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Protonated nitro group: structure, energy and conjugation

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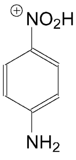
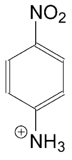
Structure of protonated nitro compounds was investigated by calculations at the levels MP2(FC)/6-311++G(2d,2p)//MP2(FC)/6-311++G(2d,2p) (nitromethane and reference compounds) or B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) (nitrobenzene and its 18 *meta*- and *para*-substituted derivatives). The group NO_2H^+ reveals many similarities with the isoelectronic group CO_2H as the preferred conformation, conformational equilibrium, and stabilization by interaction (resonance) within the group quantified by means of isodesmic reactions. However, there is a difference in the interaction with donor groups (for instance in 4-nitroaniline) that is much stronger with NO_2H^+ than with CO_2H. This interaction may be called resonance and may be described by standard resonance formulas, but these formulas predict only partially the geometry and cannot explain the great interaction energy.

Introduction

Protonation of the nitro group can be observed both in the gas phase[1] and in protic solvents (mostly in sulfuric acid).[2] In the gas phase, nitrobenzene is a medium strong base – on the scale of basicity[1] it is approximately in the middle. Recently, this protonation reaction attracted attention from several points of view. First, there were problems with the site of protonation of some bifunctional derivatives in the gas phase, the most interesting example being 4-nitroaniline. According to experience from solution chemistry, one could expect preferential protonation on the amino group (**1b**); this opinion was even supported by experiments[3] and low-level calculations.[4] However, preferential protonation on the nitro group (**1a**) has been proven.[5]



1a



1b

On the other hand, 3-nitroaniline is protonated on the amino group[5] and 3- and 4-nitrobenzonitrile on the cyano group[6] as originally anticipated.[7]

Problems of this kind can, in principle, be solved either by calculations[6,8] or by correlations with similarly substituted compounds.[5] More difficult are further problems associated with the similarity of protonated nitro compounds and carboxylic acids since the groups NO_2H^+ and CO_2H are isoelectronic. The structure of carboxylic acids has been extensively discussed recently[9–11] with the main question of whether the acidity is due mainly to the low energy of the anion or to the high energy of the acid molecule. Although complete agreement has not been reached,[9,10] we are of the opinion that the problem can be in principle solved by using suitably constructed isodesmic reactions.[11] (This term means that on both sides of the reaction there is the same number of bonds of each type, C–C, C–O, *etc.*) It turned out that, for instance, the molecule of acetic acid is stabilized[12] due to the interaction of the two groups C=O and OH by 77 kJ mol^{-1}. Interaction energy of the groups N=O and OH within the group NO_2H^+ could be investigated in the same way.

The third problem concerns the interaction energy of the NO_2H^+ group with conjugated substituents. The energy of protonated 4-nitroaniline is unexpectedly low: from experiments and semiempirical calculations it was deduced that it is by 59 kJ mol^{-1} lower than that of the *meta* isomer.[5] It may appear easy to interpret this stability by conjugation of the NH_2 and NO_2H^+ groups but it is difficult to present the pertinent resonance formulas.[5] Even the great energy difference may be puzzling since the corresponding difference between the isoelectronic molecules of 4-aminobenzoic acid and 3-aminobenzoic acid is only 9 kJ mol^{-1}.[13]

In this article we investigate the structure of protonated nitro compounds by MP2 and DFT calculations with particular respect to the isoelectronic molecule of carboxylic acids. Using the apparatus of isodesmic reactions[14] we wanted to estimate both the inner conjugation within the NO_2H^+ group and the conjugation of this group with conjugated donors. The inner conjugation was investigated on the simplest model compound, protonated nitromethane **2** (Table 1), and conjugation with donors on a series of substituted nitrobenzenes **3a**–**3s** (Table 2) within the framework of the Hammett equation.[15] Conjugation should be revealed by deviations from the Hammett dependence, as was observed in other cases and which led to the questioning of the defined range of validity.[6,13] Such deviations are apparent, particularly when the ionization reaction is decomposed into two isodesmic reactions, one describing the interaction in the ion, the other in the unionized molecule.[6,13]

In principle, energies of certain isodesmic reactions could be obtained from experiments, but the accuracy would be

Table 1 Calculated energies of protonated nitromethane and of reference compounds in eqns. (3)–(5)[a]

