Proton Affinity and Protonation Sites of Aniline. Energetic Behavior and Density Functional Reactivity Indices

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High-level theoretical methods based on both density functional and Hartree−Fock and Moller−Plesset theories have been employed in order to give better insight in the longstanding question concerning the protonation site of gaseous aniline. From the thermodynamic point of view, nitrogen and para ring carbon appear to be the preferred protonation sites. Density functional and MP4 computations show that the protonation on para ring carbon atom is the slightly favored process. The orbital Fukui indices analysis does not resolve unequivocally the *dilemma* of preferred protonation site attributing to para ring carbon and nitrogen atoms the same probability to work as nucleophilic centers. The absolute hardness values of protonated forms of aniline do not follow the maximum hardness principle. Proton affinity values closer to the experimental counterparts are obtained when the G2(MP2), B3LYP, BP, and MP4 levels of theory are used.

Introduction

The basic behavior of aniline in solution has been well established because the nitrogen-protonated form is much better stabilized by solvation than those protonated on the ring.[1] On the contrary, the question concerning the preferred protonation site of aniline in the gas phase is yet now a topic of controversy.

In principle, aniline presents four basic centers (three on the ring and one on the nitrogen of amine group), but the meta ring carbon is a strongly unfavored site for the protonation process. So nitrogen, para, and ortho ring carbons remain the only candidates for the proton attachment.

Several works[2−16] have been published in the last two decades with the attempt to solve the case. Lau and Kebarle, on the basis of its experimental gas-phase basicity determination, suggest a protonation process on the ring carbons.[2] Subsequently, this hypothesis was reinforced by a series of mass spectrometric measurements involving collisionally activated dissociation of partially deuterated aniline ions.[3−5] In the 1990, Karpas, Berant, and Stimac, using an ion mobility spectrometry/mass spectrometry experiment,[6] evidenced the presence of two isomeric ions (at atmospheric pressure), which were assigned to the nitrogen and ring protonated forms. On the basis of its lower mobility the former was indicated as the preferred structure. A more recent work,[7] based on ion−molecule reactions, inclines toward the possible existence of both nitrogen- and carbon-protonated cations, but nitrogen is the kinetically favored protonation site. Finally, Nold and Wesdemiotis[8] underline that FAB ionization yields predominately the anilinium cation, while chemical ionization with a variety of reagents gases generates primarily the ring-protonated species.

This short history of experimental works proves the difficulty to establish unambiguously if the proton attaches the aniline on nitrogen or on ring carbons. In fact, different experimental strategies and techniques can affect the final results. Furthermore, there are no indications about the preferred ring carbon in the protonation process.

Two previous theoretical studies on this argument, using the Hartree−Fock method employing minimal STO-3G basis set[9] and semiempirical AM1 approach,[12] conclude that in the gas phase aniline is a nitrogen base and that protonation on the aromatic para carbon is less stable. In particular, the work of Pollack et al.[9] estimates the energy difference between the two mentioned isomers to be 1−3 kcal/mol. Semiempirical difference is found to be 2.4 kcal/mol.[12]

Local surface ionization energy study of Sjoberg et al.[13] suggests that the para carbon atom is the most reactive site for electrophiles, while molecular electrostatic potential calculations of Richie[14] found the global minimum near the nitrogen atom.

Hillebrand et al.[15] have determined the proton affinity of aniline, performing single-point MP2 computations on HF-optimized geometries using two different basis sets. They conclude that the nitrogen is the most susceptible site to proton attack.

Very recently, Roy, de Proft, and Gerlings, on the basis of DFT-based reactivity descriptors, indicate nitrogen as the preferable protonation site.[16]

In this situation, we performed high-level theoretical studies taking into account the correlation effects using different sized basis sets. They can provide more reliable information on the energetic of the protonation process and contemporary allow to better define which is the preferred protonated isomer. This information will be then used to evaluate the proton affinity with high accuracy.

In addition, orbital Fukui indices, computed through the method recently proposed by some of us,[17−20] will be used in attempt to individuate the preferred protonation site in aniline.

For the protonated isomers, global hardnesses have been calculated with the aim to correlate their relative stabilities to

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the hardeness values in the framework of the maximum hardness principle (MHP).[21] Following the MHP, if the chemical potential remains constant, we should expect that the hardest species is the more stable protonated system.

