Protonation and Proton Affinities of Monosubstituted Benzenes: a Theoretical Study

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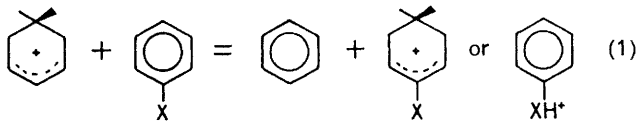
We have performed an *ab initio* study of the protonation of some monosubstituted benzenes using a minimal basis set. According to our results molecular electrostatic potentials characterize compounds that protonate exclusively on the ring or on the substituent. There is a linear correlation between the proton affinities of those compounds that protonate on the ring and the 1*s* binding energy of the *para*-carbon atom.

PROTONATION of aromatic compounds, particularly benzene derivatives, has been much studied in recent years.[1–10] Proton affinities of these compounds in solution have been known for some time,[11–13] but the influence of the solvent can be very strong [14–18] making it difficult to estimate their intrinsic basicity.

Although gas-phase proton affinities have been recently measured to a precision of ± 0.2 kcal mol^{-1} by means of high-pressure mass spectroscopy,[2,5] ion cyclotron resonance techniques (ICR) [19] and flowing-afterglow experiments,[20] interpretation of these experimental results is not straightforward. When the molecule contains more than one basic site, these methods do not provide conclusive information either on the preferred protonation-site or the proton affinity values for the other sites.

A considerable amount of theoretical work [3,8–10,21–24] has been devoted to study the intrinsic effects of the substituent on the basicity of benzene derivatives, mainly by calculating the energy change in the 'isodesmic' proton transfer reaction (1): [3,8–10,23]



(1)

One important conclusion of these studies is that ring-protonation occurs preferably on the *para*-position relative to the substituent.

A good correlation between experimental enthalpy changes for reaction (1) and the empirical substituent constants σ_p^+ was obtained [6] for a 'reasonable' set of benzene derivatives with the exception of nitrobenzene, benzaldehyde, and cyanobenzene. The conclusion was that protonation of these compounds occurs on the substituent.

We aim, in this paper, to look for some molecular property which can be easily calculated, which correlates with the relative proton affinities of monosubstituted benzenes, and which indicates unambiguously the preferred protonation site. To achieve this we calculate the electrostatic potential map for a given set of benzene derivatives since it has been shown [25,26] that this simple treatment can, qualitatively, predict protonation sites. Theoretical proton affinities will be obtained by computing SCF energies for the system plus a proton placed at the electrostatic potential minimum.

Calculations.—A set of monosubstituted benzene derivatives with known equilibrium geometries was selected to avoid time consuming geometry optimizations. They are: benzene,[27] toluene,[28] aniline,[29] phenol,[30] fluorobenzene,[31] benzaldehyde,[32] nitrosobenzene,[33] cyanobenzene,[34] and nitrobenzene.[35] This set includes all kinds of substituent effects and therefore any correlation found between proton affinities and other molecular properties, should be quite general.

As a first step we have evaluated the electrostatic potentials of these molecules in a P plane, defined as being perpendicular to the ring and containing the substituted and '*para*' carbon atoms. SCF calculations were carried out using a STO-3G minimal basis set.[36] The molecular electrostatic potential was calculated with the equations of ref. 37. We shall only present maps for the molecules which best characterize each extreme situation. We present in Figures 1—4 the results for toluene, fluorobenzene, aniline, and nitrobenzene.

It is clear that toluene (Figure 1) and nitrobenzene (Figure 4) are two extreme cases. In the first one, a single minimum appears above (and below) the ring and the line of zero potential clearly separates this region from that of the substituent, which is repulsive. Therefore, toluene should undergo ring protonation, exclusively. In nitrobenzene the reverse situation is found: there is a potential minimum on the substituent and the potential is repulsive on the ring region. In consequence, nitrobenzene should protonate on the substituent, exclusively.

