We conclude that the ACHARGE analysis yields charges that are useful in understanding chemical properties. With further refinement, and especially in combination with higher resolution spectra, the ACHARGE analysis of photoelectron data may permit prediction of the reactivities of new compounds.

A Study of Monoprotonated Nitrogen Bases Using X-Ray Photoelectron Spectroscopy (ESCA)[1]

Lawrence E. Cox, John J. Jack, and David M. Hercules*

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30601.

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Abstract: Nitrogen 1s binding energies are reported for salts (primarily hydriodides) of pyridine, monoprotonated pyrazine, 1,2-, 1,4-, and 1,5-diazanaphthalenes, 1,2- and 1,5-diaminonaphthalenes, 1,10-phenanthroline, 2,2′-bipyridine, and several other compounds. The binding energy differences between the protonated and unprotonated nitrogens are indicative of substantial electron withdrawal from the aromatic ring. Shift differences are calculated employing 1s binding energy *vs.* charge slopes obtained from self-consistent atomic field data together with atomic charges from all valence electron MO calculations. Lattice self-potentials are evaluated for pyridine hydrochloride and pyridine hydrogen nitrate. The lattice potential at nitrogen is found to be *ca.* 1.0 eV more negative than at position 4 if intra-ionic potentials are excluded. Symmetrical protonation, *i.e.*, a "chelated" proton, which would lead to a single ESCA line was not found in the chelating bases or in phthalazine.

The measurement of core electron binding energies by means of X-ray photoelectron spectroscopy (ESCA) has proven to be a powerful, albeit not completely unambiguous, tool for the elucidation of charge distribution in a variety of solid and gaseous compounds. Recent investigations[2,3] have shown that core electron binding energy shifts correlate roughly with Pauling atomic charges and somewhat better with those obtained from molecular orbital (CNDO/2) calculations, particularly if the interatomic Madelung potential is included.[3]

The difficulties associated with the interpretation of binding energy measurements on solid, electrically insulating materials have been discussed by Fadley, *et al.*[4] The principal uncertainties are (1) the location of the reference level (*i.e.*, the Fermi level) in the solid and (2) the importance of sample charging. Sample charging effects arise because photoelectron ejection produces positive sites near the surface and hence a shift in the sample potential relative to the spectrometer. The magnitude of this shift has been shown to be *ca.* 2 eV for $BaSO_4$.[5] The dependence of charging on such factors as sample type, sample thickness, and X-ray intensity has not been established, however. That charging effects are of equal importance for all samples is therefore an unwarranted assumption.

Both of the forementioned problems can be circumvented if one is interested only in binding energy differences between atoms in the same compound. In such cases shifts in the reference level are unimportant since all atomic levels are affected equally.

In a previous investigation[6] N 1s binding energies were reported for an extensive series of ionic nitrogen compounds. The present paper extends these studies to a series of singly protonated organic bases containing two or more nitrogens. Our expectation has been that these results would provide some insight into the charge distribution in these ions. Also, since several of the bases studied serve as bidentate ligands for metal ions, the existence of substantial intramolecular hydrogen bonding in their monoprotonated acids does not seem unreasonable. Should the proton be chelated, the environments of the nitrogens would be equivalent, a situation evidenced by a single line in the N 1s electron spectrum.

Experimental Section

Binding energy measurements were performed using a 30-cm double-focusing magnetic spectrometer which has been described previously[6] or an AEI ES100 electrostatic spectrometer. Samples were run as powders on double-back cellophane tape or as pellets pressed into copper mesh. The two methods gave identical results. The C 1s line of graphite (284.3 eV) was used as an external reference.

The organic bases were purchased from Aldrich Chemical Co. and were used without further purification. The salts were prepared by dropwise addition of a stoichiometric quantity of the appropriate concentrated acid to a well-stirred acetone solution of the base. Precipitation was accomplished by cooling in an ice bath and addition of diethyl ether when necessary. The salts were washed with acetone and ether, air-dried, and stored over anhydrous $Mg(ClO_4)_2$. The *N*-methyl iodides were prepared by standard methods.[7]

The deconvolution procedure of Siegbahn, *et al.*,[2b] was employed for the estimation of peak separations if they were equal to, or less than, 2.1 eV. The method requires an estimate of peak width at half-height for a single peak; a value of 1.75 eV was used. It

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(1) This work was supported by funds provided by the U. S. Atomic Energy Commission under Contract AT-(38-1)-645.

(2) (a) K. Siegbahn, *et al.*, "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967; (b) "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

(3) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **10**, 378 (1971).