	Compound	Conformation	ΔEcalc/au	ΔE_{rel}/kJ mol^{-1}
	CH_3NO_2		−244.5367358	
2A	$CH_3NO_2H^+$	sp	−244.8256488	0
2B		ap	−244.8160592	25.2
4A	CH_3CO_2H	sp	−228.6232142	0
4B		ap	−228.6146245	22.6[b]
	$CH_3N{=}O$		−169.4401081	
	$CH_3NH^+{=}O$		−169.7430113	
	$(CH_3)_2NH$		−134.8151189	
	$(CH_3)_2NH_2^+$		−135.1819081	
	$(CH_3)_2NHOH$	sc	−210.2153853	0
		ap	−210.2147453	1.7

[a] Level MP2(FC)/6-311++G(2d,2p)//MP2(FC)/6-311++G(2d,2p). [b] At the level MP4/cc-pVTZ calculated 22.52 kJ mol^{-1}, ref. 17.

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Table 2 DFT calculated energies of substituted nitrobenzenes and their protonated forms and energies of the isodesmic reactions, eqns. (3)–(5)

	Substituent	Conformation[a]	ΔE $ArNO_2$/au	ΔE $ArNO_2H^+$/au	$\Delta_{11}E$/kJ mol^{-1}	$\Delta_{12}E$/kJ mol^{-1}	Δ_6E/kJ mol^{-1}
3a	H		−436.8746070[b]	−437.1931555[c]	0.00	0.00	0.00
3b	3-CH_3	ap	−476.2029171	−476.5259218	−2.02	−13.49	−11.47
		sp		−476.5257625			
3c	3-CF_3	ap	−774.0200282	−774.3270356	10.93	41.10	30.17
		sp		−774.3271413			
3d	3-CHO	ap, ap	−550.2293612	−550.5382731	9.93	32.88	22.95
		ap, sp		−550.5382009			
		sp, ap	−550.2284017	−550.5388061			
		sp, sp		−550.5391911			
3e	3-CN	ap	−529.1356600[d]	−529.4385756	14.36	55.20	40.84
		sp		−529.4387437			
3f	3-NH_2	ap	−492.2514302	−492.5794664	−1.14	−25.15	−24.02
		sp		−492.5789325			
3g	3-NO_2	ap	−641.4315579	−641.7325462	16.85	62.61	45.76
		sp		−641.7328646			
3h	3-OH	ap, ap	−512.1209147	−512.4406421	2.20	0.36	−1.84
		ap, sp		−512.4406024			
		sp, ap	−512.1217657	−512.4405490			
		sp, sp		−512.4400854			
3i	3-F	ap	−536.1405790	−536.4515280	7.62	27.57	19.95
		sp		−536.4515311			
3j	3-Cl	ap	−896.4944599	−896.8067930	8.11	24.49	16.38
		sp		−896.8067444			
3k	4-CH_3		−476.2035274	−476.5300540	−3.62	−24.57	−20.95
3l	4-CF_3		−774.0200697	−774.3262944	10.82	43.17	32.36
3m	4-CHO	ap	−550.2285125	−550.5377803	10.31	34.64	24.34
		sp		−550.5378044			
3n	4-CN		−529.1361175[d]	−529.4407725[d]	13.16	49.64	36.48
3o	4-NH_2		−492.2557597	−492.6028566	−12.50	−87.46	−74.95
3p	4-NO_2		−641.4315816	−641.7310084	16.79	66.99	50.20
3q	4-OH	ap	−512.1239885	−512.4544247	−5.22	−36.36	−31.13
		sp		−512.4543679			
3r	4-F		−536.1422321	−536.4584149	3.28	9.49	6.21
3s	4-Cl		−896.4957460	−896.8138368	4.73	5.93	1.20

[a] Conformation on the C(1)–N(O_2) bond, followed by the conformation on the C(3)–X bond as the case may be. [b] Ref. 18; at the level MP2(FC)/6-311++G(2d,2p) calculated here −435.7908113 au. [c] Ref. 6; at the level MP2(FC)/6-311++G(2d,2p) calculated here −436.1028448 au. [d] Ref. 6.

insufficient in some cases. We preferred to obtain all values by quantum chemical calculations when their reliability was secured by anchoring on some experimental gas-phase basicities.[1] The use of quantum chemistry in our approach is thus essentially restricted to observable quantities that can be in part checked by experiments.

