Geometry Changes of Aryl Amino Groups Resulting from Changes in Electron Withdrawal: an *ab initio* Molecular Orbital Study

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Changes in the geometry of aryl amino groups in aniline, aminopyridines and protonated forms of these molecules have been studied by *ab initio* 6-31G* molecular orbital calculations. The pyramidal nature of the amino group in aniline is reduced by increased π-electron withdrawal by the ring but coplanarity with the ring (sp² hybridized nitrogen) only results when a very strongly π-electron withdrawing centre is conjugated with the amino group.

The geometry of aniline, and in particular that of its amino group, has been studied both experimentally by microwave spectroscopy[1] and X-ray diffraction[2] and theoretically[3-10] using *ab initio* molecular orbital calculations. The experimental studies indicate that the amino group is pyramidal with the NH_2 plane being tilted at an angle in the region of 40° to the ring plane. The X-ray study also indicates a small but significant displacement (0.12 Å) of the amino nitrogen from the plane of the ring. The results of the *ab initio* calculations are highly basis set dependent with regard to their predictions of the geometry of the amino group. Studies[6,7] of these basis set effects have shown that a fairly flexible basis, with d-polarization functions at least on the nitrogen, is required to describe the balance between localization of the lone pair on the nitrogen (making the nitrogen more pyramidal) and its delocalization onto the ring (tending to make the nitrogen planar). Full geometry optimization with such a basis set[6] also indicates that the C–N bond is bent out of the plane of the ring and it was pointed out that the microwave analysis was based on an assumption that the entire C_6H_5N group was perfectly planar. Microwave studies have also been performed on the aminopyridines[11,12] and their amino groups are also pyramidal, but with a flatter pyramid in the cases of 2- and 4-aminopyridines. The ability of the amino group to donate electrons to the π-system of the ring is closely related to its geometry and would be at its maximum if the amino group were coplanar with the ring. The amino group is known to exert a +M electronic effect, usually represented in text books by the resonance shown in Scheme 1.[13] It is probably for this reason that there has been an assumption that the amino group is coplanar with the ring since resonance canonical **4** implies that this electron donation occurs as a result of the nitrogen atom being planar (sp² hybridized). Even some recent theoretical studies[14,15] have assumed that aniline is planar. The pyramidal nature of aryl amino groups needs to be borne in mind in a range of situations (*e.g.* orientation effects in electrophilic aromatic substitution, base strength of amino groups, hydrogen bonding in DNA base pairs) where present descriptions and explanations often assume, at least implicitly, that nitrogen is sp² hybridized. It is the aim of the present work to perform a systematic study and comparison of electronic effects and geometry changes in aniline, protonated aniline, the aminopyridines and aminopyridinium ions using *ab initio* molecular orbital calculations with full geometry optimization and a basis set which will correctly describe the amino geometry. A study,[16] using semiempirical MNDO[17,18] calcul-

ations, has previously been performed and, where appropriate, comparisons will be made with those results.
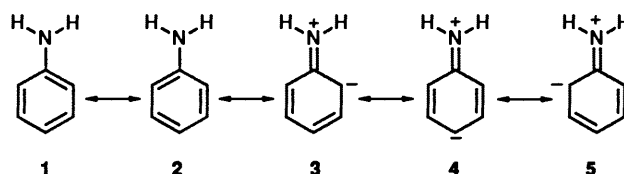
Scheme 1 Resonance description of delocalization of amino lone pair in aniline

Calculations

Unless otherwise stated, full geometry optimizations with no assumptions about symmetry were performed using the 6-31G* basis set[19] with the GAMESS program.[20] The 6-31G* basis set was selected because, being split valence and having d-polarization functions on C and N, it provides a balanced description of the localization and delocalization tendencies of the lone pair. Although a detailed study of correlation effects was not feasible within the computing resources available, MP2 calculations were performed for aniline and planar aniline at their RHF optimized geometries to provide an indication of the effect of correlation energy in determining the geometries of amino groups. Mulliken population analyses[21] are used to discuss the electron distributions. This is adequate for present purposes since it is the trends in populations and charges which are important rather than their actual values. However, for aniline two further methods of determining the atomic charge distribution were investigated. Potential derived charges,[22-26] a least squares fit of atomic charges to reproduce the electrostatic potential (obtained from quantum chemical calculations) at a set of points around the molecule. The program of Kendrick and Fox[27] was used with points on the 0.0001 electrons bohr⁻³ contour which was selected because it is outside the Van der Waals' surface of the molecule and leads to very little difference between the charges obtained whether or not the total charge is constrained to be zero. A distributed multipole analysis[28] was also performed for aniline.