(4) C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968).

(5) D. J. Hnatowick, J. Hudis, M. L. Perlman, and R. C. Ragaini, *J. Appl. Phys.*, in press.

(6) J. J. Jack and D. M. Hercules, *Anal. Chem.*, **43**, 729 (1971).

(7) J. C. E. Simpson, "The Chemistry of Heterocyclic Compounds," Vol. 5, Interscience, New York, N. Y., 1953.

is difficult to estimate the uncertainty in separations obtained in this manner, but it probably does not exceed 0.2 eV.

Results and Discussion

Nitrogen 1s binding energies for the various compounds are given in Table I. The values refer to doublet centers. Measured doublet separations are given for spectra in which this quantity exceeded 2.0 eV; otherwise the values are based on the deconvolution procedure described above.

Table I

Compound	N 1 s binding energy center,[a] eV	Peak separation, eV
Pyrazine·HI	401.6	1.8
Pyrazine·HBF_4	401.5	1.7
Pyrazine·HBr	400.8	1.7
Quinoxaline·HI	400.7	1.6
1,5-Naphthyridine·HI	400.6	2.0
Phthalazine·HI	400.8	1.2
N-Methylquinoxalinium iodide	401.0	1.8
N-Methylphthalazinium iodide	401.8	1.7
1,10-Phenanthroline·HI	400.0	2.1
1,10-Phenanthroline·HBr	399.7	2.2
1,10-Phenanthroline·HBF_4	399.9	2.2
N-Methyl-1,10-phenanthrolinium iodide	400.2	2.0
2,2′-Bipyridine·HI	400.3	2.2
2,3-Diaminonaphthalene·HI	399.8	2.0
1,5-Diaminonaphthalene·HI	400.4	2.5
4-(*p*-Nitrobenzyl)pyridine	401.8	7.1
4-(*p*-Nitrobenzyl)pyridine·HI	403.2	4.9

[a] Uncertainties are less than or equal to ±0.2 eV.

All heterocyclic compounds are listed first, followed by the diaminonaphthalenes and other miscellaneous compounds. Salts of a given cation are listed together; the slight anion effect on peak separations is noteworthy.

That a correlation exists between Mulliken atomic charges and core binding energies corrected for the interatomic Madelung potential seems well established. The results of Siegbahn for a large number of compounds in the gas phase[2b] as well as those of van der Avoird[8] for thymine, cytosine, and adenine indicate that semiempirical MO methods provide adequate accuracy for the interpretation of ESCA spectra provided the molecular potential is considered. The expression for the core shift of atom A is

$$E_A = k_A q_A + \sum_{B,B \neq A} q_B / r_{AB} + E_A{}^0 \qquad (1)$$

where k_A is the interelectronic repulsion integral for atom A, q_A is its charge, q_B is the charge of atom B, and r_{AB} represents the distance separating atoms A and B. $E_A{}^0$ is the core electron binding energy of atom A in the zerovalent state, relative to the appropriate reference level. For solids this is the Fermi level; for gases it is the vacuum level.

Unfortunately the application of eq 1 to the compounds studied here requires knowledge of the charge and position of every atom in the lattice. We have therefore adopted a somewhat less rigorous approach which, nevertheless, is helpful in assessing the importance of electron distribution in the protonated nitrogen bases studied.

In the pyrazinium monocation, for example, two limiting situations can be envisioned. The first (case 1) is designated charge localized, in which electron withdrawal from ring atoms other than nitrogen is negligible. The assumption is made, somewhat arbitrarily, that 0.5 electron migrates from the protonated nitrogen to the proton. The second (case II), or charge-delocalized model, assumes extensive electron delocalization on protonation so that the nitrogens experience the same net effect.

In order to calculate N 1s binding energy differences for the two cases from eq 1, the electron repulsion parameter k_A was evaluated for nitrogen and carbon. A modified version of the Hartree–Fock–Slater self-consistent atomic field program[9] was used to obtain 1s binding energies for five atomic charges between *ca.* −0.5 and +0.5. Some nonlinearity in the charge-binding energy relationship was evident so a least-squares quadratic fit was obtained. For nitrogen and carbon the results were (in eV)

$$\mathrm{BE(N\ 1s)} = 2.70 q_N{}^2 + 16.07 q_N + 405.0$$

$$\mathrm{BE(C\ 1s)} = 2.61 q_C{}^2 + 13.99 q_C + 291.1$$

The calculations described below utilize the linear coefficient, since only charge differences can be assumed. Shifts obtained from MO charges (*vide infra*) are based on the quadratic form.