Computational details

Energies of protonated nitromethane **2A**,**B** and reference compounds were calculated at the level MP2(FC)/6-311++G(2d,2p)//MP2(FC)/6-311++G(2d,2p) using the GAUSSIAN 03 program.[16] They are listed in Table 1. Energies of substituted nitrobenzenes **3a**–**3s** and of their protonated forms were calculated at the level B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) and are listed in Table 2. All structures were checked by vibrational analysis and behaved as energy minima. Planarity or any symmetry conditions were never anticipated. As far as possible all reasonable conformations were taken into consideration and calculations were started from the pertinent near structures; this concerns particularly the two orientations of unsymmetrical substituents in benzene *meta* derivatives **3b**–**3j**.

In the cases when several conformers were found, the reaction energies were calculated for their equilibrium mixture at 298 K. The equilibrium constant and population of conformers were estimated with the assumption $\Delta G°(298) \cong \Delta E(\mathrm{DFT})$; from these values we calculated the effective energies of the equilibrium mixture. This particularly concerns the values of Δ_6E, $\Delta_{11}E$ and $\Delta_{12}E$ in Table 2, although the corrections were minute and very similar values would be obtained taking into account only the minimum-energy conformer.

Results and discussion

Comparison with experiments

Measurements of the gas-phase basicities of nitro compounds are scarce.[1] Direct comparison with our calculation is possible for nitrobenzene and 4-nitroaniline, eqn. (1), when one accepts as granted that protonation of the latter takes place on the nitro group[5] (**1a**).

$$\begin{aligned} &C_6H_5\text{-}NO_2H^+ + 4\text{-}NH_2\text{-}C_6H_4\text{-}NO_2 \\ &\qquad = 4\text{-}NH_2\text{-}C_6H_4\text{-}NO_2H^+ + C_6H_5\text{-}NO_2 \\ &\qquad\qquad \Delta_1E(\mathrm{calc}) = -74.9\ \mathrm{kJ\ mol^{-1}} \\ &\qquad\qquad \Delta_1G°(298)(\mathrm{exp}) = -64.7\ \mathrm{kJ\ mol^{-1}} \end{aligned} \tag{1}$$

The reaction is both isodesmic and homodesmotic[19] (the corresponding bonds connect not only equal atoms but also atoms of the same hybridization). However, the calculated substituent effect is overestimated. Similarly, in the case of substituted benzonitriles,[6] the basicities calculated at the same theoretical level had to be corrected by a factor of 0.82 to reach the fit with experiments. In eqn. (1) the factor would be 0.86.

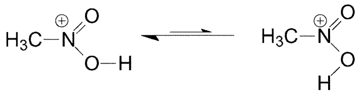
Comparison of aliphatic and aromatic nitro compounds required recalculation of the latter at the high level (Table 2, footnotes *b* and *c*). In eqn. (2) the substituent effects are also overestimated; the correction factor would be 0.79.

$$\begin{aligned} &CH_3\text{-}NO_2H^+ + C_6H_5\text{-}NO_2 = C_6H_5\text{-}NO_2H^+ + CH_3\text{-}NO_2 \\ &\qquad\qquad \Delta_2E(\mathrm{calc}) = -60.7\ \mathrm{kJ\ mol^{-1}} \\ &\qquad\qquad \Delta_2H°(298)(\mathrm{calc}) = -62.0\ \mathrm{kJ\ mol^{-1}} \\ &\qquad\qquad \Delta_2G(\mathrm{exp}) = -47.9\ \mathrm{kJ\ mol^{-1}} \end{aligned} \tag{2}$$

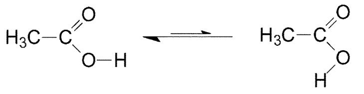
From eqns. (1) and (2) we may conclude that our calculated energies agree with the experiments fairly, with a similar accuracy as obtained previously for the acidobasic equilibria of similar compounds.[6,12,13,18] For evaluation of the relative substituent effects, overestimating of all values is of no consequence; for predicting the experimental values, scaling by an empirical factor would be suggested. Note that calculation of $\Delta_2H°(298)$ did not improve the fit as in other isodesmic reactions dealt with previously.[13]