Cyanobenzene, nitrosobenzene, and benzaldehyde present similar characteristics, explaining why protonation of these compounds takes place on the substituent. Although in the last two cases a shallow minimum appears on the ring region, ring-protonation is not very likely to occur. We shall discuss this point later.

The depth of the minima over the ring increases in the sequence: fluorobenzene, phenol, and aniline (see Figures 2 and 3) and two basic sites exist, making possible a ring and/or a substituent protonation.

In order to evaluate the proton affinities for these systems it is necessary to locate the absolute minimum in the electrostatic potential map. Only in the case of aniline must this minimum be in the P plane. We then calculated the molecular electrostatic potential in the

substituent region on the molecular plane. As an example, the results obtained for nitrobenzene, benzaldehyde, and nitrosobenzene are presented in Figures 5—7, respectively.

Nitrobenzene and benzaldehyde present two minima corresponding to the two lone pairs of the oxygen atom.

Nitrosobenzene can be a nitrogen- or an oxygen-base. In this case we have found two minima which correspond to the lone pairs of the oxygen atom; and a third (and deeper) one centred on the nitrogen atom. According to our results, nitrosobenzene must be a nitrogen base. Although we could find no experimental study of nitrosobenzene protonation in the literature, on the basis of a recent study of the base properties of this molecule, Freiser and Beauchamp [7] conclude that in nitrosobenzene–Li^+ complexes, the ion is bonded to the nitrogen.

The remaining molecules present, as expected, a single minimum.

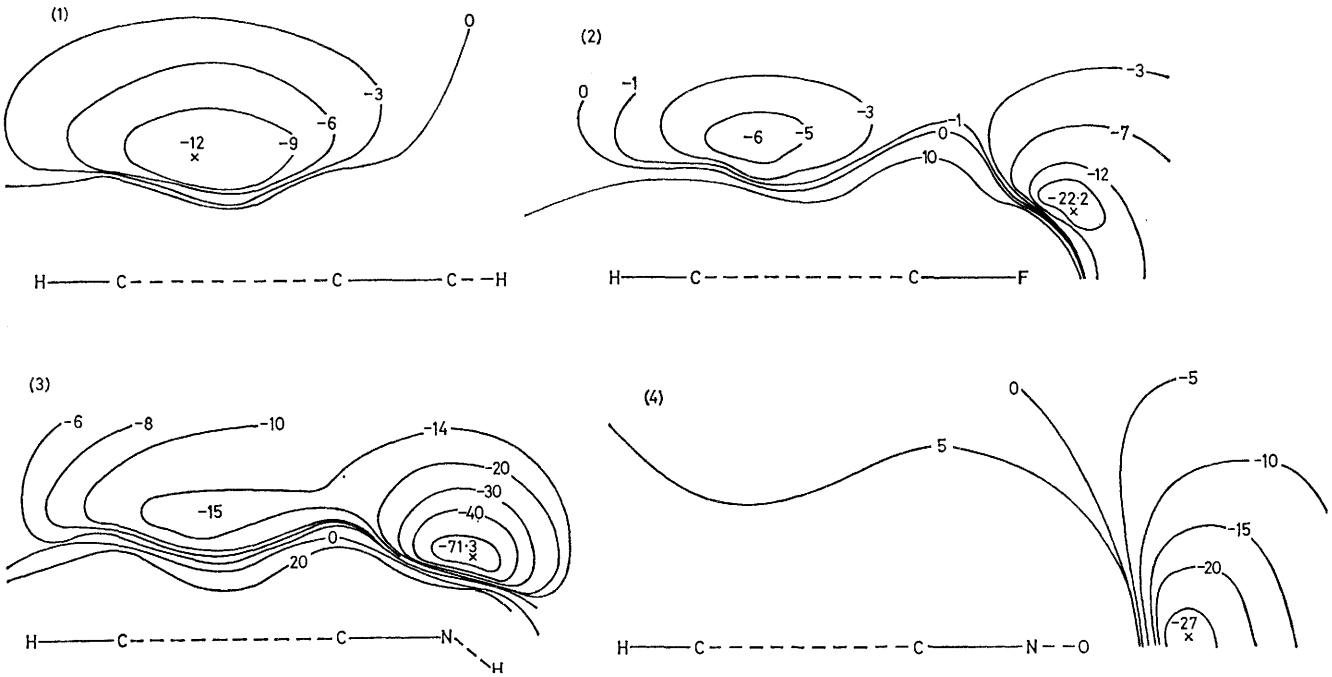
Ring Protonation.—Some benzene derivatives undergo ring protonation. To investigate this point in more detail we postulate that a change from sp^2 to sp^3 hybridization in the *p*-carbon atom is the first step in the reaction. We have restricted our study to the *para*-position because it is the most likely to undergo protonation.[3,5,23,24]