Calculation of the N 1s electron binding energy difference for protonated pyrazine was accomplished as follows: in case 1 the protonated nitrogen is shifted by 8.0 eV owing to the removal of 0.5 electron (first term of eq 1) and by an additional 7.2 eV due to the Madelung potential of the proton (second term of eq 1); the unprotonated nitrogen, whose charge is assumed to be constant, experiences a shift of 4.5 eV by virtue of its proximity to the added positive charge. The protonated and unprotonated nitrogens are shifted by 15.2 and 4.5 eV, respectively, and a binding energy difference of 10.7 eV would be expected. Case II is of course trivial, since the nitrogens are equivalent. The observed line separation in pyrazinium salts, of 1.8 eV, would seem to lend credibility to the charge-delocalized model. Case 1, on the other hand, predicts a separation some 8.9 eV too large. Moreover, inclusion of the lattice potential does not change this conclusion.

Inasmuch as semiempirical molecular orbital calculations are available for several of the nitrogen heterocyclic molecules and their cations, it is instructive to compare their predictions concerning charge delocalization. Adam, *et al.*,[10] have reported extended Hückel (EHT) calculations for a number of five- and six-membered heterocycles and have found a correlation between electron densities and both proton and ^{13}C nmr shifts. The EHT method approximates the Coulomb integral by a valence-state ionization potential (VSIP) which is not allowed to vary with changes in orbital occupation. Thus, protonation leads to rather slight withdrawal of electron density from atoms other than the protonated nitrogen. In the pyrazinium ion, for example, the delocalization amounts to only about

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(8) A. van der Avoird, *Chem. Commun.*, 727 (1970).

(9) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

(10) W. Adam, A. Grimison, and G. Rodriquez, *Tetrahedron*, 23, 2513 (1967).

0.03 electron.[10] This result is virtually the same as our charge-localized model (case 1) and predicts a binding energy difference which is much too large. In contrast, the ASMO-SCF calculation of Kato, *et al.*,[11] indicates a charge migration of 0.709 electron onto the added proton of which only 0.309 electron comes from the protonated nitrogen. Using charges reported by these authors together with HFS charge-binding energy slopes, we have calculated core shifts for pyrazinium ion. The results are given in Table II.

Table II. Calculated Core (1s) Electron Binding Energy Shifts in Pyridinium and Pyrazinium Salts

	Madelung shift		Interelectronic	
Position	Intraionic	Lattice[a,b]	repulsion	Total
		Pyridinium		
1(N)	11.28	−5.79	−3.57	1.92
2,6	4.21	−5.64	3.14	1.71
3,5	7.62	−5.21	−0.069	1.72
4	5.84	−4.76	0.48	1.56
		Pyrazinium		
1(N)	10.86	−5.79	−2.32	2.75
2,6	6.00	−5.64	2.42	2.78
3,5	3.74	−5.21	3.10	1.63
4(N)	9.18	−4.76	−5.46	−1.04

[a] Lattice self-potentials are for pyridine hydrochloride: space group is $P2_1/m$, with unit cell parameters $a = 7.63$, $b = 8.12$, $c = 4.80$ Å^3; $\beta = 90 \pm 1°$, and Z = 2. [b] Lattice self-potentials for pyridinium nitrate are −5.54, −3.83, −4.14, −4.00, −4.83, −5.47 for positions 1–6, respectively. py·HNO_3 crystallizes in space group $P2/c$ with cell parameters $a = 3.905$, $b = 12.286$, $c = 13.470$ Å^3; $\beta = 90° 30'$, and $Z = 4$.

It should be pointed out that because of neglect of lattice potentials, even the most sophisticated free ion MO calculations cannot be expected to predict accurately charge distributions in ionic solds. Perhaps it will prove advantageous to perform calculations which include a lattice potential correction to the Coulomb integral of each atom. It would appear that the ASMO-SCF method[11] accounts for the gross features of charge migration in the pyrazinium ion whereas the EHT approach seems to suffer some rather serious shortcomings.

A major difficulty in the interpretation of ESCA measurements on ionic solids is the assessment of lattice potentials at the atoms of interest and the potential due to the surface itself. Slater[12] has recently evaluated the surface or epipotential for corundum and finds it to be important for only the outermost two or three atomic layers. Therefore, use of the full Madelung potential will be appropriate provided the summation converges at distances appreciably less than the mean photoelectron escape depth.[4] Inasmuch as we were concerned primarily with differences in lattice potential at various atomic positions, these considerations are not of great importance.