Conformation

Of the two planar conformations of carboxylic acids, **4A** (sp) is much more stable[20] than **4B** (ap) and this regularity holds also quite generally for a variety of derivatives and similar molecules.[21]



2A **2B**

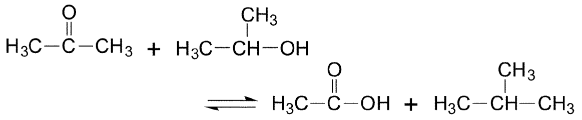


4A **4B**

We found that it also holds for protonated nitromethane **2A**,**B** and the energy differences calculated at the same level are almost equal (Table 1, last column). Several explanations of this regular conformation have been offered but none of them are satisfactory.[21] In any case the isoelectronic molecules **2** and **4** behave equally in this respect.

Conjugation within the NO_2H^+ group

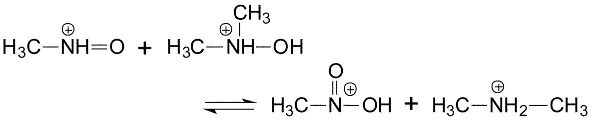
Conjugation within the carboxyl group was estimated[11,12] on the basis of eqn. (3):



$$\mathrm{H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_3C{-}\overset{CH_3}{\overset{|}{C}H}{-}OH \rightleftharpoons H_3C{-}\overset{O}{\overset{\|}{C}}{-}OH + H_3C{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_3}$$

$$\Delta_3E(\text{calc}) = -77\ \text{kJ mol}^{-1} \qquad (3)$$

This reaction is isodesmic but not homodesmotic[19] since the bonds C_{sp^3}–C_{sp^2} and C_{sp^3}–O have been replaced by the bonds C_{sp^3}–C_{sp^3} and C_{sp^2}–O; this shortcoming evidently cannot be removed. Application of this procedure to protonated nitromethane is not self-evident: comparison of carboxylic acid to alcohol as reference seems natural; nitro compounds must be compared to *N*,*N*-dialkylhydroxylamine. In our opinion, eqn. (4) is the right choice: the bonds N_{sp^2}–H and N_{sp^3}–O are replaced by the bonds N_{sp^3}–H and N_{sp^2}–O and the positive charges are retained.



$$\mathrm{H_3C{-}\overset{\oplus}{N}H{=}O + H_3C{-}\overset{CH_3}{\overset{\oplus|}{N}H}{-}OH \rightleftharpoons H_3C{-}\overset{O}{\overset{\|\oplus}{N}}{-}OH + H_3C{-}\overset{\oplus}{N}H_2{-}CH_3}$$

$$\Delta_4E\ (\text{calc}) = -129\ \text{kJ mol}^{-1} \qquad (4)$$

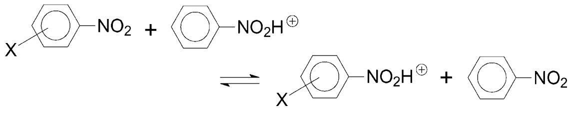
The stabilization energy Δ_4E is much higher than Δ_3E of the isoelectronic carboxylic acids when using a comparable model. Note, however, that Δ_4E could be very sensitive to the proper choice of this model. In any case the conclusion is safe that **2** is a particularly stable structure compared to simpler molecules with only one oxygen atom.

Hammett correlations

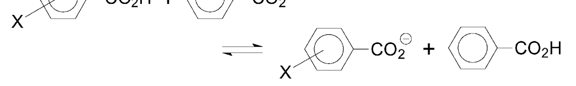
According to the Hammett equation,[15] eqn. (5), relative basicities of *meta*- and *para*-substituted nitrobenzenes are related to the relative acidities of equally substituted benzoic acids through the substituent constants σ_m or σ_p that have been derived from these acids. The reaction constants ρ and ε are determined by linear regression and ε should be not significantly different from zero.

$$\Delta E = \rho\sigma_{m,p} + \varepsilon \qquad (5)$$

In terms of isodesmic reactions, the relative basicity of substituted nitrobenzenes is represented by eqn. (6), and the relative acidity of benzoic acids by eqn. (7).