We have recalculated molecular electrostatic potentials in the P plane with the *para*-hydrogen at an angle of 55° relative to the molecular plane. The results obtained for fluorobenzene, phenol, and nitrobenzene are presented in Figures 8—10.

In the case of fluorobenzene the minimum over the *para*-position is now of the same order than that over the substituent. This is, of course, a consequence of our rough approximation, since it has been shown [38,39] that ring-protonation produces a noticeable distortion of the ring, with a considerable increase of the C–C bond lengths and a decrease of the C–C–C angle. Therefore a deeper minimum should appear on the *para*-position if some allowances were made for geometry relaxation.

The situation is less clear in the case of phenol and no prediction can be made using only this map. In aniline the minimum on the *para*-position is much smaller than the one on the substituent; in this case ring-protonation is not likely to occur.[6]

We have included nitrobenzene to study whether ring protonation is likely to take place in this system. Our results show a very small minimum on the *para*-position indicating a possible but not likely ring-protonation. Frieser *et al.*[40] pointed out that with sufficiently acidic donors protonation occurs on both the ring and the substituent.



FIGURES 1—4 Electrostatic potential map for (1) toluene, (2) fluorobenzene, (3) aniline, and (4) 4-nitrobenzene in the P plane

Proton Affinities.—Proton affinities calculated by placing the proton at the position of the electrostatic potential minimum corresponding to the substituent are given in Table 1, together with experimental values.[5]

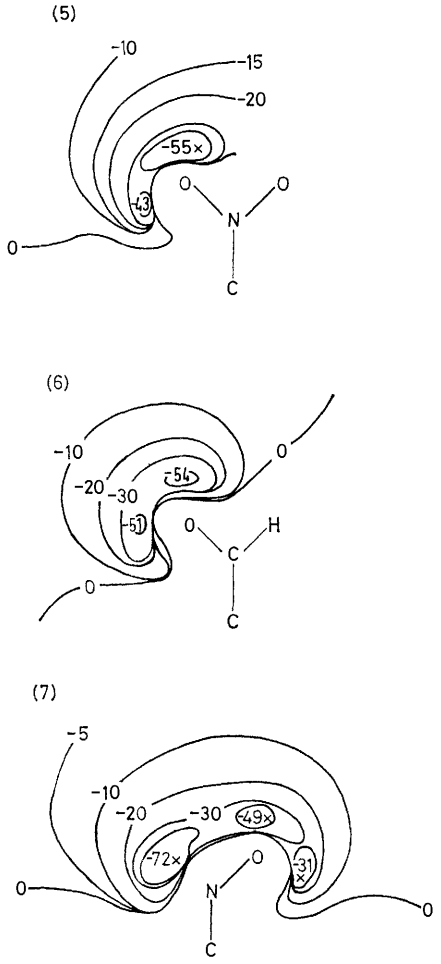
TABLE 1

Proton affinities of monosubstituted benzenes

	Calculated (kcal mol^{-1}) (for substituent protonation)	Experimental (kcal mol^{-1})
Aniline	257.1	209.3
Nitrobenzene	250.3	192.6
Benzaldehyde	241.0	199.1
Nitrosobenzene	239.4	
Cyanobenzene	230.1	195.1
Phenol	229.6	195.0
Fluorobenzene	183.1	182.9

1 kcal = 4.184 kJ.

