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Commentationes

An *ab initio* Molecular Orbital Study of the Protonation of Amines

A. C. Hopkinson
Department of Chemistry, York University, Downsview, Ontario, Canada

Imre G. Csizmadia
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada

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Ab initio molecular orbital calculations using an 8^s, 3^p; 3^s Gaussian basis set, with contraction, have been used to study a series of primary amines XNH_2, where $X = H$, CH_3, OH, F, CN, CHO, and NO_2. The geometries of the corresponding ammonium ions have been optimised and the energy differences have been used to estimate relative proton affinities. The 1^s orbital energies for both the amines and ammonium ions, when corrected for the effects of charges on the other atoms in the molecule by use of an ESCA equation, give a good correlation with the computed charge on the nitrogen atom.

Key words: Amines, protonation of – Protonation of primary amines

1. Introduction

Protonation equilibria for both aromatic [1–3] and aliphatic amines [4] have been studied extensively and are well characterised. Most amines are found to protonate in the pH range but introduction of electron-withdrawing groups reduces their basicities and 2,4,6-trinitroaniline is only half protonated in 96.5% H_2SO_4 [1]. The nitroanilines vary markedly in basicity and by choosing a variety of substituted anilines it is possible to obtain a series of compounds which ionise over the whole range of aqueous sulphuric acid mixtures. This class of compounds has therefore been useful in the construction of acidity functions in a variety of aqueous and non-aqueous solutions of strong mineral acids [1–3, 5].

Molecular orbital calculations are for isolated molecules at 0 °K and without any zero-point energy. Energy differences obtained from such calculations are therefore much closer to the experimental values from the gas phase than to those from solution work. Unfortunately the only gas phase study is for alkylamines, [6] varying both the size and number of the alkyl groups on the nitrogen atom and the majority of the compounds are too large to be subjected to *ab initio* calculations at this time. As part of our study of organic bases [7, 8] we have therefore examined a series of primary aliphatic amines, varying the substituent in

$$NH_2X + H^+ \rightleftharpoons \overset{+}{N}H_3X$$

where X = H, CH_3, F, OH, CN, CHO, and NO_2. In these molecules the substituent is very close to the reaction site and, as the basicity of the anilines is very substituent dependent, it was expected that the computed proton affinities for these amines would show a similarly large variation.

2. Computational Details

All the calculations were carried out on an IBM 360-65 computer using the IBMOL-IV program: [9]. The Gaussian basis set consisted of 8^s and 3^p functions on C, O, N, and F and 3^s functions on hydrogen, contracted to 2^s, 1^p, and 1^s respectively [10].

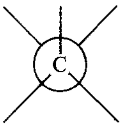
All the amines, with the exception of fluoramide, have been subjected to microwave structure determinations and the geometries from these studies [11–16] were used in the molecular orbital calculations. The geometry of fluoramide was estimated from that of the difluoro derivative, NHF_2 [17]. The geometries of the ammonium ions were optimised, varying the conformations and bond lengths in a systematic manner until a minimum energy was obtained. Further details of these optimisations are given in the first part of the results section.

This policy (optimising the geometries of the amonium ions and assuming experimental geometries for the neutral amines) leads to some systematic error, particularly because of the limited basis set used. This systematic error manifests itself in the over-estimation of the proton affinity values; however, it is hoped that the relative order of gas phase basicities remain uneffected.

3. Results

3.1. Geometry Optimisations

Rotation about the C-X bond of methylamine showed the rotamer in which one of the hydrogens on the methyl group is staggered between those on the nitrogen atom (1) to be the most stable as observed in a previous theoretical treatment [18].



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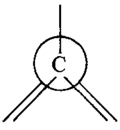

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Structure 2, in which the hydrogens almost eclipse one another, was computed to be less stable by 2.2 kcal/mole.

A similar rotational study on hydroxylamine showed the eclipsed structure to be less stable than the staggered one by 7.3 kcal/mole.