(6)



(7)

Mutual dependence of the calculated energies Δ_6E (this paper) and Δ_7E (ref. 13) is shown in Fig. 1. The values of Δ_7E on the *x*-axis have the same meaning as the constants σ but their merit is that they relate to isolated molecules. Fig. 1 confirms the previous results reached both from the calculated energies[6] and from the gas-phase reactivities:[22] The Hammett equation is valid with a high accuracy for *meta* derivatives. When *para* derivatives are included, one half of them usually deviates, either donors when the functional group is an acceptor or *vice versa*. This defect was formally solved either by introducing dual substituent constants for the proper class of substituents[15b,23] or by excluding this subclass from the validity range.[24] In this way the number of empirical parameters may increase and in any case a certain arbitrariness cannot be avoided. As a radical alternative, restriction of the validity range only to *meta*-substituents was considered;[6,22] the restricted version should be used at least when comparing the substituent effects in various reactions, *i.e.* comparing the reaction constants ρ. Note that in eqn. (6) the classical range of validity of the Hammett equation is not exceeded: protonation proceeds on the second atom from the benzene ring, at the same distance as in reaction eqn. (7).

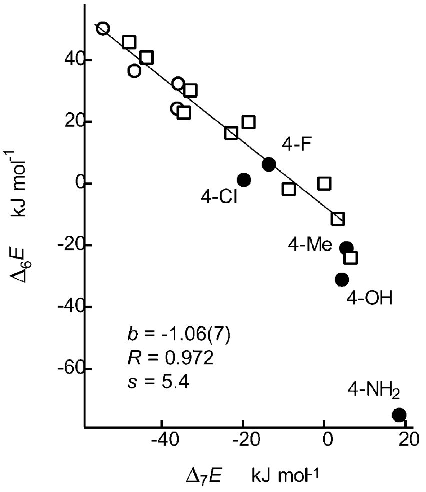


Fig. 1 Hammett plot of the calculated basicities Δ_6E of substituted nitrobenzenes **3a**–**3s** *vs.* the acidities of equally substituted benzoic acids Δ_7E: □ *meta* derivatives, ○ *para* derivatives with an acceptor substituent, ● *para* derivatives with a donor substituent; the statistics and the regression line relate to the groups □ + ○.

The traditional access improving the accuracy is Dual Substituent Parameter (DSP) treatment.[23,25] Application to our case yields eqns. (8) and (9); the inductive and resonance parameters σ_I and σ_R were taken from ref. 26.

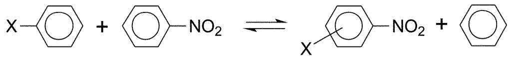
$$\Delta_6E(meta) = -3\pm2 + (69\pm4)\sigma_I + (40\pm5)\sigma_R \quad R = 0.993 \quad s = 2.9\ \mathrm{kJ\ mol^{-1}} \qquad (8)$$

$$\Delta_6E(para) = -8\pm5 + (75\pm12)\sigma_I + (86\pm9)\sigma_R \quad R = 0.979 \quad s = 8.6\ \mathrm{kJ\ mol^{-1}} \qquad (9)$$

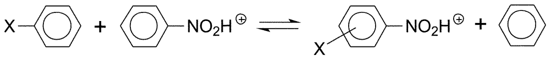
Improvement has been reached (compare the statistics in Fig. 1), but it is at the cost of more parameters and it is not proportional to this effort. There are not two parameters compared to one as commonly said, but four compared to one, since the main improvement is in separating *meta* and *para* derivatives.[22] Eqn. (8) is overparametrized and improvement compared to the Hammett equation is not very significant. The lower accuracy of eqn. (9) can be still somewhat improved by using the dual constants[26] $\sigma_R{}^+$, eqn. (10), but the arbitrariness in choice between several sets of constants is a matter of consequence.

$$\Delta_6E(para) = -4\pm4 + (65\pm8)\sigma_I + (74\pm3)\sigma_R{}^+ \quad R = 0.991 \quad s = 5.6\ \mathrm{kJ\ mol^{-1}} \qquad (10)$$

A more significant analysis is based on separating the substituent effect in non-protonated nitrobenzenes and in their protonated forms as expressed by the isodesmic reactions, eqns. (11) and (12).



