituted anilines or *N*,*N*-dimethylanilines, the amino group would be expected to be the most basic according to the basicity of monosubstituted derivatives. However, a reversal is not excluded, particularly in *para* derivatives in which the mutual influence is greater.

We expected that at least some of these problems can be resolved within the framework of correlation analysis. For a derivative AC_6H_4B, this approach requires us to investigate two reaction series, XC_6H_4B and AC_6H_4X, where X is a variable substituent, itself of weak basicity compared with A or B. From correlations of the gas-phase basicity (GB) with suitable empirically selected substituent constants, GB can be predicted for protonation into both $AC_6H_4BH^+$ and $H^+AC_6H_4B$. A comparison with experiment can then be decisive. In a thorough analysis of gas-phase substituent effects [1], GBs were correlated by a multiparametric relationship (eq 1), including field/inductive (F), resonance (R), and polarizability (α) constants.

$$\mathrm{GB} = \mathrm{GB}^\circ + \rho_F\sigma_F + \rho_R\sigma_R + \rho_\alpha\sigma_\alpha \qquad [1]$$

The last term was often insignificant ($\rho_\alpha \approx 0$). Furthermore, one of three different sets of values can be introduced for σ_R; they are denoted σ_R^0, σ_R^+, and σ_R^-. Taking into account the complexity of eq [1], the predicted values may become less dependable. We assumed

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Table I. Gas-phase basicities (GB in kJ mol^{-1}, 298 K) of some substituted anilines, experimental and estimated for the protonation on either side.

Compound	Substituent X	GB^{a}_{exp}	GB (Hammett)		GB (AM1)		GB (AM1) corr[b]		Site of protonation[c]	
			NR_2H^+	XH^+	NR_2H^+	XH^+	NR_2H^+	XH^+	Hammett	AM1
Anilines $XC_6H_4NH_2$										
1	4-NO_2	833.5	798	837	792.1	814.6	780.2 [785.4][e]	827.2	NO_2	NO_2
2	3-NO_2	811.3[d]	804	781	805.8	774.7	793.9 [797.1][e]	787.3	NH_2	?
3	4-CN	830.1[d]	807	830	822.3	829.1	810.4 [803.8][e]	825.5	CN	CN
4	3-CN	807.1	811	791	828.2	804.0	816.3 [809.6][e]	800.4	NH_2	?
5	4-CO_2Me	857.7	822	859 [858.6][f]	830.9	856.7	819.0	865.6	CO_2Me	(CO_2Me)
6	3-CO_2Me	839.6[d]	828	829 [840.2][f]	842.9	827.0	831.0	835.9	?	?
N,N-dimethylanilines $XC_6H_4NMe_2$										
7	4-NO_2	865.3	856 [852.7][f]	855	804.3	825.2	838.6	837.8	?	?
8	3-NO_2	864.0	860 [863.5][f]	781	819.2	782.1	853.5	794.7	NMe_2	(NMe_2)
9	4-CN	859.4	860 [865.1][f]	842	833.3	836.4	867.6	832.8	NMe_2	NMe_2
10	3-CN	864.4	865 [870.8][f]	792	835.3	809.7	869.6	806.1	NMe_2	NMe_2
11	4-CO_2Me	888.3[g]	876 [883.8][f]	865	841.6	864.9	875.9	873.8	NMe_2	?
12	3-CO_2Me	897.0	881 [894.3][f]	829	853.7	834.1	888.0	843.0	(NMe_2)	(NMe_2)
Compounds for comparison										
	$PhNH_2$	847.3			859.2					
	$PhNMe_2$	901.2			866.9					
	$PhNO_2$	776.6				764.0				
	PhCN	787.8				791.4				
	$PhCO_2Me$	824.2				815.3				

[a] Ref [7] unless otherwise noted.

[b] Corrected empirically according to the comparison of calculated and experimental values for the pertinent mono-derivative.

[c] The site of protonation is considered as "determined" if the disagreement for the correct structure, δ, does not exceed 5-10 kJ mol^{-1} (in any direction) and if the prediction for the incorrect structure is lower by at least 3δ; between parentheses, less reliable determinations if the difference between the two calculated values is at least 15 kJ mol^{-1} (irrespective of the experimental value).

[d] This work.

[e] Obtained from relative values, respective to aniline, calculated *ab initio* at the STO-3G level [18].

[f] Calculated according to eq 1, using ρ and σ values given in ref 1.