Planar formamide was computed to be *less* stable by 0.2 kcal/mole than that with the experimental geometry. However calculation of inversion barriers

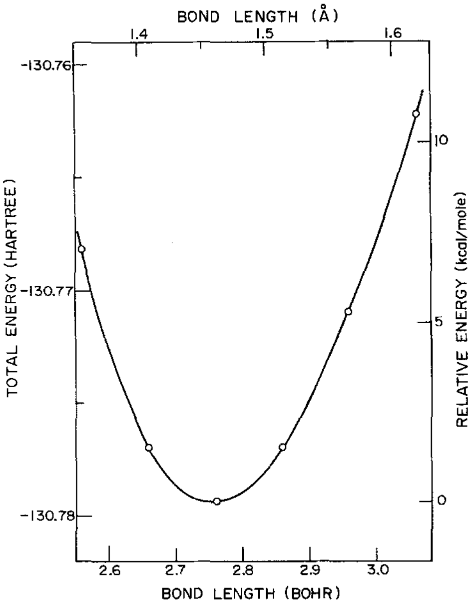


Fig. 1. Plot of nitrogen-oxygen bond length against the computed total energy in the optimisation of the geometry of $\overset{+}{N}H_3OH$

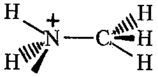
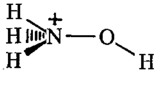
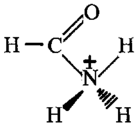
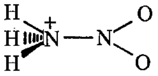
about the nitrogen atom have been shown to be improved by inclusion of *d* functions on the nitrogen and *p* functions on the hydrogens [19] attached to the nitrogen.

Inclusion of these types of functions in the relatively small Klessinger basis set would provide an unbalanced basis set, so the inversion about nitrogen was not investigated further.

The geometries of the ammonium ions were optimised by determining which rotamer was the most stable, then optimising the N-X bond and finally varying any bonds within the substituent group X. All bond optimisations included at least six points and the minimum energy and optimum bond length were obtained graphically (see Fig. 1). Previous studies have shown that the computed total energy only varies a little with changes in the bond angles [20] so it was decided to conserve computer time by assuming that all bond angles were ideal (tetrahedral, trigonal or 180°). Also the N–H bond lengths were all taken to be 1.038 Å as in NH_4^+ [21].

The rotational barriers for the ammonium ions, listed in Table 1, are all very small permitting free rotation about the N–X bond at room temperature. The ions formed by protonation of nitramide and formamide prefer the eclipsed rotamer probably caused by internal hydrogen bonding between the oxygen atom on the substituent and a hydrogen on the $\overset{+}{N}H_3$ group. Neither of the free bases display this type of interaction although in formamide the amino hydrogen cis to the oxygen atom is much closer to the NCO plane than the other one, suggesting that there is a weak interaction between the hydrogen and oxygen.

Table 1. Optimised conformations and N-X bond lengths (Å) in ammonium ions

Cation (in optimum conformation)	N-X bond length[a]	Other bond lengths[a]	N-X rotational barrier (kcal/mole)
NH_4^+	1.038 (1.014)[b]		
	1.553 (1.474)[c]		0.36
	1.46 (1.46)[d]		1.29
$\overset{+}{N}H_3F$	1.400 (1.400)[e]		
$\overset{+}{N}H_3CN$	1.478 (1.346)[f]	C–N (cyano) 1.197 (1.16)	
	1.569 (1.376)[g]	C–O 1.343 (1.193)	1.3
	1.639 (1.427)[h]	N–O 1.259 (1.206)	0.02

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[a] Bond lengths of corresponding free base in parentheses.
[b] Ref. [11].
[c] Ref. [12].
[d] Ref. [13].
[e] Ref. [17].
[f] Ref. [15].
[g] Ref. [14].
[h] Ref. [16].

Positively charged species have very acidic hydrogens which form strong hydrogen bonds and this is apparently sufficient to change the preferred conformation about the N–X bond.

Protonation on the nitrogen atom was found to usually result in an increase in the N–X bond length with the major changes occurring for X = HCO, CN and NO_2. For these three electron-withdrawing substituents the N–X bond lengths in the free bases are shorter than in the corresponding fully hydrogenated species (CH_3NH_2 [22] and NH_2NH_2 [23]) and a substantial rotational barrier about this bond in amides has been observed (see Ref. [24]). These data suggest that there is considerable double bond character in the N–X bond, caused by donation of the lone pair on the amino group to the electron-withdrawing substituent.