Results and Discussion

General.—The total energies for all species and the energy changes on protonation are shown in Table 1. The barrier to inversion (difference in energy between planar and fully optimized geometries) of the amino group in aniline is calculated to be 1.63 kcal mol⁻¹* in close agreement with both experimental estimates[8,29-32] and calculations using a similar

Table 1 Energies, geometries and electron distributions for aniline and aminopyridines

	Energies		Angles/°				Distance/Å	Electron populations				Electronic effects		
	Total/ hartree	Protonation/ kcal mol^{-1}	ΣN	Tilt^a	H–N–H	R–C–N^b	C–N^c	Atom 1 π	Ring π	NH2 π	NH2 Total	Ring gain π	NH2 loss π	NH2 gain total
Planar aniline	−285.728 225		360.0	0.0	117.7	0.0	1.374	0.885	6.123	1.877	9.205	0.123	0.123	0.205
MP2	−286.678 821													
Aniline	−285.730 820		339.3	43.7	110.7	2.1	1.397	0.906	6.094		9.171	0.094		0.171
MP2	−286.681 931													
2-Protonated	−286.086 959	−223.4	360.0	0.0	116.5	0.1	1.302	0.622	4.396	1.652	8.951	0.396	0.348	−0.049
3-Protonated	−286.041 506	−194.9	343.9	38.4	111.5	3.6	1.385	0.993	4.208		9.097	0.208		0.097
4-Protonated	−286.095 562	−228.8	360.0	0.0	116.5	0.2	1.301	0.640	4.406	1.647	8.966	0.406	0.353	−0.034
Anilinium	−286.087 762	−223.9					1.455		5.987			−0.013		
1-Aminopyridinium	−302.063 417		330.3	53.5	110.9		1.401	1.507	6.008		8.768	0.008		−0.232
2-Aminopyridine	−301.734 923		344.2	38.8	113.8	1.7	1.378	0.835	6.121		9.146	0.121		0.146
2-Aminopyridinium	−302.118 618	−240.7	360.0	0.1	116.7	0.0	1.328	0.756	6.229	1.771	9.044	0.229	0.229	0.044
3-Aminopyridine	−301.721 697		338.5	44.4	110.4	2.3	1.398	0.947	6.092		9.166	0.092		0.166
3-Aminopyridinium	−302.101 767	−238.5	353.0	25.4	114.6	2.1	1.361	0.906	6.160		9.094	0.160		0.094
4-Aminopyridine	−301.729 166		344.8	37.6	112.6	1.8	1.379	0.841	6.120		9.157	0.120		0.157
4-Aminopyridinium	−302.125 660	−248.8	360.0	0.1	116.8	0.1	1.323	0.734	6.263	1.736	9.040	0.263	0.264	0.040

^{a} Angle between extension of C–N bond and NH2 plane. ^{b} Angle between C–N bond and the plane of the ring. ^{c} N–N distance for 1-aminopyridinium.

Table 2 Atomic charges in aniline

Atom	Mulliken π	Mulliken Total	PDC total	DMA total
C1	0.094	0.297	0.523	0.327
C2,6	−0.097	−0.255	−0.370	−0.191
C3,5	0.037	−0.179	−0.083	−0.021
C4	−0.068	−0.232	−0.228	−0.156
H2,6		0.192	0.184	0.076
H3,5		0.198	0.144	0.082
H4		0.194	0.147	0.082
N		−0.890	−0.953	−0.918
H		0.359	0.381	0.366
NH2		−0.171	−0.192	−0.187

basis set.[8] The MP2 calculations show that correlation contributes significantly (596.7 kcal mol⁻¹) to the stability of aniline but that there is only a small difference (0.3 kcal mol⁻¹) between the correlation contribution for planar and non-planar aniline, leading to an inversion barrier of 1.95 kcal mol⁻¹.