Method

Gaussian94,[22] DGauss,[23] and deMon[24] program codes have been used to perform calculations on neutral and protonated species of aniline. Geometries have been fully optimized with different nonlocal functionals. In particular, gradient corrected Perdew and Wang[25] (exchange) and Perdew[26] (correlation) (PWP), Becke[27] (exchange) and Perdew[26] (correlation) (BP), Becke[27] (exchange) and Proinov[28] (correlation) (BPROY), Perdew and Wang[29] (exchange) and Perdew[30] (correlation) (PP91), and hybrid Becke3 (exchange)[31] and Lee, Yang and Parr[32] (correlation) (B3LYP) potentials have been employed. Full geometry optimization and single-point calculations have been performed at second (MP2) and fourth (MP4) order Moller−Plesset perturbation level, respectively. The G2MP2 procedure has been also used.

Triple-ζ (TZVP) C, N(7111/411/1*) and H(41/1) orbital with the C, N (4,4;4,4) and H(5,1;5,1) auxiliary basis sets[33] have been used in the gradient-corrected calculations. The same orbital and C, N(8/4/4), and H(4/1) auxiliary basis set have been considered to perform BP calculations with the DGauss program. B3LYP, MP2, and G2MP2 optimizations have been obtained by using the 6-311++G**[34] basis as implemented in Gaussian94 code. The same basis set has been used to obtain the MP4 energy starting from MP2 optimized geometry. In addition B3LYP optimization has been done with the TZVP basis set.

Harmonic vibrational frequencies have been obtained numerically by the finite difference procedure in the gradient-corrected calculations while analytical second derivatives have been employed in the B3LYP, MP2, and G2MP2 computations.

Proton affinity (PA) has been assumed as the negative of the enthalpy (ΔH) for the process:

$$\mathrm{B} + \mathrm{H}^+ \rightarrow \mathrm{BH}^+$$

The variation in zero-point vibration energies and thermal corrections from zero degrees to 298 K has been considered[35] in the calculations.

The reactivity indices have been computed following a procedure described elsewhere.[17−19]

Results and Discussion

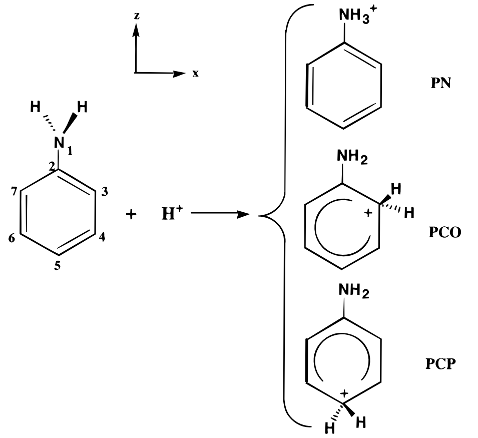
The protonation of aniline can occur on nitrogen as well as in meta, ortho, and para carbons of the ring.

It is well-known from basic organic chemistry that meta carbon is the less favored in the electrophilic reaction. Previous semiempirical computations,[12] performed at the AM1 level, have shown that the cation arising from meta ring carbon protonation lies at a very high energy with respect to all other forms generated by proton attack to the remaining sites. For this reason we have neglected this possibility, thus concentrating our attention on the other three sites as shown in Scheme 1. Energetic data are reported in Table 1.

All density functional (DF) based calculations indicate that the preferred protonated site is the para ring carbon (PCP) while MP2 level of theory suggests a proton attack on nitrogen (PN). The ortho ring carbon (PCO) is unambiguously always unfavored.

In order to verify a possible basis set dependence on the computed energy difference (ΔE), we have considered, at the B3LYP level, different basis sets including the 6-311++G** optimized in the framework of Hartree−Fock method[34] and the TZVP obtained from local density functional optimization.[33] In addition, single-point computations on the 6-311++G** optimized geometry have been redone using the extended cc-pvTZ set.[36]

SCHEME 1



The obtained results indicate that the preferred protonation site is always the para ring carbon and the relative energies of the other two minima are not effected by the nature and size of the employed basis sets. Both 6-311++G** and TZVP bases are able to reproduce the energetic path.

MP2/6-311++G** optimization indicates the nitrogen-protonated aniline as the most stable conformer followed by those protonated at para (6.2 kcal/mol) and ortho (10.9 kcal/mol) carbons of the ring. The inversion is surely not due to the slightly different MP2 geometry. Our MP2/6-311++G** single-point calculation on B3LYP/6-311++G** optimized structures, as well as the previous MP2/6-311+G**//HF/6-31G* study of Hillebrand et al.,[15] propose the same trend of stability indicating that the various approximations for the electron correlation plays a significant role.