Protonation of the amino group removes the lone pair and the positively charged ammonium group is repelled by the electron-withdrawing substituent, causing a considerable lengthening of the N–X bond.

All the bond lengths *within* the substituents X were also increased by protonation of the amino group. These optimum bond lengths are included in Table 1.

3.2. Charge Distribution

All the nitrogen atoms of the amino and ammonium groups are computed to carry net negative charges due to the electronegativity of the nitrogen atom (Fig. 2). In the free amines this net charge does not vary in a predictable

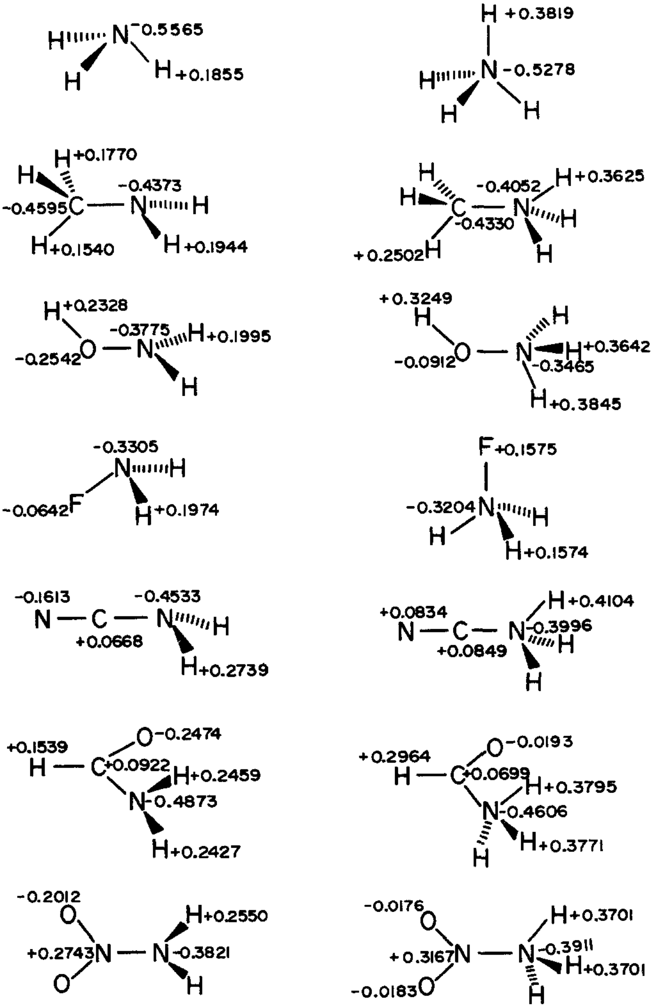
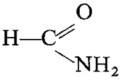


Fig. 2. Computed charge distributions

Table 2. Dipole moments for amines (debyes)

Molecule	Computed value	Experimental value[a]
NH_3	2.22	1.47
NH_2OH	0.44	—
NH_2F	1.98	—
NH_2CN	3.78	4.3
 $H-C(=O)-NH_2$	2.70	3.73
NH_2NO_2	3.14	3.57

[a] Handbook of physics and chemistry, 49th Ed. (1968/1969).

manner as illustrated by the fact that the nitrogen atom of the amino group of cyanamide has a larger negative charge than that of methylamine.

Protonation causes a small decrease in the electron density on the nitrogen atom, with the exception of nitramide. Most of the positive charge associated with the incoming proton remains on the three hydrogen atoms on the nitrogen of the ammonium ions. In nitramide the oxygen atoms also lose an appreciable amount of electron density.

Molecular orbital calculations with this basis set usually underestimate the dipole moment [8]. This has again been found to be true for the amines (Table 2), although the value calculated for ammonia is larger than the experimental one. The computed value for cyanamide is much closer to the experimental one than that reported in a previous *ab initio* treatment of this molecule [25].

3.3. Protonation Energies

The computed total energies for the amines and ammonium ions are recorded in Table 3. There have been many previous *ab initio* studies on the amines, several of them using more extensive basis sets in attempts to calculate the inversion barriers for the amino groups. The emphasis in the present work, however, is on protonation and the only cation for which previous calculations have been reported, is the parent ammonium ion [26].