In all cases the rings, including hydrogens, were calculated to be essentially planar. The maximum deviation of a ring atom from the plane defined by ring atoms 1, 2 and 6, where atom 1 is bonded to the amino nitrogen, was 0.016 Å for a carbon and 0.024 Å for a hydrogen. Two methods of measuring the pyramidal nature of the amino group have been used. A frequently used measure is the pyramidalization angle which is the angle between the extension of the C–N bond and the NH₂ plane (0° for planar sp² hybridization and 54.7° for sp³ hybridization with all bond angles 109.47°). The second method [2,16] is to take the sum of all three bond angles at the nitrogen (360° for planar and 328.4° for sp³ hybridization with 109.47°). Both measurements of degree of pyramidalization are reported in this work. The subsequent numerical values quoted in discussions refer to the sum of angles at the amino nitrogen, which allows direct comparison with the MNDO results. The choice of method has no effect on the conclusions reached.

Geometry of the Amino Group.—The details of the calculated amino group geometries are listed in Table 1. In all the non-protonated species the amino group is calculated to be pyramidal and also the C–N bond is bent out of the plane of the ring by 1.7 to 2.3°. Protonation at the *ortho* or *para* carbons of aniline or the ring nitrogens of 2- and 4-aminopyridines causes the amino nitrogen to become planar with the amino group coplanar with the ring. The presence of the ring nitrogen in 2- and 4-aminopyridines causes the amino pyramid to flatten by about 5° compared with aniline, while the amino group in 3-aminopyridine is very similar to that in aniline. *meta* protonation of aniline also flattens the pyramid by about 5° and so it is surprising that protonation of 3-aminopyridine flattens the pyramid by the much larger amount of 14°. The amino group with the highest degree of pyramidalization is in the 1-aminopyridinium ion with angles very close to the tetrahedral bond angles of sp³ hybridization. This is the only species in which the amino group is rotated so that the hydrogens are above and below the ring thereby excluding any possibility of the lone pair being delocalized onto the ring. This rotation is presumably a result of repulsion of the lone pair by the much higher π-electron population of N1 (1.51) compared with that at C1 in the other species, Table 1. The microwave spectrum of 2-aminopyridine[11] indicated that one of the amino hydrogens was 0.08 Å closer to the plane of the rest of the molecule and it was suggested that this was the hydrogen closer to the ring nitrogen. The optimized geometry is in agreement with this assignment with the two hydrogens being displaced from the plane of the ring by 0.36 and 0.20 Å.

The angle by which the C–N bond is bent out of the plane of the ring although small also shows interesting variations, the bending being generally greater the greater the pyramidal nature of the amino group. The two exceptions to this are *meta*-protonated aniline and 3-aminopyridinium ion where the bending is much greater than expected for their degree of pyramidalization. The C–N bond distances shorten (indicating stronger bonding) as the amino group flattens and for those species where the amino group is coplanar with the ring the C–N bond is shorter where there is greater π-electron release to the ring. Throughout the series, however, neither π-electron release nor total electron withdrawal by the amino group follow the precisely same sequence as C–N distance.

Electronic Effects.— *General.* The amino group is normally considered to be π-electron donating and σ-electron withdrawing. For maximum π-electron donation the nitrogen atom would need to be sp² hybridized and the amino group coplanar with the ring and it is this concept which has probably lead to the slow acceptance of the pyramidal nature of aryl amino groups, particularly in standard textbooks[13] which only rarely[13e,f] acknowledge the pyramidal geometry. The amount of π-electron donation to the ring is conveniently measured by considering the total π-electron populations (*i.e.* the populations of the p_y, d_{xy} and d_{yz} orbitals since the rings were in the x-z plane) on the sp² hybridized ring atoms. For no π-electron donation the population would be 6.0 electrons for all cases except the ring-protonated anilines when it would be 4.0. Where the amino group is planar and coplanar with the ring the π-electron donation can also be measured by the loss of π-electrons from the amino group which would have a π-population of 2.0 for no π-donation. The amino group is also σ-electron withdrawing and the total electron gain or loss from the amino group provides an indication of the balance between the π-donation and σ-withdrawal, the total population being 9.0 for no electron gain or loss from NH₂. Table 1 shows the π-electron population at the atom to which the amino group is bonded, the π-electrons gained by the ring, the π-electrons lost by planar amino groups and the total electron gain by the amino group.