G2MP2 procedure gives again aniline PN favored by 0.7 kcal/mol over the aniline PCP. The ΔE of aniline PCO (5.6 kcal/mol) is now half-order of the MP2 value.

Fourth-order Moller−Plesset (MP4/6-311++G**//MP2/6-311++G**) single-point computation indicates the para ring carbon as the energetically preferred site for the H^+ attack. The ΔE with respect to the aniline PN is of only 0.5 kcal/mol.

Because of the very small energy difference between the two isomers, high level of accuracy in the evaluation of electron correlation is required for obtaining reliable results.

It is worth noting the agreement between the MP4 and DF trends, although the ΔE values of the two lowest isomers differ. In fact, MP4 indicates a very low energy gap while both gradient-corrected and hybrid exchange correlation functionals show higher differences. In particular, the BP and PWP functionals overestimate this quantity of 1.3 kcal/mol, while the BPROY one indicates a more substantial difference (6.8 kcal/mol). PP91 potential gives a result (1.8 kcal/mol) very close to the B3LYP ones. Finally, we note that the energy difference between the aniline PCP and aniline PCO is almost the same in MP4, B3LYP, PWP, BP, and PP91 levels, but BPROY seems to overestimate this gap.

On the basis of our accurate energetic pathway, we can conclude that both amino nitrogen and para ring carbon in aniline are the most probable candidates for the proton attack and the latter is slightly favored. The way of accounting for

TABLE 1: Absolute (au) and Relative Energy (Δ*E*, kcal/mol) for Aniline and Its Protonated Isomers

	aniline	aniline PN	aniline PCP	aniline PCO
PWP/TZVP				
total energy	−288.046459	−288.400456	−288.402216	−288.393300
Δ*E* (298 K)		2.8	0.0	5.8
BP/TZVP				
total energy	−287.697387	−288.042756	−288.044460	−288.038197
Δ*E* (298 K)		2.8	0.0	4.2
PP91/TZVP				
total energy	−287.751150	−287.926149	−287.926186	−287.92061
Δ*E* (298 K)		1.8	0.0	3.7
BPROY/TZVP				
total energy	−287.460310	−287.822213	−287.830355	−287.818233
Δ*E* (298 K)		6.8	0.0	7.8
B3LYP/6-311++G**				
total energy	−287.687739	−288.034587	−288.035481	−288.028542
Δ*E* (298 K)		1.9	0.0	4.2
B3LYP/TZVP				
total energy	−287.695936	−288.043505	−288.044138	−288.037207
Δ*E* (298 K)		1.7	0.0	4.2
B3LYP/cc-pVTZ// B3LYP/6-311++G**				
total energy	−287.711919	−288.061798	−288.062681	−288.055498
Δ*E* (298 K)		0.6	0.0	4.5
MP2/6-311++G**// B3LYP/6-311++G**				
total energy	−286.815707	−287.163788	−287.151699	−287.144194
Δ*E* (298 K)		0.0	6.2	10.9
MP2/6-311++G**				
total energy	−286.816290	−287.164107	−287.151936	−287.144436
Δ*E* (298 K)		0.0	6.3	10.9
MP4/6-311++G**// MP2/6-311++G**				
total energy	−286.852078	−287.204146	−287.201876	−287.194508
Δ*E* (298 K)		0.5	0.0	4.6
G2MP2/6-311++G**				
total energy	−287.045076	−287.378282	−287.377205	−287.369383
Δ*E* (298 K)		0.0	0.7	5.6

the electron correlation together with the accuracy in the computations of vibrational corrections can play a significant role in the establishment of the absolute minimum, but, in any case, the very small energy difference suggests that both isomers can be populated in the gas phase. We think that for this reason experimental studies ambiguously predict the protonation site, because the experimental conditions can favor the prevalence of one of the two isomers.

Further indications on this problem can be obtained from the computation of the DFT-based reactivity descriptors[37] such as the softness (s), hardness (η), and Fukui indices ($f_{\rm i}$). Very recently, Roy, de Proft, and Geerlings applied these concepts in order to establish the gas-phase protonation site in aniline and some substituted anilines.[16] In this study, the total hardness and softness were obtained through the computation of the vertical ionization potential (IP) and the electron affinity (AE) of aniline, and the local softnesses are estimated from the finite difference between the electron population on each atom for neutral and charged species. On the basis of this procedure, the authors conclude that the preferred protonation site in aniline is the nitrogen atom, but do not report the stability order and PA values of different protonated isomers.