The calculated values are much higher than the experimental ones, but it has been established,[26,41] that minimal basis sets significantly overestimate protonation energies. There is correlation between both sets of values as shown in Figure 11, with two clear exceptions: fluorobenzene and nitrobenzene. In the first case the very small calculated value of the substituent proton affinity confirms that fluorobenzene protonates on the ring.



FIGURES 5—7 Electrostatic potential map in the substituents region on the molecular plane for (5) nitrobenzene, (6) benzaldehyde, and (7) nitrosobenzene

This explanation does not hold for nitrobenzene, since this compound protonates on the substituent.

Benoit and Harrison [42] have shown that the linear relationship (proposed independently by Martin and Shirley [43] and Davis and Rabalais [44]) between proton affinities and inner-shell ionization energies for oxygen- and nitrogen-containing molecules, holds for a considerable number of organic compounds.

We present in Table 2 the O_{1s} binding energies for those compounds that can be oxygen-bases.

Linear correlation between these energies and calculated proton affinities given in Table 1 is very good (see Figure 12) with the only exception of nitrosobenzene, confirming our previous result that this molecule is a nitrogen-base.

TABLE 2

O_{1s} binding energies (a.u.)

Nitrobenzene	−20.255 21
Benzaldehyde	−20.278 93
Phenol	−20.297 14
Nitrosobenzene	−20.342 63

1 a.u. of energy (Hartree) = $4.359\,8 \times 10^{-18}$ J.

This correlation indicates again that proton affinity for nitrobenzene must be greater than those of benzaldehyde and phenol, although this point has not yet been experimentally confirmed.

As we have indicated, ring protonation takes place on the *para*-carbon atom. We have found a good linear correlation between the 1*s* binding energy of the *para*-carbon atom (Table 3) and the experimental proton affinities for those compounds that protonate on the ring (see Figure 13).

A least-square fitting of the data yields equation (2):

$$\text{P.A.} = 1\,035.75\,E(C_{1s}) + 1\,160.97 \qquad (2)$$

where the proton affinity is in kcal mol^{-1} and the C_{1s} binding energy, $E(C_{1s})$, in atomic units.

Equation (2) can be used to predict ring protonation energies from *evaluating only* the 1*s* binding energy of the *para*-carbon atom for the molecule in its ground state. We present these results in Table 4.

TABLE 3

1*s* Binding energies (a.u.) of the *para*-carbon atom

Phenol	−11.020 08
Toluene	−11.022 58
Benzene	−11.029 09
Fluorobenzene	−11.031 53
Aniline	−11.011 15
Benzaldehyde	−11.044 34
Nitrosobenzene	−11.054 63
Cyanobenzene	−11.059 00
Nitrobenzene	−11.064 56

1 a.u. of energy (Hartree) = $4.359\,8 \times 10^{-18}$ J.