Aniline. As expected for aniline, the electron donation to the ring π-system is greater when the ring is constrained to be coplanar with the ring, but only by a very small amount (0.03 e). Overall, however, the amino group is electron withdrawing and despite the slightly greater donation to the ring π-system when planar, the increased σ-electron withdrawal by the sp² hybridized nitrogen dominates making the planar amino group more negative than the pyramidal. Table 2 shows the atomic charges in aniline obtained from Mulliken population analyses, potential derived charges and the point charge term of a distributed multipole analysis, although only the Mulliken charges can be divided into σ and π contributions. The π-electron populations of the ring carbons indicate small negative π-charges at the *ortho* and *para* positions (−0.10 and −0.07 respectively) and small positive π-charges at the *meta* and *ipso* positions (0.04 and 0.09 respectively). When the total population is considered all ring carbons, except *ipso* (+0.30), carry an overall negative charge but with the *ortho* and *para* (−0.25 and −0.23) being larger than *meta* (−0.18). The *ipso* carbon carries the largest charge of any ring atom, losing σ-electrons as a result of the inductive effect of the amino nitrogen, but not gaining any electrons by π-donation from the amino group. The potential derived charges also clearly indicate a large positive charge on the *ipso* carbon (0.52), with large negative charges *ortho* and *para* (−0.37 and −0.23) and a small negative charge on the *meta* carbon (−0.08). The charges from the distributed multipole analysis suggest a zero charge for the *meta* carbons, a large positive charge for the *ipso* carbon and negative charges

Scheme 2 Electrophilic attack at the *meta* and *para* positions of aniline

for *ortho* and *para*. Although there are significant differences in detail between the methods of charge calculation, they all clearly illustrate the expected build-up of negative charge at the *ortho* and *para* positions and the same general pattern of π-electron distribution is observed using an atoms-in-molecules approach.[33,34]

Comparison of all species. In all cases the amino group is a π-electron donor, the greater the electron demand from the ring, the greater the donation, the order being 2- and 4-protonated aniline > 2- and 4-aminopyridinium > 3-protonated aniline > 2-and 4-aminopyridine and planar aniline > 3-aminopyridine and aniline. In the cases of greatest electron donation the nitrogen has become sp^2 hybridized and the amino group is coplanar with the ring allowing maximum interaction of its lone pair with the π-system. In the cases of 2- and 4-protonated aniline the difference between the increase in ring π-population and decrease in amino π-population results from a small donation (about 0.05 e) to the π-system from the ring CH_2 group. With the exception of 3-protonated aniline, increase in donation to the ring π-system is associated with a reduction in π-population at atom 1, the build up being on alternating atoms. In all cases except the very high π-electron withdrawal in 2- and 4-protonated aniline and high σ-electron withdrawal in 1-aminopyridinium, the σ-electron withdrawing effect of the amino group is greater than the π-electron donation giving the amino group an overall negative charge.

Protonation Reactions.—General. The simple differences in energies between protonated and unprotonated species do not give accurate estimates of the experimental proton affinities (*e.g.* for aniline the calculated is 229 kcal mol⁻¹ and the experimental[35] is 208.8 kcal mol⁻¹) and cannot be used directly for reliable comparisons except in a series of closely related reactions where the bond formed is of the same type in each case. Valid comparisons can therefore be made between protonation at the three ring carbons of aniline or protonation of the three aminopyridines. Isodesmic reactions[36] combined with experimental reference proton affinities have been used to compare N and C4 proton affinities of aniline[37,38] but further evidence was required before concluding that *N*-protonation occurred.

Basicity of aniline. The lower basicity of aniline, and other aryl amines, compared with alkyl amines is usually ascribed to stabilization from resonance, Scheme 1, which cannot occur when the nitrogen is protonated or, that as a result of this resonance, the lone pair is delocalized and not available for protonation. Experiment and calculation have shown that the nitrogen is pyramidal and that π-electron donation to the ring is small. These explanations should therefore be viewed with caution.

Electrophilic substitution. The *ortho/para* directing properties of the amino group are usually ascribed to the greater resonance stabilization of the intermediate cation, and hence of the transition state, for *ortho* and *para* attack compared with *meta*. Scheme 2 shows this for *para* and *meta*. Ring protonation of aniline serves as a model for electrophilic attack and the calculations are in agreement with this explanation. For *ortho* and *para* attack the nitrogen of the amino group becomes planar (sp^2 hybridized) and there is a large donation of π-electrons to the ring. For *meta* attack, however, the amino group remains pyramidal, although flattened somewhat, and the donation from the amino group to the π-system is much less. This is consistent with resonance canonical **12** as the major contributor to the stability of the cation for *para* (and the equivalent for *ortho*) substitution compared with *meta*. It appears, however, to be contrary to recent investigations into the contributions of initial and final state effects in protonation and deprotonation reactions which suggest that for a charge gain or loss process the energy is governed by the initial charge distribution and that changes in resonance stabilization make very little contribution.[39–42] This conclusion was reached by analogy with potential and relaxation energy contributions to shifts in core electron binding energies obtained both experimentally and theoretically. The reactions considered involved loss of a proton without any change in the hybridization of the atom from which the proton was lost and without any change in the number of atoms/electrons (if any) of the π-system. Extending this to electrophilic aromatic substitution[43] which involves changes in hybridization of a ring carbon and the consequent removal of one atom and two electrons from the π-system may not be valid. Indeed for aniline not only does the substituent amino group donate electrons to stabilize the positive charge but it also changes its geometry to do so more effectively.