(11)



(12)

Eqns. (11) and (12) exceed the range of validity of the Hammett equation as originally defined[15] since the reactions do not proceed in the side-chain but directly on the benzene ring. Nevertheless, extension to such reactions, *i.e.* aromatic substitution, is common provided that dual constants σ are used for the conjugated *para* substituents, which are different according to whether the substitution is nucleophilic or electrophilic.[27] For equilibria, there is no material for comparison, but it was pointed out that the Hammett equation may be poorly valid for equilibria between uncharged particles.[28] The Hammett plot of $\Delta_{11}E$, Fig. 2, reveals an essentially similar picture as Fig. 1: the same substituents deviate, *viz. para* standing donor groups, only the deviations are smaller since also the whole range of the values of $\Delta_{11}E$ is narrower. The Hammett plot of $\Delta_{12}E$ is not shown: it would be rather similar to Fig. 1 since $\Delta_{12}E = \Delta_{11}E + \Delta_6E$ and Δ_6E preponderates in the sum.

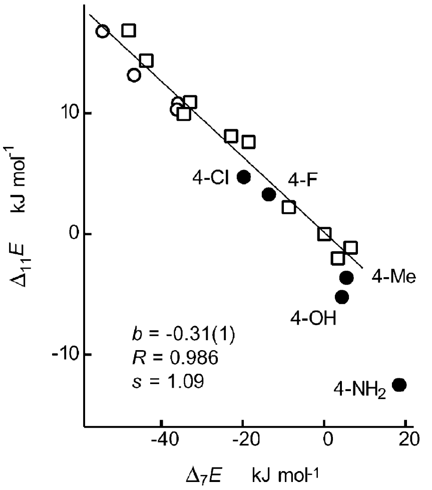
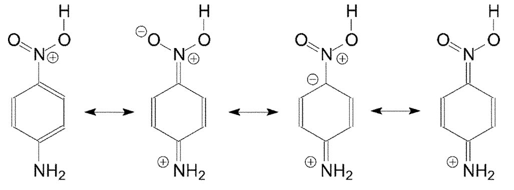


Fig. 2 Hammett plot of the calculated interaction energies $\Delta_{11}E$ in substituted nitrobenzenes, eqn. (11), *vs.* the acidities of substituted benzoic acids Δ_7E: definition of points is as in Fig. 1.

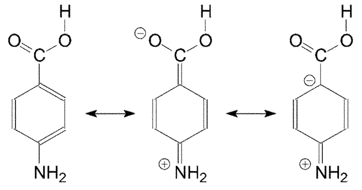
Definition of the exact range of validity of the Hammett equation may be mainly a matter of convention. A broader range is always accompanied by a lower accuracy and the proper definition will depend on the intended purpose. In our opinion, the problem requires still further data, experimental or calculated. In any case, protonation of nitrobenzenes is a good example on which the limitation of the Hammett equation is evident, even when the classical range of validity is maintained [eqn. (6) and Fig. 1]. The most deviating point is that of 4-nitroaniline. Its deviation corresponds roughly to the dual substituent constant σ^+ for the NH_2 group as given by Charton[26] but many different values can be found in the literature.

Structure of the conjugated molecules

Since the conjugation in the protonated 4-nitroaniline **1a** is particularly strong, we shall choose this example for structure investigation. Classical theory of resonance describes this conjugation by the resonance formulas **1A** ↔ **1B** similarly as in the case of isoelectronic 4-aminobenzoic acid, **5A** ↔ **5B**. There is no evident reason why the resonance should be stronger in **1**.



1A **1B** **1C** **1D**



5A **5B** **5C**

Some experimental proofs can be searched in the geometric parameters. Table 3 confirms that the formulas **1B** and **5B** have same predicative value: both the bonds C2–C3 and C–NH_2 are significantly shortened and the angles H–N–H widened (hybridization nearer to sp^2). However, similarity of the two isoelectronic molecules is only qualitative: in the quantitative respect conjugation in **1** is several times stronger than in **5** and seems to be more dependent on the positive charge than on the isoelectronic structure (see the similarity with the $C{\equiv}NH^+$ group, Table 3, in the next to last line). Also, the interaction energies of the substituents expressed by isodesmic reactions like in eqns. (11) and (12) give the same picture (Table 3, last column): for **1** the energy is much greater in the absolute values

Table 3 Calculated geometric parameters and stabilization energies of some substituted anilines

Substituent	C2–C3^a/Å	C–NH_2/Å	∠HNH/°	ΔE^b/kJ mol^{-1}
H	1.391	1.398	112.2	0
4-CO_2H	1.384	1.383	114.0	−10.3^c
4-NO_2	1.383	1.369	117.7	−12.5
4-$C{\equiv}NH^+$	1.368	1.343	117.1	−59.4^d
4-NO_2H^+	1.362	1.334	116.9	−87.5

[a] Average values for the bonds C2–C3 and C5–C6. [b] Stabilization energies as, for instance, in eqn. (11) or (12). [c] Ref. 13. [d] Ref. 6.