TABLE 4

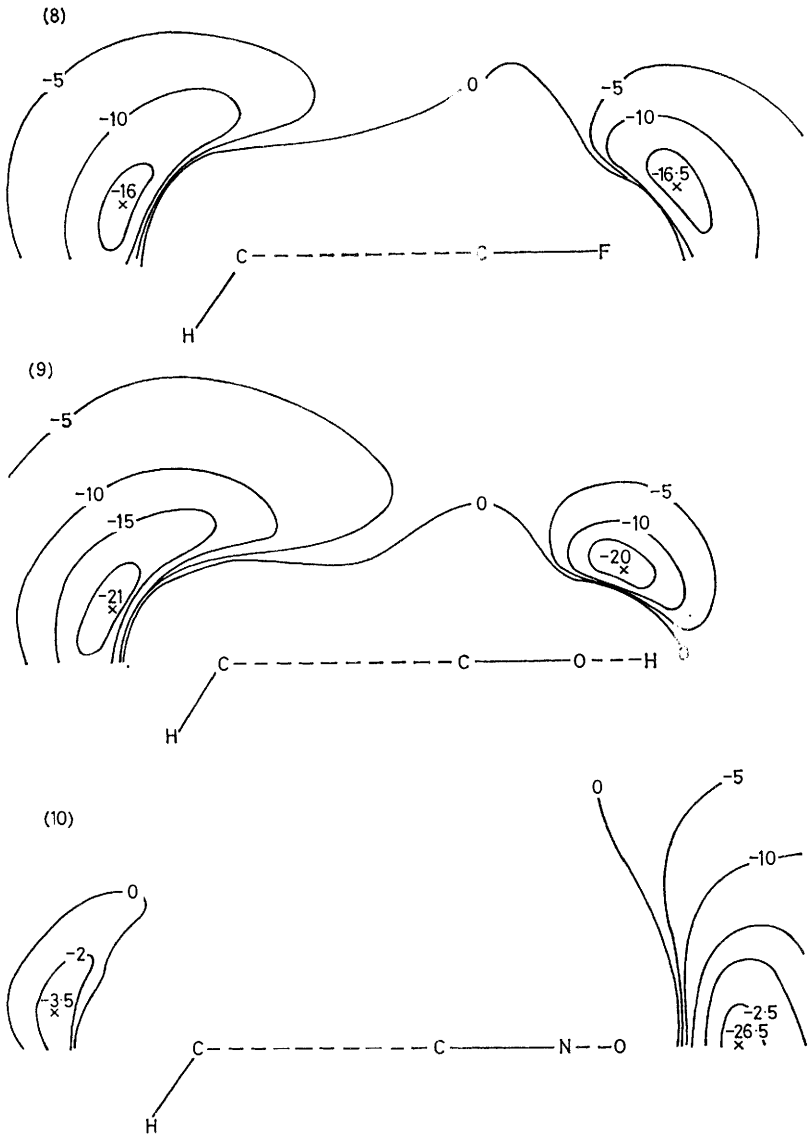
Ring proton affinities (kcal mol^{-1}) obtained using equation (2)

Aniline	203.2
Benzaldehyde	168.7
Nitrosobenzene	158.1
Cyanobenzene	153.5
Nitrobenzene	147.7
Phenol	193.8
Toluene	191.2
Benzene	184.5
Fluorobenzene	182.9

1 kcal = 4.184 kJ.

It is interesting to note that the ring proton affinity predicted for aniline is only 5 kcal mol^{-1} smaller than that corresponding to substituent protonation, in good agreement with previous results.[9]

In phenol we have found a good correlation between the experimental proton affinity and *both* the O_{1s} and C_{1s} binding energies, indicating that ring- and substituent protonation involve about the same energy. Calcu-



FIGURES 8—10 Electrostatic potential map for (8) fluorobenzene, (9) phenol, and (10) nitrobenzene in the P plane, with the *para* hydrogen bent below the molecular plane

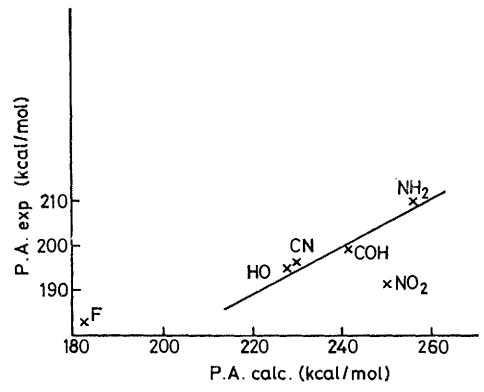


FIGURE 11 Correlation of calculated proton affinities (for substituent protonation) with experimental proton affinities. Correlation coefficient: $r = 0.991$

