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Small steric effects in isolated molecules: alkyl-substituted benzonitriles

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A series of seven alkyl-substituted benzonitriles was investigated as a model for small steric effects (van der Waals tension) excluding any steric inhibition due to resonance. The energies were calculated at a B3LYP/6-311+G(d,p) level and the gas-phase basicities of some compounds were measured by Fourier-transform ion cyclotron resonance. Substituent effects were evaluated separately for neutral molecules and protonated forms by means of isodesmic reactions, and dissected into polar and steric effects by comparing *ortho* and *para* derivatives. One or two *ortho* methyl groups have a relatively small steric effect operating almost exclusively in the protonated form which leads to weakened basicity. An *ortho tert*-butyl group exerts a strong steric effect both in the protonated and nonprotonated forms, manifested also in a rather strong distortion of geometry. The effect on basicity is then a small difference of two large values and is base strengthening. Acid–base properties are in such cases a poor measure of substituent effects and cannot be interpreted in simple terms.

Introduction

Acid–base properties of sterically congested molecules have been customarily explained[1] in classical terms: a primary steric effect or van der Waals tension[2] (vdW), and steric inhibition of resonance or secondary steric effect (SIR). More recently, these effects have also been investigated on isolated molecules in the gas phase, using mostly benzene *ortho* derivatives as model systems. The methyl,[3,4] isopropyl,[5] and *tert*-butyl[6] alkyl groups were chosen as substituents as they exert increasing steric effects and negligible polar effects. The constant functional groups were the acidic groups CO_2H[3–6] or OH,[3] and the basic groups $COCH_3$,[7] NH_2 or $N(CH_3)_2$.[8] These groups are conjugated with the benzene ring and prefer a coplanar or near-to-coplanar conformation unless this is distorted by steric hindrance. We obtained previously[4–6] some results at variance with the classic interpretation[1] based mainly on reactivity in solution. In particular, SIR is not always present when it has been assumed that it is since some pertinent molecules possess planar conformations (for instance 2-methylbenzoic acid[4] or 2-methylacetophenone[7b]). Acidity or basicity of these molecules is not due to vdW tension since the volumes of the carboxy and carboxylate groups (or of acetyl and protonated acetyl) are virtually equal. We preferred modelling the acid–base properties as electrostatic interactions. This model assumes that the substituent effect takes place mainly in the ion and only to a small extent in the neutral molecule. In the case of the carboxylate anion, one can imagine this interaction as a pole–induced dipole interaction of the negative charge with a polarizable alkyl group,[3,9] or alternatively as a pole–dipole interaction between the charge and C–H bond dipole.[10] In the case of the protonated acetyl group, only the latter interpretation is possible (destabilizing the cation) since the *ortho* effect is base weakening. The difference may be understood in terms of a different charge distribution of negative and positive charges.

Other molecules, which are more sterically hindered, are nonplanar and SIR can be detected and calculated within the framework of isodesmic reactions (for instance in 2,6-dimethylbenzoic acid[9] or 2,6-dimethylacetophenone). Even in these molecules, SIR is also present in the ions and has a relatively small effect on the resulting acidity or basicity.

Our conclusions have been based only on a limited number of molecules and are supported in part by experiments, and also by quantum chemical calculations, particularly in the case of species which are not in the minimum-energy conformation.[9] In this paper, we intend to support these conclusions by reference to a simpler model in which any SIR is *a priori* excluded and the steric effect can be identified with the vdW tension. We chose alkyl-substituted benzonitriles **2**–**7** (Table 1) and anticipated that the steric effects would be small but still detectable in isolated molecules. The structure of 2-methyl- (**2**) or 2,6-dimethyl-benzonitrile (**5**) seemed unquestionable and has not been investigated in detail, except for an X-ray analysis of **5**.[11] No steric effect has ever been claimed: it does not seem possible from the inspection of space-filling (Stuart–Briegleb) models as well as from molecular mechanics calculations.[2] The absence of steric effects was explicitly claimed on the basis of $\nu(C\equiv N)$ stretching frequencies and their absorption intensities,[12] or on the basis of H-bond basicities.[13] A small steric effect in these compounds is also expected from the values of various steric constants of the CN group; they are between the values for F and Cl,[14] or between OH and NH_2.[15] Most significant is a recent analysis[16] calculating the van der Waals radius perpendicular to the substituent axis: it is significantly lower for CN compared to Cl or CH_3. As far as we know, the only implication of any steric effect might be the statement[17] that rotation of the methyl group is observable in **3** but not in **2**. Some steric effect, merely stabilizing, could also be deduced from the anticipated most stable conformation of **2** with one methyl