[g] Attention is drawn to **11** in ref 7 with the mention "this compound given twice in 86Taft". Two GB values (897.0 and 888.3 kJ mol^{-1}) are reported therein. The latter corresponding to that is given by Taft and Topsom in ref 1 is retained here.

that meaningful results could be obtained with the simple Hammett equation (eq 2) which can be directly represented by a linear plot (see for instance reference 4).

$$GB = GB^0 + \rho\sigma_{m,p} \qquad [2]$$

Nevertheless, even with this equation, one must decide which of the possible types of constants [6] is appropriate : σ_p, σ_p^+ or σ_p^-. For this purpose, the set of substituents X must include strong donors or strong acceptors in the *para* position.

An alternative, more direct, procedure would be the correlation of the GB values with GBs of another reaction series in which the site of protonation is not variable. However, suitable data are seldom available.

Using eq [2], we reexamined the 12 aniline derivatives listed in table I. Their GBs were mostly known [7]. For three additional compounds, we report equilibrium measurements by Fourier transform ion cyclotron resonance (FT-ICR). Further measurements were necessary to establish the Hammett plots for substituted nitrobenzenes and benzonitriles. As a second approach, we used semiempirical AM1 calculations [8]. We calculated both the enthalpy and entropy of protonation on each group and compared the corresponding Gibbs energy with experiment. The AM1 approach was recently found to be satisfactory for problems of a similar kind [9, 10].

Table II. Experimental gas-phase basicities (in kJ mol^{-1}) of substituted anilines and auxiliary compounds.

B	Ref	ΔGB(338 K)[a]	GB(B)[b]
2	*n*-$PrCO_2Me$	$+6.7 \pm 0.2$	
	Et_2CO	$+1.3 \pm 0.2$	
	t-BuCOMe	-3.8 ± 0.1	811.1
3	(*i*-Pr)$_2$CO	$+7.7 \pm 0.1$	
	(*i*-Pr)$_2$O	$+1.1 \pm 0.5$	
	PhCOMe	$+0.4 \pm 0.2$	830.1
6	(*n*-Pr)$_2$S	$+6.2 \pm 0.4$	
	pyrrole	$+1.9 \pm 0.6$	839.6
1,3-Dinitrobenzene	MeCHO	$+0.6 \pm 1.0$	
	MeCN	-6.3	748.2 (746.8)[c]
3-Chloronitrobenzene	HCO_2Me	$+3.5 \pm 0.1$	
	EtCHO	$+2.8 \pm 0.1$	761.3
4-Nitromethoxybenzene	*t*-BuCOMe	$+1.3 \pm 0.1$	
	c-$PrCO_2Me$	$+1.3 \pm 0.1$	816.4
4-Methylbenzonitrile	$MeCO_2Me$	$+7.2 \pm 0.1$	
	cyclopentanone	$+1.8 \pm 0.1$	
	MeCOEt	$+1.0 \pm 0.1$	
	tetrahydrofuran	-1.8 ± 0.1	802.7
4-Chlorobenzonitrile	HCO_2Et	$+6.9 \pm 0.2$	
	t-BuCN	$+3.1 \pm 0.1$	
	1,4-dioxane	$+2.5 \pm 0.2$	
	c-PrCN	-1.8 ± 0.4	782.0
4-Methoxybenzonitrile	cyclohexanone	-0.3 ± 0.1	
	c-$PrCO_2Me$	-1.0 ± 0.1	
	t-BuCOMe	-1.3 ± 0.1	813.1

[a] Gibbs energies for the reaction $BH^+ + Ref = RefH^+ + B$; quoted uncertainties correspond to the standard deviation for 3 or 4 measurements.

[b] Absolute Gibbs energies of basicity ($BH^+ \rightarrow B + H^+$) referenced to the literature GB (298 K) data [7] for the reference compounds (Ref) (no temperature correction).

[c] A statistical correction ($-RT \ln 2$) has been applied. This data is to be used in correlation analysis.

Experimental section

The substituted benzonitriles were described in a previous paper [11]. The remaining compounds were of commercial origin (Aldrich or Fluka).

Proton transfer equilibria were monitored by FT-ICR as previously [9]; details of this technique have been described elsewhere [12]. The results are listed in table II. With protonation of nitrobenzenes, a technical difficulty was the presence of strong peaks due to the protonated molecules of the corresponding nitroso compounds and anilines, increasing with the reaction time. Since the purity of starting compounds was reexamined by gas chromatography, the only reasonable explanation is a reduction of nitro compounds in the inlet system by an unidentified mechanism. Nevertheless, the precision of the results was acceptable, as follows from the consistency of individual experiments shown in table II.