Although amines are some of the strongest and most common organic bases and their protonation behaviour has been extensively studied in solution, only the alkyl substituted amines have been investigated in the gas phase [6]. Experimental proton affinities are therefore only available for two of the amines examined in this study and there is insufficient data to test the accuracy of the computed proton affinities (Table 4). However from previous studies it is possible to predict that the computed proton affinities will be larger than the experimental values, as there is a monotonic decrease in the computed proton affinity as the basis set is increased with Hartree-Fock wavefunctions reproducing the experimental value quite accurately [26]. The computed values for methylamine and ammonia are both about 50 kcal/mole greater than the experimental values and more importantly, methylamine is predicted to be the more basic in

Table 3. Computed total energies (hartrees)

	Present calculations	Previous calculations
a) Amines XNH_2		
$X=H$	−55.9452	−56.1812[g], −56.2109[b], −56.2268[e]
CH_3	−94.8474	−94.3235[d], −95.1127[e], −95.1087[f]
OH	−130.3964	−129.7061[g], −130.8975[h]
F	−154.1815	−154.9772[i]
CN	−147.2851	−144.5448[j], −147.8655[i]
CHO	−168.1299	−168.8684[k], −168.872[l]
NO_2	−258.3827	−259.1724[m]
b) Ammonium ions $X\overset{+}{N}H_3$		
$X=H$	−56.3513	−56.5320[a]
CH_3	−95.2672	
OH	−130.7794	
F	−154.5523	
CN	−147.6351	
CHO	−168.5259	
NO_2	−258.7518	

[a] Ref. [26].
[b] Body, R. G., McClure, D. S., Clementi, E.: J. Chem. Phys. **49**, 4916 (1968).
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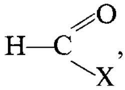
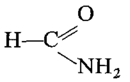
keeping with the experimental gas phase results which showed that the order of basicity for amines is tertiary > secondary > primary > ammonia [8].

The range of proton affinities from methylamine, the most basic, to cyanamide, the least basic, covers 44 kcal/mole. This is a slightly smaller range than that found for protonation of the carbonyl compounds  $H{-}C\overset{\displaystyle\nearrow O}{\underset{\displaystyle\searrow X}{}}$, using the same basis set, a surprising result as the protonation in this latter class of compounds is further removed from the substituent than in the amines.

In solution secondary amines are more basic than either the primary or tertiary ones [27], solvation changing the order of basicity from that found in the gas phase. This illustrates the dangers in attempting to correlate the experimental pK values for dissociation of the ammonium ions with the computed (or experimental) proton affinities. Nevertheless the pK values for the ammonium ions of methylamine (10.66) [28], ammonia (9.25) [28], hydroxylamine (6.03) [28],

Table 4. Computed proton affinities (kcal/mole)[a]

Amine	Computed value	Experimental value
NH_3	−254.9	−207[b]
CH_3NH_2	−263.5	−211[b]
NH_2OH	−240.4	
NH_2F	−232.8	
NH_2CN	−219.7	
	−248.6	
NH_2NO_2	−231.7	

[a] Not corrected for changes in zero-point energy or thermal energies.

[b] Haney, M. A., Franklin, J. L.: J. Phys. Chem. 73, 4328 (1969).

and cyanamide (1.1) [29] follow the same order as the computed proton affinities. Formamide, however, is much less basic in solution (pK has been estimated as −2.60 and −2.75) [30] than would be expected from the computed proton affinities and the site of protonation, although there is some conflicting evidence [31], is almost certainly the oxygen atom and not the amino group [32–34].

3.4. Effect of Protonation on Orbital Energies

All the molecular orbitals, including the inner shells, are more tightly bound in the ammonium ions than in the corresponding amines. Even the 1^s atomic orbitals on the oxygen atoms of nitramide, which are situated on atoms not directly bonded to the site of protonation, are changed by 9.40 eV.

By way of illustration of this phenomenon the energies of all the molecular orbitals of nitramide and its ammonium ion are recorded in Table 5. Valence shell calculations, which assume no change in the inner shells of atoms during a reaction, clearly are making an invalid approximation as the inner core orbitals are stabilised by a similar amount as the outer ones by the addition of an extra proton.