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Table 1 Calculated energies of substituted benzonitriles and their protonated forms[a]

				Substituent		Rel. basicity Δ_3E		Steric effects		
Comp.	Substituents	E(DFT) au	E(DFT) cation au	Δ_1E	Δ_2E	Calc.	Exp. $\Delta_3G^{\circ c}$	Base SE$_4$	Cation SE$_5$	Basicity SE$_6$
1	H	−324.5777606	−324.9015658	0	0	0	0	0	0	0
2	2-Me	−363.9057384	−364.2334543	−1.1	−11.4	−10.3	−10.8	1.6	6.0	4.4
3	3-Me	−363.9058859	−364.2327799	−1.5	−9.6	−8.1		0	0	0
4	4-Me	−363.9063460	−364.2357428	−2.7	−17.4	−14.7[d]	−14.9[e]	0	0	0
5	2,6-Me$_2$	−402.2341298	−403.5649435	−3.6	−22.0	−18.4	−17.2	2.1	13.1	11.0
6	2-*t*-Bu	−481.8659371 (−481.642839)[f]	−482.1992781 (−481.965020)[f]	+20.0	−5.1	−25.0		23.3 (23.2)[f]	19.1 (18.9)[f]	−4.2 (−4.3)[f]
7	4-*t*-Bu	−481.8747935 (−481.651685)[f]	−482.2065434 (−481.972208)[f]	−3.3	−24.1	−20.8		0	0	0

[a] In kJ mol^{-1} unless otherwise noted; the subscripts at the energies agree with the numbers of defining equations. [b] Calculated from columns 3 or 4, respectively, and from E(DFT) of the following compounds (au): benzene −232.3112375, methylbenzene −271.6387778, 1,3-dimethylbenzene −310.9662298, *tert*-butylbenzene −389.6070228. [c] Relative values of the gas-phase basicity given as the Gibbs energy, $\delta\Delta G°(298)$, determined in this work, referenced to benzonitrile, GB = 780.9 kJ mol^{-1}, ref. 22. [d] From the data of ref. 24 one would get −10.3 kJ mol^{-1} at an MP2/6-31(d) level, or −10.6 for $\Delta H°(298)$ with a thermal correction. [e] From the gas-phase basicity of **4** from ref. 23 (omitted in ref. 22). [f] Values of the sums of electronic and thermal enthalpies, $\Delta H°(298)$, and quantities derived from them.

Table 2 Determining the gas-phase basicities of methyl-substituted benzonitriles from proton transfer reactions (kJ mol^{-1}, 298 K)

Compound B	Reference compound	GB(reference)[a]	ΔGB[b]	GB[c]
2	$CH_3CO_2CH_3$	790.7	+2.15 ± 0.18	
	Cyclopentanone	794.0	−3.50 ± 0.86	
	Tetrahydrofurane	794.7	−2.85 ± 0.03	791.7 ± 1.4
5	$C_2H_5COCH_3$	795.5	+0.60 ± 0.16	
	$C_2H_5CO_2CH_3$	799.2	−1.19 ± 0.46	
	$(C_2H_5)_2O$	801.0	−2.49 ± 0.46	798.1 ± 1.8
	$CH_3CO_2C_2H_5$	804.7	−4.82 ± 0.25	