The approach used here is based on the fractional occupation number concept in DFT.[38] This allows the computation of the internally resolved hardness tensor, the softness tensor, and the orbital Fukui indices, as described in refs 17−19. In such a way the reactivity analysis can be provided using the values for orbital reactivity indicators of the neutral species only. Following this approach, we have computed the Fukui indices at PWP level of theory, considering all the eighteen occupied valence orbitals plus the LUMO one for neutral aniline.

TABLE 2: Valence Orbital Fukui Indices ($f_{\rm i}$) and Orbital Energies ($\epsilon_{\rm I}$ in eV) for Neutral Aniline[a]

$\epsilon_{\rm i}$	$f_{\rm i}$	$\epsilon_{\rm i}$	$f_{\rm i}$	$\epsilon_{\rm i}$	$f_{\rm i}$
−22.529	−0.31	−12.063	0.33	−8.541	0.55
−20.873	−0.41	−11.641	−0.23	−6.413	0.38
−18.529	−0.72	−11.228	−0.22	−6.273	0.42
−18.057	−0.34	−10.603	0.37	−6.075	0.36
−15.086	−0.53	−10.387	0.41	−1.448	0.63
−14.714	0.00	−8.974	−0.21		
−12.917	−0.01	−8.839	0.52		

[a] Results have been obtained using a fractional occupation number of 0.875 for the occupied orbitals and of 0.125 for LUMO.

Although the internal orbitals are not directly involved in the reaction, they must be taken into account in the Fukui indices computation, because of their relaxation.[17−19] From the Fukui indices values, presented in Table 2, it is worth noting that the low-lying valence orbitals are characterized by negative values of the Fukui indices. These orbitals will not participate in the proton attack as follows from the charge sensitivity analysis.[39] The few orbitals showing positive Fukui values are, however, quite low in energy. For this reason, our discussion will be essentially concentrated on the frontier (HOMO, HOMO-1, and HOMO-2) orbitals. In Figure 1, these molecular orbitals are plotted for the neutral and the three protonated species considered here. Since we are interested in the proton electrophilic attack, the hardest orbital is expected to be the most reactive one. The Fukui indices are proportional to the local softness and hence the orbitals showing lower $f_{\rm i}$ values should be more reactive in the protonation process. Looking at the figure, it is evident that three orbitals of aniline are representative of the π system of the ring carbons and of nitrogen. HOMO and

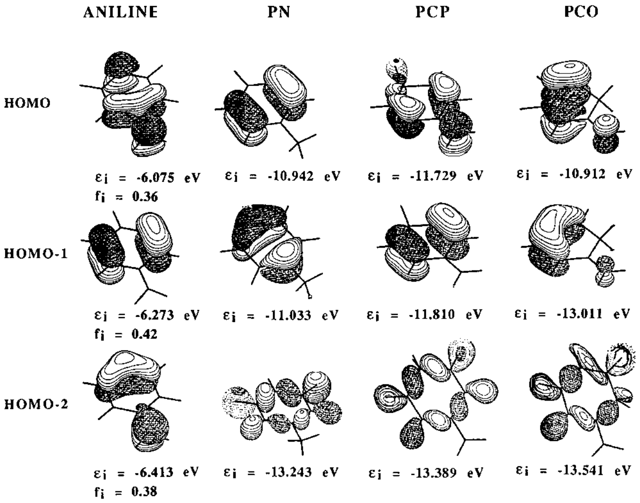


Figure 1. Molecular orbital coefficients (cutoff = 0.225, step = 0.0125) for HOMO, HOMO-1, and HOMO-2 in aniline and its protonated forms. Dark shading represents negative coefficients.

HOMO-2 are characterized by the lowest and very similar Fukui indices (0.36 and 0.38, respectively). The molecular coefficients plot shows that HOMO is composed by out-of-plane atomic orbitals of nitrogen and para carbon, as well as by a bond combination, involving the two ortho carbons and the substituted one. A nitrogen atomic contribution emerges also in the HOMO-2 picture, where a π system formed by the two meta and para carbons is also present. On the basis of the composition and Fukui indices values of these orbitals, one can conclude that nitrogen and para carbon are good candidates for the H^+ attack. The Fukui index of the HOMO-1 (0.42) predicts a less probability of proton attack to this orbital. This is not surprising because its electrons are shared between ortho and meta carbons, forming a π bond.