The AM1 calculations were carried out using the MOPAC package, version 6.0 [13], on a 486 DX50 personal computer. Calculations were performed on the neutral, and protonated forms, starting from standard bond lengths and bond angles. All geometries were fully optimized by minimizing the energy with respect to geometrical variables without symmetry constraint, using the keywords PRECISE and GNORM = 0.0 for a better precision. In the final structures, no negative vibration frequencies were disclosed.

The calculated enthalpies of formation and entropies were combined with $\Delta_f H^0$ (H^+, g, 298.15 K) = 1 536.246 kJ mol^{-1} [14] and S^0 (H^+, g, 298.15 K) = 108.946 J mol^{-1} [15]. The results are listed in table I.

Hammett correlations were carried out graphically since the number of points and the low accuracy do not allow an efficient statistical treatment. All correlations are shown in graphs (figs 1-6).

Results and discussion

The substituted anilines with a questionable site of protonation are listed in table I. In each case the experimental GB can be compared with the values anticipated for the respective sites of protonation as estimated both from the Hammett correlations (columns 4 and 5) and AM1 calculations (columns 6 and 7). The latter disagree, sometimes considerably, as far as the absolute basicity is concerned. Hence, an empirical correction was obtained by calculating the difference between GB(AM1) and GB_{exp} for the pertinent monofunctional compound. This difference is then subtracted from the GB(AM1) of the disubstituted derivative protonated on the appropriate function. The corrected values are given in table I, columns 8 and 9.

From the point of view of mathematical statistics, the problem is to decide between two hypotheses on the basis of one measured quantity. This is not always trivial [16]. In our particular case, there is still a strict condition that the accepted hypothesis must give a higher predicted GB than the rejected alternative. We have preferred a simple, rather arbitrary treatment. A hypothesis is considered as proven when the calculated value differs from experiment by a value δ, not exceeding

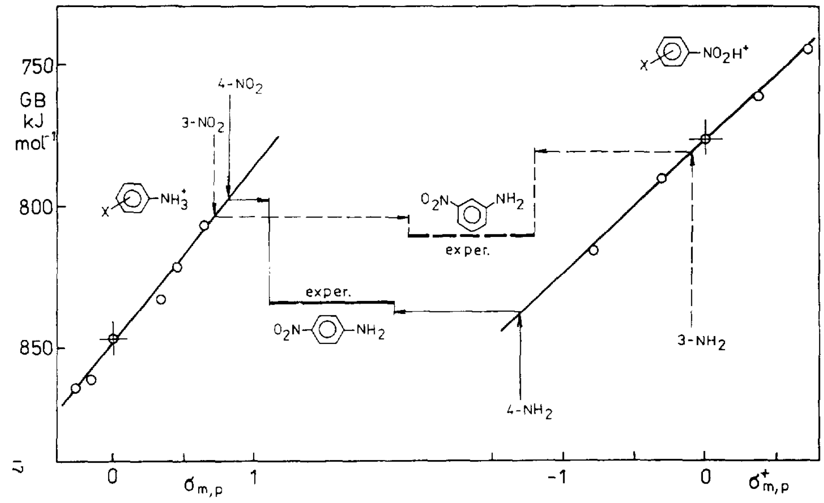


Fig 1. Determining the site of protonation of 4- and 3-nitroanilines. Left : GB of substituted anilines *vs* σ constants; right : GB of substituted nitrobenzenes *vs* σ^+ constants, the pertinent experimental values in the middle; all experimental data from ref 7 and this work.

10 kJ mol^{-1} (in any direction) and the rejected alternative is lower (weaker basicity) by at least 3δ. Table I reveals nine such cases for the Hammett correlations and four for AM1 calculations. With a lower degree of reliability, we can be satisfied with an estimate of which group is more basic, regardless of the agreement with experiment. In this case, the difference between the two calculated values may be at least 15 kJ mol^{-1} (table I, the decisions given in parentheses).

In general, AM1 appears to be less efficient than the Hammett correlations. Most important is the fact that there is no disagreement between the two methods in any single case. Two cases remain unresolved, compounds **6** and **7**, and the following compounds deserve discussion.

4-Nitroaniline 1

From ionization energies and metastable dissociation spectra, Rolli and Houriet [17] came to the conclusion that protonation occurs at the amino group. This was also assumed in STO-3G calculations [18]. However, in standard tables [7] the site of protonation is not defined. A plot of GBs of substituted anilines [7] *vs* σ constants [6] contains few points and exhibits some scatter with the point for 4-NO_2 deviating very distinctly (fig 1, left). One reason for the scatter could be heterogeneity of data obtained by two techniques [2, 3] differing in temperature and pressure. The use of σ and not σ^-, constants does not follow from fig 1, and is substantiated only subsequently with respect to figure 4. The second plot, GBs of substituted nitrobenzenes *vs* σ^+ [6], must be restricted to weakly basic substituents (fig 1, right). Nevertheless, the extrapolated value for substituent 4-NH_2 agrees reasonably well with the experiment (fig 1, table I). When evaluating this agreement, we must take into account that the σ^+ value for 4-NH_2 [19] is rather uncertain. Even so, the conclusion that 4-nitroaniline is protonated on the nitro group is safe. This is also strongly supported by AM1 calculations (table I).