Table 4 Some calculated geometric parameters of substituted nitrobenzenes and their protonated forms (bond lengths in Å, bond angles in degrees)

		Nitrobenzenes				Protonated forms			
	Substituent	C2–C3	C–N(O)	N=O	∠ONO	C2–C3	C–N(O)	N=O	∠ONO
3a	H	1.392	1.481	1.225	124.7	1.380^a	1.401	1.194	119.3
3r	4-F	1.390	1.477	1.225	124.7	1.374^a	1.393	1.196	119.2
3k	4-CH_3	1.391	1.477	1.225	124.5	1.375^a	1.390	1.199	118.9
3q	4-OH	1.386^a	1.469	1.227	124.4	1.368^a	1.380	1.203	118.8
3o	4-NH_2	1.383	1.459	1.229	124.1	1.362^a	1.368	1.208	118.4

^{a} Average values for the bonds C2–C3 and C5–C6.

than for **5** and is nearer to the interaction energy of the charged group $C\equiv NH^+$.

Since formula **1B** does not predict the unusual stability of the molecule, two additional theoretical conceptions will mentioned that were suggested in the case of non-protonated 4-nitroaniline. On the one hand, it was assumed that only the NH_2 group is actually conjugated and the NO_2 group acts only by its inductive effect and strengthens this conjugation;[29] this suggestion was later somewhat weakened.[30] A picture corresponding to this concept would be the formula **1C** and its analogy **5C**. On the other hand, it was pointed out that the two N=O bonds in the NO_2 group possess practically a double-bond character and one piece of speculation was about the possibility that the nitrogen atom could accommodate more than eight electrons;[31] this idea was extended to further molecules.[32] Its representation would be the *a priori* low probability formula **1D**. We searched an experimental test in the geometry of several nitrobenzene derivatives with variable donor substituents (Table 4). Conjugation is evident from the shortened bonds C2–C3 as required by all theories; shortening is rather small in nitrobenzenes, greater in their protonated forms. Even the C–N(O) bond is shortened – more in the protonated form – in accord with **1B** or **1D** but not with **1C**. Lengthening of the N=O bond would be in agreement with **1B** but is rather small as expected from the participation of **1C** or **1D**. Narrower angles O–N–O could be predicted by **1B** but the observed changes are almost negligible. In conclusion, the calculated geometry gives good proof for the existence of conjugation as pictured by the formula **1B**, some features perhaps by a small participation of **1D**. For **1C** there is no support; an analogous form could come into consideration for non-protonated 4-nitroaniline. Strong conjugation as it follows from the calculated energies is not predicted by any simple theory. We agree with the opinion[30] that real structures of the individual molecules can be only very roughly described in simple terms as an inductive effect and resonance or by means of simple formulas.

Conclusions

In our opinion, the principle of isoelectronic structures should not be overestimated, particularly when the two species are differently charged. Protonated nitro compounds display several similarities with the isoelectronic carboxylic acids but also strong differences particularly in the quantitative respect. These features cannot be explained in terms of simple resonance formulas but quantum chemical calculations are very helpful.