The crystal structures for most of the compounds included in this study are not known; only pyridine hydrochloride[13] and pyridine hydrogen nitrate[14] have been determined. Therefore these compounds are used as models to interpret the ESCA shifts of pyrazinium salts. For our purposes it is the potential gradient, *i.e.*, the lattice potential as a function of distance from the anion along the C_2 axis of the ion, that is of interest. The assumption is made that this quantity is very similar in pyrazinium and pyridinium salts. Evaluation of the lattice Madelung potential at the *j*th ion involves, in the point-charge approximation, a summation over all ions in the lattice.

$$E_m(j) = e^2 \sum_{i,i\neq j} q_i/r_{ij}$$

q_i refers to the charge (electronic charge units) on the *i*th ion and r_{ij} to the distance between ions *i* and *j*.

A computer program to evaluate lattice self-potentials and Madelung constants has been described by Van Gool and Piken.[15] This program together with the atomic charges reported by Kato, *et al.*, has been used to calculate lattice self-potentials for pyridine hydrochloride and pyridine hydrogen nitrate. Because the positions of the hydrogen atoms were not determined, each ring atom was assigned a charge equal to its own charge plus that of the associated hydrogen. The contribution to the site potentials from intraionic terms will of course be somewhat unrealistic, so these terms were evaluated separately and subtracted from the computed result. Then, using an ideal geometry and a C–H bond length of 1.0 Å, more accurate molecular potentials were obtained.

It is noteworthy that the lattice potentials at nitrogen and at position 4 differ by 1.03 eV in pyridine hydrochloride and by 1.54 eV in pyridine hydrogen nitrate, despite the fact that the structures are quite dissimilar. This is consistent with our observation that the anion has only a slight effect (at most 0.2 eV) on the N 1s binding energy separations in the compounds studied.

Clearly, the variation in lattice potential from atom to atom in the pyridinium ion is not negligible. As one might expect, the lattice self-potential (exclusive of intraionic terms) is most negative at nitrogen and increases with distance from the anion. Thus, the energy difference between the 1 and 4 positions in the free ion should be reduced by *ca.* 1.0 eV due to the lattice potential. If this correction is applied to the N 1s free ion binding energy difference for pyrazinium ion as in Table II, the predicted difference becomes 3.8 eV, still somewhat larger than the experimental value of 1.8 eV. It is striking that the nitrogen binding energy differences for the compounds studied span a range of only 1.3 eV, although the N–N distances vary from 1.4 Å in phthalazine to *ca.* 6.4 Å in 1,5-diaminonaphthalene.

Interestingly, the C(1s) spectra of the three pyrazinium salts studied all contain two lines of approximately equal intensity (making the assignment of either line as contaminant unlikely) with a separation of 1.8 ± 0.2 eV. This agrees rather well with the calculated separation for pyrazinum salts of 1.15 eV. Also, the C 1s line of both pyridinium salts was found to consist of an unresolved multiplet with full width at half mean height *ca.* 2.5 eV for the hydrochloride and 3.0 eV for the nitrate. Such a result is by no means conclusive, but it is what would be expected on the basis of the calculation for the pyridinium ion, shown in Table II.

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(11) H. Kato, H. Kato, H. Konishi, and J. Yonizawa, *Bull. Chem. Soc. Jap.*, **42**, 923 (1969).

(12) R. R. Slater, *Surface Sci.*, **23**, 403 (1970).

(13) P. C. Rerat, *Acta Crystallogr.*, **15**, 427 (1962).

(14) A. J. Serewicz, *et al.*, *J. Phys. Chem.*, **69**, 1915 (1965).

(15) W. Van Gool and A. G. Piken, *J. Mater. Sci.*, **4**, 95 (1969).

The pyridinium salts are hygroscopic and volatile so the latter results are not as reliable as are those for the pyrazinium compounds.

As mentioned above, the interpretation of binding energy differences in the diaza heterocyclic compounds and the diaminonaphthalenes is hampered by a lack of structural information as well as uncertainty about the extent of reasonance interaction between the nitrogens. The latter ambiguity can be avoided if one studies a molecule in which the reference nitrogen (unprotonated) is isolated from the protonation site insofar as inductive or resonance effects are concerned. N 1s binding energy measurements have been performed on 4-(*p*-nitrobenzyl)pyridine and its hydriodide with the expectation that they would meet this requirement. The last two entries in Table I reveal that protonation of the pyridyl nitrogen results in a N 1s shift of only 2.2 eV relative to the nitrogen of the nitro group.