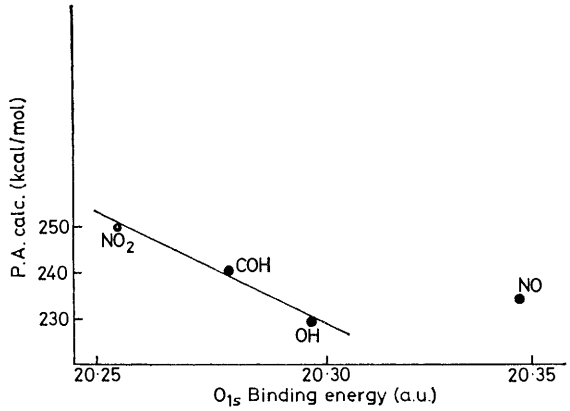


FIGURE 12 Calculated proton affinities *vs.* O_{1s} binding energies. Correlation coefficient: $r = 0.991$

lations by DeFrees *et al.*[8] gave an oxygen-proton affinity 15 kcal mol^{-1} smaller than that corresponding to ring protonation. The experimental results are not conclusive: Freiser *et al.*[40] found by deuterium exchange that ring protonation is favoured but Martinson and Butrill[45] concluded from chemical ionization studies that protonation occurs on the substituent.

Ring protonation energies calculated with two hydrogen atoms located on the P plane and symmetric

TABLE 5

Calculated ring proton affinities (kcal mol^{-1})

Aniline	240.0
Phenol	229.9
Toluene	224.0
Benzene	216.0
Fluorobenzene	218.2

1 kcal = 4.184 kJ.

with respect to the molecular plane * confirm (see Table 5) our previous conclusions. Protonation of fluorobenzene must occur on the ring.

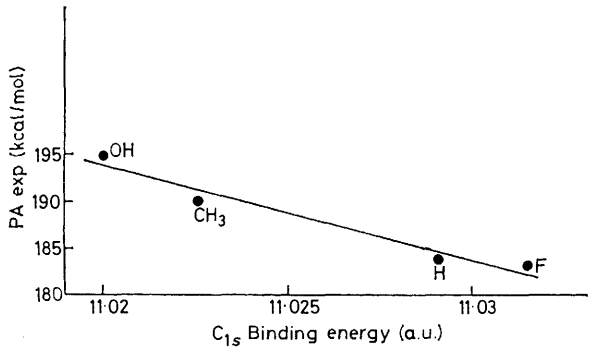


FIGURE 13 Experimental proton affinities *vs.* 1*s* binding energies of the *para*-carbon atom. Correlation coefficient: $r = 0.977$

We believe that equation (2) is very general because the environment of the *para*-carbon atom is somewhat constant from one compound to another and only the substituent should have an influence on the 1*s* binding energy of that carbon atom.

We conclude from our results that electrostatic potential maps permit a clear distinction between those molecules that protonate exclusively on the ring or on the substituent. The proton affinities obtained calculating the SCF energy placing the proton at the potential minimum correlate well with experimental values. For oxygen- (or nitrogen-) bases there is also a linear correlation between proton affinities and calculated O_{1s} (or N_{1s}) binding energies. Finally we have observed that a similar relationship exists between the proton affinities of those compounds that protonate on the ring and the 1*s* binding energy of the *para*-carbon atom.

All calculations were performed on the I.B.M. 360/65 computer at the UAM/IBM Center (Madrid).

[8/939 *Received*, 19*th May*, 1978]

* A rigorous calculation of ring proton affinities would require an expensive geometry optimization due to the distortion that undergoes the ring under protonation; but we are interested in relative values of ring proton affinities.

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