[a] Absolute gas-phase basicities of the reference base, ref. 22. [b] Gibbs energy of the reaction $BH^+ + Ref \longrightarrow RefH^+ + B$, experimental temperature 338 K; the uncertainties given are standard deviations from three to four measurements. [c] No temperature correction applied; the uncertainties given are standard deviations corresponding to the overlap quality.

hydrogen oriented towards the CN group.[18] In a reversed sense, the substituent effects in **2** were described as an effect of the substituent CN on the $^1J_{13C,H}$ coupling constant in the methyl group;[19] even in this case no steric effect was claimed.

As in our preceding work,[4–8] we intended to calculate the substituent effects with the aid of isodesmic reactions[4,20] and to separate steric effects by comparison of *ortho* derivatives **2**, **5** and **6** with *para* derivatives **4** and **7** (Table 1). Since the enthalpies of formation are not known (except for an estimate[21] for **2**) we calculated the energies of isolated molecules within the framework of density functional theory (DFT) at a B3LYP/6-311+G(d,p) level. In order to estimate steric effects separately in the protonated forms, we also calculated the energies of the latter. The DFT method was chosen for two reasons. Firstly, we wanted to have results compatible to some previous[6b] and parallel[7b] investigations; secondly, orientation calculations at the MP2 and MP4 levels were very pretentious and their results were less consistent.

Experimental gas-phase basicities of benzonitrile[22] and 4-methylbenzonitrile **4**[23] have been reported. When investigating the proton transfer reactions involving derivatives **2** and **5** by Fourier-transform ion cyclotron resonance, we were faced with secondary reactions lowering the precision of results. Nevertheless, this precision was still sufficient since the calculated and experimental relative basicities agreed well for the three derivatives experimentally investigated. Our calculations are thus experimentally supported.

Experimental

The gas-phase basicity measurements (GB) were performed using Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry. Relative basicities ΔGB were determined from the equilibrium constant of proton exchange between the base under study and a reference base of known absolute basicity. The experimental technique has been described in more detail.[4a,5,23]

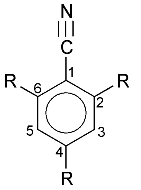
The experimental results are listed in Table 2; comments on the method of calculation are given as footnotes. Note that the uncertainties concern relative values which are deciding within the narrow range of basicities. Some ΔGB values exhibited larger uncertainties than usual. We found that the main cause of errors were secondary reactions (*i.e.* other than proton transfer between the two bases), in particular formation of proton-bound dimers and adducts of fragment ions with a neutral molecule. When these reactions proceed at a rate comparable with the proton transfer, they may impede precise determination of the equilibrium constant. Consequently, the uncertainties in Table 2 are larger than the usual value ±0.5 kJ mol^{-1}.

Results and discussion

Calculations

The DFT calculations at the B3LYP/6-311+G(d,p) level were performed according to the original proposal[25] using the GAUSSIAN94 program.[26] Vibrational analysis was carried out in all cases: all structures belonged to the energy minimum. In the case of conformations with frozen rotation of a methyl or *tert*-butyl group, all remaining geometry parameters were optimized with internal coordinates. Calculations of the sum of electronic and thermal enthalpies, $\Delta H°(298)$, by statistical thermodynamics were made using the same program.[26] The calculated energies are listed in Table 1, some important geometrical parameters in Table 3. Orientation calculations at the MP2/6-311+G(d,p) and MP4 levels were performed using the same program.[26]

Table 3 Calculated geometric parameters of some substituted benzonitriles and their protonated forms[a]