In order to rationalize this observation, it is instructive to consider the binding energy shifts which would be expected for the hydriodide as an isolated ion pair. The calculation is based on several assumptions. The angle between the rings is taken to be 110°, and the $N(1)-I^-$ distance to be 3.3 Å. The pyridyl nitrogen is designated N(1) and the nitro nitrogen N(2). The positive charge is approximated by a point charge 1.5 Å from N(1) along the C_2 axis of the pyridyl moiety. The N 1s shift of N(1) (free ion) is taken to be +9.0 eV, based on a calculation using charges from Kato, *et al.* Other distances are based on ideal geometries and standard bond lengths. Thus N(2) experiences a shift of −1.32 eV due to the iodide ion and a shift of +1.89 eV due to the positive charge. N(1) is shifted by −4.36 eV due to iodide. Its net shift is thus +4.64 eV, or +4.07 eV relative to N(2). Considering the crudeness of the calculation, this result is surprisingly close to the measured value. Even this degree of agreement is somewhat fortuitous, however, since the free-ion shift of N(1) is undoubtedly too large and the difference in potential at N(1) and N(2) is overestimated by the ion-pair model. The point to be emphasized is that N 1s binding energy separations in compounds of the type studied here are rather insensitive to the distance between the nitrogens. In this respect the predictions of the isolated ion pair model are conceptually even if not quantitatively useful. Unfortunately, this effect limits the structural information which can be gleaned from measurements of this kind. It is possible, however, to distinguish between symmetrical and unsymmetrical protonation in compounds possessing basic centers in close proximity. Our results for phthalazinium ion, for example, rule out a structure with the proton situated on the bisector of the N–N bond.[2a] The spectra of the diazanaphthalenes and diaminonaphthalenes are explicable qualitatively in that increasing physical separation of the nitrogens is accompanied by increasing binding energy separation. Nevertheless, the reasoning that was applied to pyrazine leads to the conclusion that substantial electron delocalization occurs in these cations as well.

It is possible that a comparison of the nitrogen binding energies of the parent bases with those of the salts would be valuable. However, since the binding energies obtained for the salts are clearly dependent upon the anion, it is not clear what interpretation could be placed on this type of information. Any comparison of binding energies of atoms in ionic in covalent solids is necessarily based on the assumption of a common reference level. Until this sort of speculation can be substantiated, such a comparison would have limited value.

For comparative purposes spectra of the *N*-methyl iodides of several compounds have been obtained. Except for 1,10-phenanthroline, replacement of the proton by a methyl group produces a slightly larger separation of the N 1s lines. It seems unlikely that methylation would lead to a greater positive charge on nitrogen than would protonation since there is a progressive lowering of the N 1s binding energy in the series NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$. The increased separation is more probably attributable to difference in lattice structure and hence lattice potentials.

The largest N 1s binding energy separation found was in the monohydriodide of 1,5-diaminonaphthalene. This is probably due to smaller charge migration from the aromatic ring than occurs in the heterocyclic molecules. Also, there are undoubtedly significant differences in lattice structure between the two types of compounds. The rather slight difference in the shift differences between 1,5- and 2,3-diaminonaphthalenes (2.5 and 2.0 eV, respectively) again emphasizes the insensitivity of binding energy differences to distance between the protonation site and the reference nitrogen.

The monocations of 2,2′-bipyridine and 1,10-phenanthroline, both good chelating ligands, might be expected to show significant intramolecular hydrogen bonding. Indeed, Joris and Schleyer[16] find that the pK_a of 1,10-phenanthroline fails to correlate with the shift in OH stretching frequency of hydrogen-bonded methanol, although such a correlation works quite well for a number of similar but nonchelating bases. This they attribute to a strong intramolecular hydrogen bond in the protonated base. Such bonding should lead to an abnormally small difference in electron binding energies. We find peak separations of 2.1 eV in both compounds as well as in *N*-methyl-1,10-phenanthrolinium iodide in which no hydrogen bond formation is possible. It must be concluded that hydrogen bonding, if it does occur, is substantially less important than electron withdrawal from the ring system in determining the binding energy difference. In aqueous solution, of course, one is dealing with hydronium ions rather than simple protons as is the situation in the solid salts. It is quite possible that hydrogen bonding is more important in solution than in the solid state.

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[16] L. Joris and P. v. R. Schleyer, *Tetrahedron*, **24**, 5991 (1968).