4-Cyanoaniline 3

This compound has not been investigated experimentally to date, but in the STO-3G calculations, protonation at the amino nitrogen was assumed as self-evident [18]. According to figure 2 and AM1 calculations (table I), there is no doubt that it is protonated on the cyano group. In the plot of GBs of substituted benzonitriles (fig 2, right), a problem may arise of whether the σ or σ^+ constants are more appropriate. Evidently, the best solution is the Yukawa-Tsuno approach [5, 20], using values intermediate between σ and σ^+ according to eq 3 where σ and σ^+ only differ for *para* substituents.

$$GB = GB^0 + \rho[\sigma + r(\sigma^+ - \sigma)] \qquad [3]$$

Our data allow the ρ constant (the slope of the straight line in fig 2, right) to be determined with some reliability on the basis of acceptor substituents. However, r can be estimated roughly on the basis of two substituents, 4-CH_3 and 4-OCH_3. We used the estimate $r = 0.6$. Let us stress that this value is not critical for a safe determination of the protonation site.

*4-Nitro-*N,N*-dimethylaniline* 7

By the same token, this compound was believed to be protonated on the amino nitrogen, as is the case for 4-nitroaniline [17]. However, it was not included in a correlation of GBs of 4-substituted *N*,*N*-dimethylanilines [1] with σ constants, based on eq [1]. A simple Hammett plot (fig 4, left) gives quite a satisfactory result and use of a three-term equation is not substantiated in this case. Note that this correlation is much more reliable than that for substituted anilines in figure 1, due to a greater number of available data [1]. Figure 4 is also decisive for using the σ and not σ^- constants (see the substituent SO_2CF_3). For this reason the normal σ constants were used even in figure 1. Any decision regarding the site of protonation of 4-nitro-

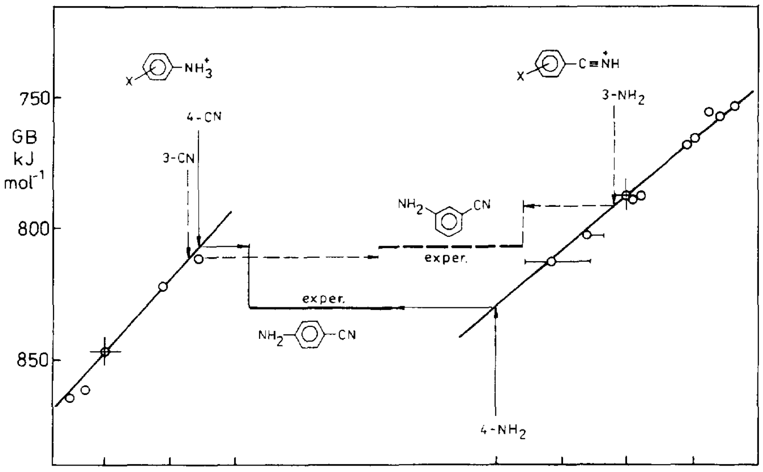


Fig 2. Determining the site of protonation of 3- and 4-cyanoanilines in a similar way as in figure 1. In the plot for substituted benzonitriles (right), the Yukawa-Tsuno equation (eq 3) was used with $r = 0.2$, the horizontal lines show the distance between σ_p and σ_p^+ values; experimental data from refs 1, 7, 24 and this work.

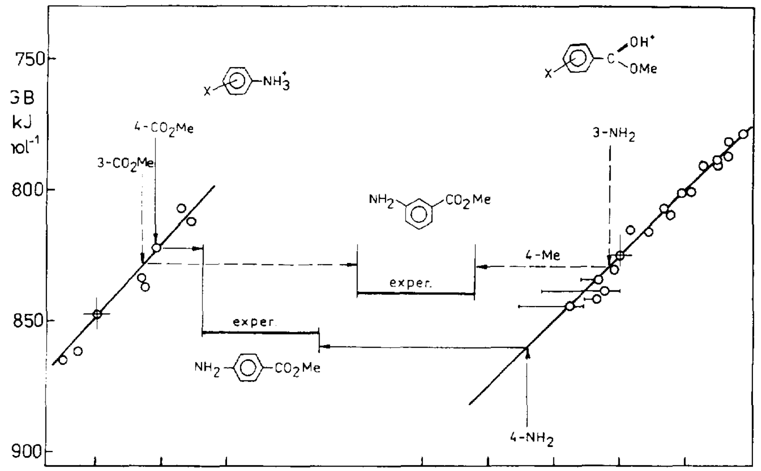


Fig 3. Determining the site of protonation of methyl 4- (or 3-) aminobenzoates in the same way as in figure 2 with $r = 0.2$ for substituted methyl benzoates; experimental data from refs 1, 7 and this work.