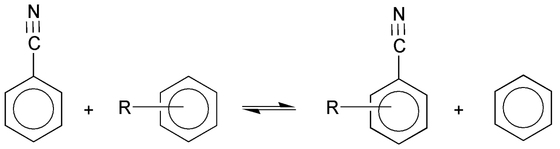


	C1–C2	C6–C1–C2	C1–C2–C3	C(N)–C1–C2	C1–C2–CH_3	C–C–N	C–N–H	C ··· H	N ··· H
1	1.402	120.1	119.7	119.9	—	180	—	—	—
1H^+	1.414	121.7	118.5	119.2	—	180	180	—	—
2	1.409	121.0	117.5	120.7	122.4	179.2	—	2.494	2.918
2H^+	1.424	122.6	116.2	119.7	122.0	179.3	179.8	2.915	3.410
6	1.414	120.9	115.9	125.7	127.1	173.5	—	2.588	2.865
6H^+	1.425	122.4	114.9	125.9	126.6	170.8	175.9	2.551	2.863

[a] Bond lengths in Å, angles in °.

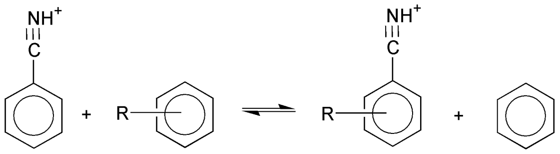
Substituent effects

As in previous work,[4a,b,5,6] the substituent effects were estimated separately in the uncharged molecules of nitriles **2**–**7** and in their protonated forms **2**H^+–**7**H^+. The difference between the two is the substituent effect on the basicity. In the neutral molecules, the interaction of alkyl groups with the nitrile group is expressed by the reaction enthalpy of the reaction eqn. (1) that is both isodesmic and homodesmotic.[20] The pertinent reaction enthalpies are not available from experiments and were substituted for by calculated energies $\Delta_1 E$ (Table 1, column 5). Note that experimental values would be of little help in this case and an efficient comparison of $\Delta_1 E$ with experiments would not be possible since enthalpies of combustion cannot be measured with the necessary accuracy. Most of the $\Delta_1 E$ values are slightly stabilizing and may be interpreted only in terms of an inductive effect (somewhat extending the usual definition of this term[27]) or of hyperconjugation but the latter seems to be negligible in uncharged isolated molecules.[28] An exception is the *tert*-butyl derivative **6** in which a destabilizing effect due to steric crowding is evident.



(1)

The substituent effect in the protonated forms is expressed by eqn. (2); only calculated values, $\Delta_2 E$, are available (Table 1, column 6). These values are evidently stabilizing and can be interpreted in terms of the alkyl group's polarizability or hyperconjugation.



(2)

Substituent effects on the gas-phase basicity, $\Delta_3 E$, can now be expressed as a difference between the effects in protonated and in neutral molecules, eqn. (3).

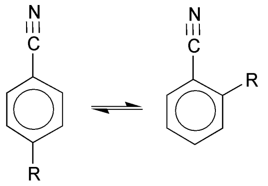
$$\Delta_3 E = \Delta_2 E - \Delta_1 E \qquad (3)$$

The values of $\Delta_3 E$ (Table 1, column 7) can be compared with our experimental relative gas-phase basicities in three cases (see Table 1, column 8). The basicities are given in terms of the original experimental quantities, Gibbs energies $\Delta_3 G°(298)$, since their recalculation to $\Delta_3 H°(298)$ would not change their relative values. The agreement is very good, in spite of the experimental difficulties. In our opinion, we can also regard the remaining calculated energies as reliable. Theoretical interpretation of the relative basicities is not straightforward; however it is evident that in most cases they are controlled by the effects in the protonated forms.

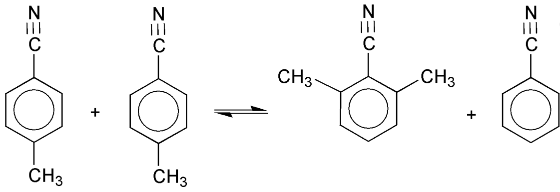
Separation of steric and polar effects

For a better understanding of substituent effects, we attempted to dissect them into steric effect on the one hand and inductive and/or hyperconjugative effects on the other. This was achieved as previously[4–6] by simple comparison of *ortho* and *para* derivatives. For monoalkyl derivatives, the steric effect SE_4 is expressed simply by eqn. (4); for the bis derivative **5** the equation takes a more complex form, eqn. (4a).