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References

1 E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413–656.
2 M. Liler, *J. Chem. Soc.*, 1962, 4272–4282; J. C. D. Brand, J. C. Horning and M. B. Thornley, *J. Chem. Soc.*, 1952, 1374–1383; R. J. Gillespie, T. E. Peel and E. A. Robinson, *J. Am. Chem. Soc.*, 1971, **93**, 5083–5087.
3 E. Rolli and R. Houriet, *Spectrosc. Int. J.*, 1984, **3**, 177–183.
4 M. Taagepera, K. D. Summerhays, W. J. Hehre, R. D. Topsom, A. Pross, L. Radom and R. W. Taft, *J. Org. Chem.*, 1981, **46**, 891–903.
5 P.-C. Maria, I. Leito, J.-F. Gal, O. Exner and M. Decouzon, *Bull. Soc. Chim. Fr.*, 1995, **132**, 394–401.
6 O. Exner and S. Böhm, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3864–3871.
7 M. Decouzon, O. Exner, J.-F. Gal and P.-C. Maria, *J. Phys. Org. Chem.*, 1994, **7**, 615–624.
8 O. Castaño, R. Notario, K. Hori and J.-L. M. Abboud, *Struct. Chem.*, 1996, **7**, 321–327.
9 M. R. Siggel and T. D. Thomas, *J. Am. Chem. Soc.*, 1986, **108**, 4360–4363; K. B. Wiberg, J. Ochterski and A. Streitwieser Jr., *J. Am. Chem. Soc.*, 1996, **118**, 8291–8299.
10 M. J. S. Dewar and K. L. Krull, *J. Chem. Soc., Chem. Commun.*, 1990, 333–334; R. W. Taft, I. A. Koppel, R. D. Topsom and F. Anvia, *J. Am. Chem. Soc.*, 1990, **112**, 2047–2052; C. L. Perrin, *J. Am. Chem. Soc.*, 1991, **113**, 2865–2868; P. Burk and P. v. R. Schleyer, *J. Mol. Struct. (Theochem.)*, 2000, **505**, 161–167; P. R. Rablen, *J. Am. Chem. Soc.*, 2000, **122**, 357–368; J. Holt and J. M. Karty, *J. Am. Chem. Soc.*, 2003, **125**, 2797–2803.
11 O. Exner, *J. Org. Chem.*, 1988, **53**, 1812–1815; O. Exner and P. Čársky, *J. Am. Chem. Soc.*, 2001, **123**, 9564–9570.
12 S. Böhm and O. Exner, *New J. Chem.*, 2005, **29**, 336–342.
13 O. Exner and S. Böhm, *J. Org. Chem.*, 2002, **67**, 6320–6327.
14 A. Pross, L. Radom and R. W. Taft, *J. Org. Chem.*, 1980, **45**, 818–826; O. Exner, *Org. Reactivity (Tartu)*, 1995, **29**, 1–6.
15 (*a*) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 2nd edn., 1970, ch. 11.9; (*b*) O. Exner, *Correlation Analysis of Chemical Data*, Plenum Press, New York, 1988, ch. 2.
16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr.., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh, PA, 2003.
17 M. L. Senent, *Mol. Phys.*, 2001, **99**, 1311–1321.
18 O. Exner and S. Böhm, *Collect. Czech. Chem. Commun.*, 2001, **66**, 1623–1637.
19 P. George, M. Trachtman, C. W. Bock and A. M. Brett, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1222–1227.
20 E. M. S. Maçôas, L. Khriachtchev, M. Pettersson, R. Fausto and M. Räsänen, *J. Am. Chem. Soc.*, 2003, **125**, 16 188–16 189.
21 O. Exner, in *The Chemistry of Functional Groups, Supplement A3: The Chemistry of Double-Bonded Functional Groups*, S. Patai, ed., Wiley, New York, 1997, pp. 261–307 and refs. cited therein.
22 M. Ludwig, S. Wold and O. Exner, *Acta Chem. Scand.*, 1992, **46**, 549–554.
23 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.
24 M. Sjöström and S. Wold, *Chem. Scr.*, 1976, **9**, 200–210.
25 R. W. Taft, *J. Phys. Chem.*, 1960, **64**, 1805–1815; S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1–80.
26 M. Charton, *Prog. Phys. Org. Chem.*, 1981, **13**, 119–251.
27 Ref. 15*b*, pp. 124–125.

28 K. Palát Jr, S. Böhm, G. Braunerová, K. Waisser and O. Exner, *New J. Chem.*, 2002, **26**, 861–866.

29 P. C. Hiberty and G. Ohanessian, *J. Am. Chem. Soc.*, 1984, **106**, 6963–6968; T. M. Krygowski and J. Maurin, *J. Chem. Soc., Perkin Trans. 2*, 1989, 695–698.

30 S. Irle, T. M. Krygowski, J. E. Niu and W. H. E. Schwarz, *J. Org. Chem.*, 1995, **60**, 6744–6755.

31 S. D. Kahn, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, 1987, **109**, 1871–1873.

32 O. Exner, *J. Phys. Org. Chem.*, 1990, **3**, 190–194.