The orbital energies of all the pairs of bases and conjugate acids behave in a similar fashion and the easiest orbitals to treat quantitatively are the 1^s atomic orbitals, as these are almost completely localised on one atom. The ease with which an electron is removed from an orbital (its ionisation potential) should be related to the energy of the orbital. Koopmans' theorem [35] simply equates the ionisation potential to this orbital energy thereby neglecting the stabilisation resulting from reorganisation of the positive ion formed in the ionisation process. This approximation then overestimates ionisation potentials but Hartree-Fock calculations have been shown to accurately predict the *changes* in ionisation relative to some standard molecule [36] (for nitrogen atom, N_2 is usually taken as standard).

The change in the ionisation potential of a 1^s electron, as measured by photoelectron spectroscopy, is related to the charge on that atom in the molecule

Table 5. Computed orbital energies (eV) for nitramide and its conjugate acid

NH_2NO_2	$\overset{+}{N}H_3NO_2$
561.42	570.82
561.42	570.79
435.26	442.71
427.19	438.40
43.09	49.34
37.08	43.88
32.95	41.74
23.15	31.14
19.29	27.64
19.21	27.32
18.94	26.37
16.36	24.58
11.80	23.80
10.82	18.58
10.41	18.26
8.95	16.24

and a plot of the computed charge on the nitrogen atom against the 1^s orbital energy should therefore be linear. Such a plot for the nitrogen atom of the amines and ammonium ions gave two straight lines, with considerable scatter, one for the free bases and the other for the conjugate acids. The lines were about 13 eV apart with the cations being the more bound.

An equation accounting for the effect of the charge on the *other atoms*, *j*, in the molecule on the electron in the 1^s atomic orbital on atom *i* has been very successful in correlating experimental "chemical shifts" of core binding energies with the charge distributions. The so called ESCA equation [37] is

$$E^i = E^i_0 + kq_i + \sum_{i \neq j} \frac{q_i}{r_{ij}}$$

where E^i is the experimental binding energy for atom i in the molecule under study, E^i_0 is for the same atom in some standard molecule, q_i is the charge on atom i and k is a proportionality constant. The summation term represents the potential created at atom i by all the other atoms in the molecule.

We have recently used this equation to obtain k values for carbon and oxygen atoms by plotting the computed binding energies minus the correction for the other atoms against the computed charge on a carbon or oxygen atom [8]. k values obtained in this way compared very favourably with those calculated by other methods [37]. The results of this kind of a plot for the nitrogen atoms of the amines and ammonium ions are shown in Fig. 3. The points for both the neutral compounds and the cations *now fall on the same line* given by the equation

$$E_{\text{corrected binding energy}} = 26.01\, q_i + 430.89$$

(least squares correlation coefficient = 0.989).

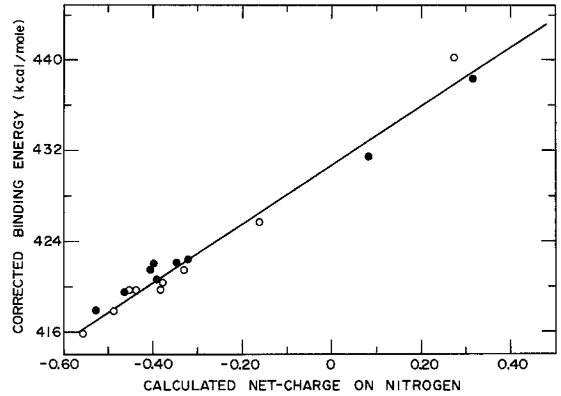


Fig. 3. Plot of binding energy, corrected for the force created by the charges on the other atoms, against the computed charge. ● inidcates ammonium ions and ○ is for amines

This shows that the above formula successfully correlates orbital energy shifts with charge distribution in molecular systems even when there is a difference in charge on the species. The value of 26.01 eV for *k* compares favourably with the values of 21.5 and 26.4 eV [37] obtained from plotting corrected *experimental* binding energies against charges calculated by more empirical methods than the calculations used in the present work.

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Prof. Dr. J. G. Csizmadia
Lash Miller Chemical Laboratories
80 St. George St.
Toronto, Canada M5S 1A1