Studying the behavior of these three orbitals after the protonation, one can note from figure that the HOMO and HOMO-2 orbitals undergo significant variations for all the three isomers. Indeed, the HOMO-2 changes the character going from π- to a σ-bond, while the composition of HOMO-1 orbital remains almost unchanged and it seems the protonation process does not influence this orbital.

The fact that the HOMO and HOMO-2 orbitals show the lowest Fukui indices values, or equivalently, are the hardest ones can be a possible explanation for the small energy differences between the PCP and PN aniline species despite the fact that HOMO orbital becomes the most stable indicating a para carbon site as the slightly preferred one. All these reasons can account also for the experimental difficulties in establishing the most stable aniline protonated isomer.

Finally, we have calculated the global hardness (η) for all the considered cationic species. The results show that the MHP principle is not applicable in this case because the computed chemical potential for the three protonated isomers cannot be considered constant. In fact, we found a μ of 8.5, 9.9, and 9.6 eV, respectively for PN, PCP, and PCO aniline. The corresponding global η are 5.38, 5.49, and 5.45 eV.

From these data it is possible to conclude that only protonation on para carbon is favored with respect to that on ortho carbon because the two species have similar chemical potential.

Table 3 collects the theoretical proton affinities (PA) at 298 K together with the experimental counterparts.[40,41] As was expected, the calculated PA on different sites reflect the energetic behavior (see Table 1). G2MP2 gives the PA value closer to experimental data (209.1 vs 209.5[40] and 208.8[41] kcal/mol). Good agreement with highest experimental value is obtained at B3LYP level employing both the 6-311++G** (211.9 kcal/mol) and TZVP (211.6 kcal/mol) basis sets and at MP2/6-311++G** (210.6 kcal/mol) one. A difference of about 4 kcal/mol between theory and experiment is found for BP/TZVP and B3LYP/cc-pVTZ computations. Gradient-corrected PWP/TZVP and PP91/TZVP PA's are similar (218.4 and 218.0 kcal/mol, respectively) and overestimated by about 9 kcal/mol with respect to the value reported by Lias et al.[40] Looking at both values obtained considering the two most favored protonation sites, all the theoretical values seem to be close to the experimental indications.

TABLE 3: Proton Affinity (PA) at 298 K in kcal/mol for Aniline from Different Theoretical Methods and from Experiment

method	aniline PN	aniline PCP	aniline PCO
PWP/TZVP	215.6	218.4	212.6
BP/TZVP	210.2	213.0	208.8
PP91/TZVP	216.2	218.0	214.2
BPROY/TZVP	220.6	227.4	219.6
B3LYP/6-311++G**	210.0	211.9	207.7
B3LYP/TZVP	209.7	211.6	207.3
B3LYP/cc-pVTZ	211.9	213.8	209.4
MP2/6-311++G**// B3LYP/6-311++G**	210.8	204.5	199.9
MP2/6-311++G**	210.6	204.3	199.7
MP4/6-311++G**// MP2/6-311++G**	213.3	213.8	209.2
G2MP2/6-31++G**	209.1	208.4	203.5
expt		209.5,[a] 208.8[b]	

[a] From ref 40. [b] From ref 41.

Conclusions

The problem of determining the preferred protonation site of aniline in the gas phase has been investigated by computing the energetic parameters at different levels of theory and the DFT-based reactivity descriptors.

It is observed that total energy computations at high level of theory indicate the para ring carbon as the most favored protonation site, although the small energy difference between this protonated form and that protonated on nitrogen atom suggests a probable coexistence of both isomers.

The values of orbital Fukui indices for neutral aniline follow the same pattern of energetic data, indicating that the para ring carbon and amine nitrogen are the better candidates for the electrophilic attack of proton. For delocalized systems such as aniline it is difficult to identify unequivocally the preferred protonation site expecially if the relative stability of protonated isomers is comparable.

The derived proton affinities agree well with the available experimental values. In particular, the G2MP2 and B3LYP data fit very well to the experimental measurements.

Because of the same order of stability of para ring carbon and amine nitrogen cations, it is possible to hypothesize that different experimental conditions favor one of the isomers or populate both in different ratios.

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