N,*N*-dimethylaniline is not possible either from Hammett plot or from the AM1 calculations (table I). Since the correlation for substituted *N*,*N*-dimethylanilines (fig 4, left) seems rather dependable, we prefer the more reliable hypothesis that the source of uncertainty is the imprecise value [19] of σ^+ for the substituent 4-$N(CH_3)_2$. In this case, protonation would occur on the nitro group. Note that in 4-nitro-*N*,*N*-diethylaniline the nitro group is also the site of hydrogen bond basicity [21].

Methyl 4-aminobenzoate 5 *and 4-(dimethylamino) benzoate* 11

These compounds were treated in the basicity studies as essentially different : the former as a substituted methyl benzoate, protonated on the ester group [1, 5]; the latter as a substituted dimethylaniline protonated at nitrogen [1]. These assumptions are confirmed from figures 3 and 6. From these figures, we estimated the Yukawa-Tsuno parameter r as equal to 0.2. When the NH_2 group was not present, the OCH_3 group was of decisive importance. From a different set of compounds, an estimate of $r = 0.45$ was obtained [5]. This mainly proves the low accuracy of this parameter, but does not reverse the resulting determination of the site of protonation. The AM1 calculations were less efficient in this case.

Methyl 3-aminobenzoate 6

This compound has not been investigated, either experimentally or theoretically. The two Hammett plots yield

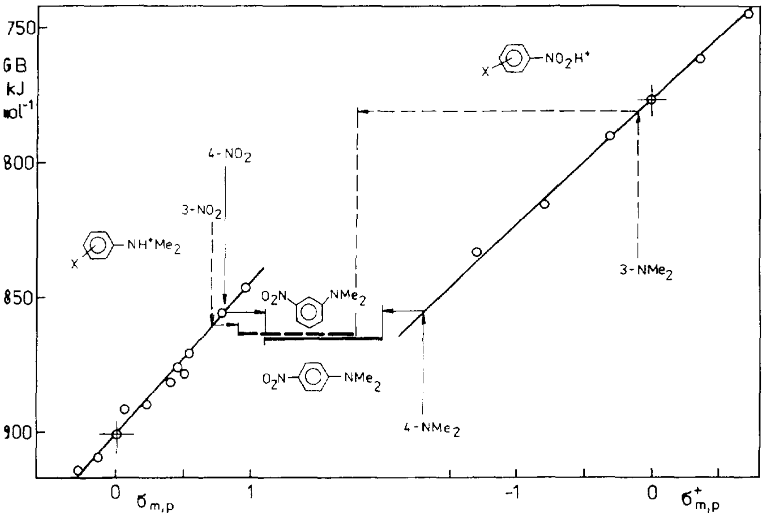
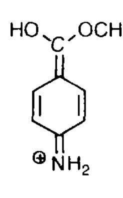


Fig 4. Determining the site of protonation of 4- and 3-nitro-N,N-dimethylanilines in the same way as in figure 1; experimental data from ref 1, 7 and this work.

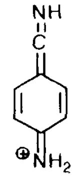
practically the same prediction of GB for the two potential sites of protonation. The AM1 calculations suggest protonation on the ester group, but the difference is not sufficient according to our criteria.

Concerning the Hammett correlations

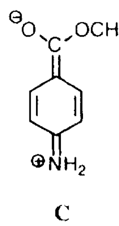
The Hammett correlations shown in figures 1-6 can also yield some new insights from the values of their slopes, some significant deviations and application of dual σ constants, *etc.* Using the presently available data, we shall discuss only the values of r in the Yukawa-Tsuno treatment, eq [3]. The values of 0.2 or 0.6 for substituted methyl benzoates or benzonitriles, respectively, are clearly explained in terms of resonance formulas **A** and **B** of the cation ("through resonance"). This resonance is evidently much stronger than in neutral molecules, **C** and **D**, where charge separation takes place.