There is a fundamental assumption that electrical effects are

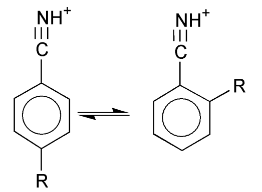


(4)



(4a)

equal in the positions *ortho* and *para*. It is based on an old tradition and has been supported quantitatively by Taft polar constants of *ortho* substituents which are approximately equal to the constants for the *para* position.[29] Still more significant are the substituent effects in reaction series in which a steric effect is impossible.[14b] However, this assumption was challenged more recently on the basis of chemometrical analysis of ionization data in solution.[30] The problem is not important when we restrict ourselves to alkyl substituents since their polar effects are very small. For this reason also our previous results with this procedure[4b,5,6,9] were reasonable. When the above assumption is accepted, the steric effect in protonated benzonitriles is represented by eqn. (5) and the steric effect on the basicity by the difference, eqn. (6). In these cases, the assumption is somewhat less safe since electronic effects in protonated forms are no longer small and cannot be predicted.



(5)

$$SE_6 = SE_5 - SE_4 \quad (6)$$

Values of SE_4, SE_5 and SE_6 are listed in Table 1, columns 9, 10, 11, respectively. They reveal in the first approximation what was expected. The difference between the behaviour of methyl and *tert*-butyl derivatives is striking. In methyl derivatives, steric effects are quite small in the base and much greater in the protonated form. The steric effect SE_4 in **2**, estimated here to be 1.6 kJ mol^{-1} (Table 1) could lie within the uncertainty of the approach but we calculated a similar value, 2.5 kJ mol^{-1}, within the framework of MM2 force field[2a] for the total vdW interaction of all nonbonded atoms. The effect on the basicity SE_6 is base-weakening and is controlled by the effect in the cation SE_5. The picture is similar to the acidity of carboxylic acids which is controlled by the effect in the anion and this effect is acid-strengthening.[4a,b] We offered an explanation according to which the vdW interaction is equal in the carboxylic acid molecule and in the carboxylate anion; the acid-strengthening effect was explained by a pole–induced dipole interaction.[9] The alkyl groups were represented in this model as a polarizable medium. One important piece of evidence was the equally distorted geometry of 2-methylbenzoic acid and of its anion which shows that the carboxy and carboxylate groups are equally bulky. In the present case of benzonitriles, there is also a negligible difference in the geometry between **2** and its anion **2H**$^+$. In **2** there is virtually no difference compared with benzonitrile: a small vdW interaction can be seen from the energy but not from the geometry. Note also that in the minimum-energy conformation no methyl hydrogen atom is oriented in the proximity of the cyano group, in contrast to the conformation suggested by the NMR spectra.[18] However, this finding is very weak since the energy calculated for the fixed conformation with one hydrogen atom in the ring plane is higher by only 0.01 kJ mol^{-1}. Taking into account some uncertainty in the calculations of fixed conformers, one could say that the methyl group is freely rotating.

Compared to carboxylic acids, there is a difference in that the methyl group in nitriles cannot be treated here as a polarizable moiety since the protonated form is destabilized (the methylated bases are weaker). Within the framework of electrostatics, one can represent the methyl group as a dipole with the positive end toward the hydrogen atoms. This is, however, an *ad hoc* explanation and only reveals the inadequacy of any electrostatic model.