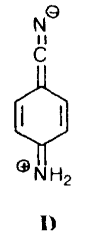
A



B

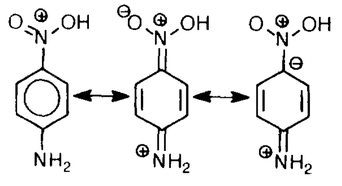


C

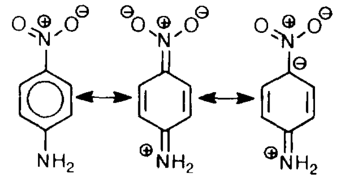


D

However, we do not see any obvious reason why the σ^+ constants are necessary for substituted nitro benzenes (figs 1 and 4, right), corresponding thus to the value $r = 1$. The resonance represented by the formulas **E** ↔ **F** should not be much stronger than in neutral molecules, **H** ↔ **J**. The latter is very weak in the gas phase [22], as also follows from using normal σ constants in the plots for substituted anilines (figs 1-3) and N,N-dimethylanilines (figs 4-6). Recently, the preferred explanation [11, 23] was that the nitro group itself is only slightly conjugated with the benzene nucleus. The stability of compounds like 4-nitroaniline is due to the strengthened conjugation of the amino group; the nitro group merely contributes by its inductive effect (formulas **G** and **K**). In terms of this theory, it is somewhat more understandable from the charge distribution that structure **G** is more important than **K**.



E **F** **G**



H **J** **K**

In an attempt to give these considerations a more quantitative character, we calculated a rough estimate of the resonance energy by reference to *meta* derivatives, using the classical approximation stating that the inductive effect is equal in the *para* and *meta* positions [24]. The reaction enthalpy for the isomerization reaction, eq [4], is obtained directly from the heats of formation [25]. For eqs [5-7] it was obtained by thermodynamic cycles from the gas-phase basicities. For certain processes it was necessary to use the values estimated from Hammett correlations (table I) when the respective reactions are not experimentally accessible.

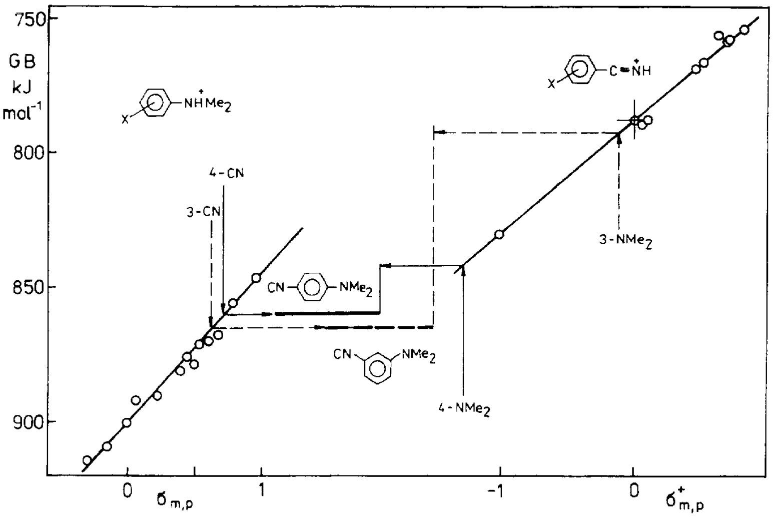


Fig 5. Determining the site of protonation of 3- and 4-cyano-*N*,*N*-dimethylanilines in the same way as in figure 2.

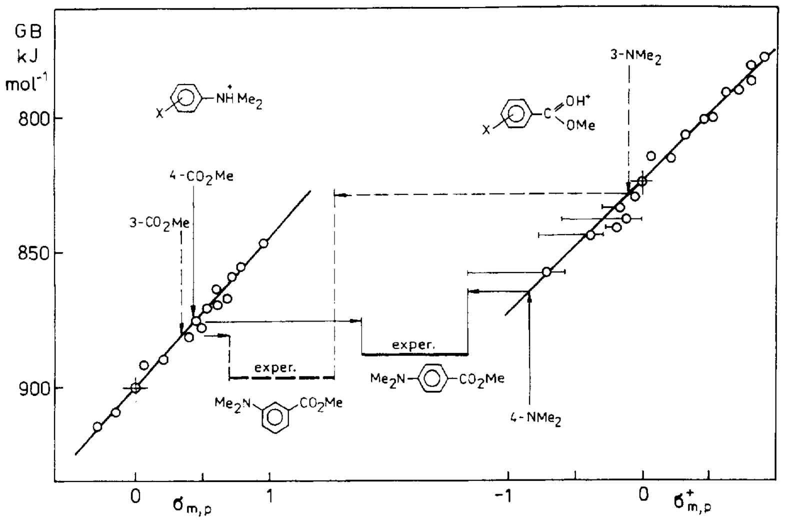


Fig 6. Determining the site of protonation of methyl 4-(dimethylamino)benzoate and methyl 3-(dimethylamino)benzoate in the same way as in figure 3.

$$3\text{-}O_2NC_6H_4NH_2 \rightarrow 4\text{-}O_2NC_6H_4NH_2 \qquad \Delta H = -9 \text{ kJ mol}^{-1} \quad [4]$$

$$3\text{-}O_2NC_6H_4NH_3^+ \rightarrow 4\text{-}O_2NC_6H_4NH_3^+ \qquad \Delta H = -3 \text{ kJ mol}^{-1} \quad [5]$$

$$3\text{-}HO_2N^+C_6H_4NH_2 \rightarrow 4\text{-}HO_2N^+C_6H_4NH_2 \qquad \Delta H = -59 \text{ kJ mol}^{-1} \quad [6]$$

$$3\text{-}HOCOC_6H_4NH_2 \rightarrow 4\text{-}HOCOC_6H_4NH_2 \qquad \Delta H = -5 \text{ kJ mol}^{-1} \quad [7]$$

$$3\text{-}^-OCOC_6H_4NH_2 \rightarrow 4\text{-}^-OCOC_6H_4NH_2 \qquad \Delta H = -3 \text{ kJ mol}^{-1} \quad [8]$$

In spite of these uncertainties, it is evident that the differential inductive effect is negligible (eq 5), and that resonance is rather weak in the neutral molecule (eq 4), and very strong in the protonated form (eq 6).

Comparison can be made with aminobenzoic acids, which are isoelectronic with **E**, while their anions are isoelectronic with **H**. The resonance energies revealed in eqs [7] and [2] are small, and almost disappear in experimental errors [26]. The large value in eq [6] is without comparison.

The resonance should also appear in the bond lengths. The AM1 calculations always yield too short C–N bond lengths (by 0.02 to 0.04 Å (1 Å = 0.1 nm) compared with the experimental values in the crystal [27]), but suggest a rather strong resonance : these bonds appear to be shortened upon protonation by 0.05 Å in nitrobenzene, 0.07 Å in **1** and 0.08 Å in **7**. In our opinion, the structure of protonated nitrobenzene and its derivatives remains not completely understood. An interesting suggestion is that the nitrogen atom can, in certain cases, allocate more than eight electrons [28]. This could partly explain the unexpected contribution of the structures **F** and **G** to the actual electron distribution.

Conclusions

The results presented here may appear as surprising when one thinks in terms of solution chemistry. In the gas phase, the site of protonation should be examined in every case. Some literature reports and/or assumptions inherent in the correlations of basicity may be in error (see compounds **1**, **3** and **7**).

Concerning the methods used, we can state that the knowledge of the true site of protonation, which is so important in correlation analyses, can often be obtained within the framework of this discipline. This approach is at least as efficient as quantum chemical calculations on a semiempirical level. Note that several cases remain undecided (for instance, compound **12**), for the reason that the two basicities predicted for each potential site of protonation are almost equal. In this case a mixture of comparable amounts of two cations would be produced under equilibrium conditions. These cases do not introduce any problem in the correlation analysis. When the two predicted values are almost equal, the experimental value can be used in any of the two correlations without any significant error.

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References and notes

1 Taft RW, Topsom RD, *Prog Phys Org Chem* (1987) 16, 1-83

2 Pollack SD, Devlin JL, Summerhays KD, Taft RW, Hehre WJ, *J Am Chem Soc* (1977) 99, 4583-4584; Summerhays KD, Pollack SK, Taft RW, Hehre WJ, *J Am Chem Soc* (1977) 99, 4585-4587; Freiser BS, Woodin RL, Beauchamp JL, *J Am Chem Soc* (1975) 97, 6893-6894

3 Lau YK, Nishizawa K, Tse A, Brown RS, Kebarle P, *J Am Chem Soc* (1981) 103, 6291-6295

4 Harrison AG, Houriet R, Tidwell TT, *J Org Chem* (1984) 49, 1302-1304; Marcuzzi F, Modena G, Paradisi C, Giancaspro C, Speranza M, *J Org Chem* (1985) 50, 4973-4975

5 Mishima M, Fujio M, Tsuno Y, *Tetrahedron Lett* (1986) 27, 939-942, *ibid* 951-954

6 Exner O, *Correlation Analysis of Chemical Data*, Plenum, New York, 1988, Chaps 2.2 and 4.1

7 a) Lias SG, Liebman JF, Levin RD, *J Phys Chem Ref Data* (1984) 13, 695-808; addition and corrections, personal communication (1987)
b) Lias SG, Bartmess JE, Liebman JF, Holmes TL, Levin RD, Mallard WG, *J Phys Chem Ref Data* (1988) 17, Suppl 1