The behaviour of the *tert*-butyl derivatives was unexpected. The steric effect SE_4 in **6** is great and its distorted geometry deserves a picture (Fig. 1). The steric interaction in **6** has been estimated to be 23 kJ mol^{-1} (Table 1) while MM2[2a] calculations yield the vdW effect of 28.4 kJ mol^{-1}. Agreement of the two fundamentally different approaches is good. We can conclude with certainty that steric effect SE_4 in **2** is almost negligible while in **6** it is at least greater by one order of magnitude. Note that the two methyl groups in **6** facing the CN group seem not to lie in the ring plane, minimizing in this way the steric interactions. However, calculation of fixed conformers did not reveal any energy difference nor any rotational barrier. The best description is again that the *tert*-butyl group is freely rotating. In any case, the conformation suggested from the NMR spectra[18] was not confirmed even for this compound.

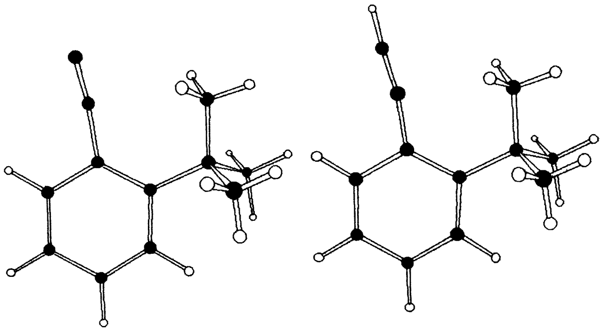


Fig. 1 Calculated geometry of 2-*tert*-butylbenzonitrile **6** and of its protonated form **6H**$^+$.

The protonated form **6H**$^+$ shows a similar steric effect (Table 1) and virtually equal deformations (Fig. 1), see for example the equal C(N)–C1–C2 and C1–C2–CH_3 bond angles and slightly different C1–C2 bond lengths (Table 3). When the two relatively large steric effects in **6** and **6H**$^+$ are subtracted, one gets the steric effect on basicity which is slightly base strengthening; this is unexpected and qualitatively different from the effect of a methyl group. We examined the possibility that this small effect could be partly due to contributions of the zero-point energy or thermal enthalpy. Hence, we calculated the sums of electronic and thermal enthalpies, $\Delta H°(298)$, of **6** and **7**, and their protonated forms (Table 1). The steric effect resulting from these values was equal to those from *E*(DFT) energies: as in similar cases the effect of thermal corrections was negligible in the isodesmic reactions. We conclude that the acid–base properties may be a poor measure of substituent effects unless they are separated into the effects in the neutral molecule and in the ion; this concerns particularly steric effects.

Our approach made possible the detection of steric effects of *ortho* substituents even in substituted benzonitriles in which the functional group is sterically unpretentious. These effects were observed separately on isolated molecules and still more clearly on the protonated forms, while the basicities themselves may be difficult to interpret and sometimes misleading. Previous analysis within the framework of the dual substituent parameters approach[12b] failed to detect steric effects, probably for the reason that sufficiently bulky substituents were not included.

We also wanted to test to what extent the results are dependent on the used DFT method. When we applied the MP approach to eqn. (4) with R = CH_3, we obtained the steric effects SE_4 which were also very small but of opposite sign to those in Table 1: −4.4 kJ mol^{-1} at the MP2/6-311+G(d,p) level and −2.6 kJ mol^{-1} at the MP4(SDT)/6-311+G(d,p)//MP2/6-311+G(d,p) level instead of +1.6 kJ mol^{-1} in Table 1. The difference is less with the more advanced theoretical model but we were not able to proceed to still more sophisticated models for technical reasons. In particular, we were unable to apply the MP method to *tert*-butyl derivatives which are essential for this work. In our opinion, DFT is the method of choice.

Conclusions

Although our results were obtained on only one particular model system and by a single method (DFT), we would suggest the following more general conclusions can be put forth. Some weak steric effects are observable on isolated molecules even when they are not evident from molecular models or from molecular mechanics. These weak effects, as well as stronger effects due to the bulkier groups, are not well estimated from the acidities or basicities since the steric hindrance may be similar in neutral molecules and in the ions. The acidity or basicity is controlled by short-range effects in the ions which may be denoted as being electrostatic, although any simple description in terms of simple electrostatic equations hardly seems possible.

Acknowledgements

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