8 a) Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP, *J Am Chem Soc* (1985) 107, 3902-3909
b) Dewar MJS, Dieter KM, *J Am Chem Soc* (1986) 108, 8075-8086

9 Decouzon M, Ertl P, Exner O, Gal JF, Maria PC, *J Am Chem Soc* (1993) 115, 12071-12078

10 Sotomatsu T, Murata Y, Fujita T, *J Comput Chem* (1989) 10, 94-98; Karaman R, Huang JL, Fry L, *J Comput Chem* (1990) 11, 1009-1016

11 Exner O, Budesinsky M, *Magn Reson Chem* (1989) 27, 27-36

12 Berthelot M, Decouzon M, Gal JF, Laurence C, Le Questel JY, Maria PC, Tortajada J, *J Org Chem* (1991) 56, 4490-4494

13 Stewart JJ (1990) : Quantum Chemistry Program Exchange, (QCPE), Department of Chemistry, Indiana University, Bloomington, IN 47405, USA

14 For $\Delta_f H^0$ (H^+, g, 298.15 K), the experimental value of 1 536.3 kJ mol^{-1} [15] is used here, as recommended by Dewar and Dieter [8b]. This value corresponds to the so-called "electron convention" for which the electron is treated as a moving particle [15]. Dewar and Dieter cited the ref 7a as their source of PA and $\Delta_f H^0$ (ion). In this compilation the "ion convention" (electron at rest) is used. In fact the experimental $\Delta_f H^0$ (ion) used by Dewar and Dieter are the values from ref 7 corrected by +6.197 kJ mol^{-1} and are therefore of the "electron convention" type

15 Chase Jr MW, Davies CA, Downey Jr JR, Frurip DJ, McDonald RA, Syverund AN, "JANAF Thermochemical Tables, Third Edition, Part I and II", *J Phys Chem Ref Data* (1985) 14, Suppl 1

16 Exner O, *Collect Czech Chem Commun* (1970) 35, 187-211

17 Rolli E, Houriet R, *Spectrosc Int J* (1984) 3, 177-183

18 Taagepera M, Summerhays KD, Hehre WJ, Topsom RD, Pross A, Radom L, Taft RW, *J Org Chem* (1981) 46, 891-903

19 Brown HC, Okamoto Y, *J Am Chem Soc* (1958) 80, 4979-4987

20 Yukawa Y, Tsuno Y, *Bull Chem Soc Jpn* (1959) 32, 965-970, *ibid* 971-981. This well-known equation was recently renamed the Young-Jencks equation : Toullec J, Milin D, *J Org Chem* (1994) 59, 2840-2847, but without a fundamental reason, since the modification suggested only consisted of an algebraic transformation : Young PR, Jencks WP, *J Am Chem Soc* (1977) 99, 8238-8248

21 Laurence C, Berthelot M, Luçon M, Morris DG, *J Chem Soc Perkin Trans 2* (1994) 491-493

22 The concept of specific solvent-assisted resonance (SSAR) concluded that the weight of through-resonance formulas is strongly enhanced by hydration : Fujio M, McIver RT, Taft RW, *J Am Chem Soc* (1981) 103, 4017-4029. However, the discussion relies on the relative values of σ constants. In fact, resonance is strongly attenuated in solution but the inductive effect is even more attenuated

23 Politzer P, Lane P, Jayasuriya K, Domelsmith LN, *J Am Chem Soc* (1987) 109, 1899-1901; Krygowski TM, Maurin J, *J Chem Soc Perkin Trans II* (1989) 695-698

24 The common assumption that inductive effects are equal in the *meta* and *para* position is not exact : Decouzon M, Exner O, Gal JF, Maria PC, *J Phys Org Chem* (1994) 7, 615-624. Nevertheless, it is sufficient for the approximate comparison presented here

25 Nishiyama K, Sakiyama M, Seki S, *Bull Chem Soc Jpn* (1983) 56, 3171-3172

26 Nabavian M, Sabbah R, Chastel R, Laffitte M, *J Chim Phys-Chim Biol* (1977) 74, 115-126

27 Boese R, Bläser D, Nussbaumer M, Krygowski TM, *J Mol Struct* (1988) 172, 413-421

28 Kahn SD, Hehre WJ, Pople JA, *J Am Chem Soc* (1987) 109, 1871-1873; Exner O, *J Phys Org Chem* (1990) 3, 190-194