*Aminopyridinium Ions and Basicity of Aminopyridines.—*The energy changes on protonation, Table 1, indicate that 4-aminopyridine is more basic than 2-aminopyridine which is slightly more basic than 3-aminopyridine. This is in agreement with the experimentally determined pK_a values of 6.82, 6.04 and 9.11[44] for 2-, 3- and 4-aminopyridine respectively in aqueous solution. The amino nitrogen becomes planar to satisfy the increased electron demand in both 2- and 4-aminopyridinium ions and the π-electron donation to the ring is similar in both cases despite the difference in basicity. It is interesting to note that all four aminopyridinium ions are isoelectronic with aniline but that on increasing the nuclear charge of a ring atom by one unit different electronic effects transmitted to the amino group can change the hybridization of the amino nitrogen or cause the rotation of the amino group through 90°.

*Comparisons with MNDO and other Calculations.—*Equations (1)–(4) show the relationship between four quantities calculated previously using MNDO (sum of angles at amino nitrogen, C–N bond distance, C–N out of plane bending, and π-electrons donated to the ring) V_{MNDO} and those calculated in the present work using the computationally much more expensive 6-31G* *ab initio* calculations V_{6-31G*}. The MNDO calculations correctly predict the trends in these properties but overestimates all values except the C–N bond distance.

Sum of angles at amino nitrogen [eqn. (1)],

$$V_{6-31G*} = \underset{(\pm 0.04)}{0.65}\ V_{MNDO} + \underset{(\pm 13.18)}{128.03} \quad r^2 = 0.97 \quad (1)$$

C–N bond distance [eqn. (2)],

$$V_{6-31G*} = \underset{(\pm 0.08)}{1.06}\ V_{MNDO} - \underset{(\pm 0.12)}{0.11} \quad r^2 = 0.95 \quad (2)$$

Out of plane bending of C–N bond [eqn. (3)],

$$V_6\ {}_{31G*} = 0.42\ V_{MNDO} - 0.05\ r^2 = 0.87 \qquad (3)$$
$$\phantom{V_6\ {}_{31G*} = }(\pm 0.06)\phantom{V_{MNDO}} (\pm 0.24)$$

π-electrons donated to the ring [eqn. (4)],

$$V_{6-31G*} = 0.74\ V_{MNDO} + 0.04\ r^2 = 0.99 \qquad (4)$$
$$\phantom{V_{6-31G*} = }(\pm 0.03)\phantom{V_{MNDO}} (\pm 0.01)$$

A recent comparison[45] of MNDO, AM1 and PM3 results with experimental data has shown that of these methods AM1 yields the best description of the pyramidalization of aryl amino groups. For aniline the sum of angles at the amino nitrogen was found to be 341.5 by AM1, slightly greater than the value of 339.3 from the 6-31G* calculations. The importance of the geometry of the aryl amino groups in DNA bases and its implications with respect to base pairing and the propeller twist of base pairs has also been studied recently[45] using AM1, and an *ab initio* study of the geometry of adenine, with particular reference to the amino group, has been performed.[46]

Correlation Effects.—The MP2 calculations indicate that, by analogy with aniline, correlation effects will slightly stabilize (approximately 0.3 kcal mol^{-1}) the pyramidal geometries with respect to the planar. This will slightly decrease the tendency for the amino pyramid to flatten compared with the predictions from the RHF calculations. A more accurate indication of the effect of correlation on the barrier to inversion, and also the effect on the geometries, would be obtained by performing MP2 geometry optimizations, and this is an area where further work would be of interest.

Conclusions

The geometry of an aryl amino group is very sensitive to the electronic properties of the group to which it is bonded. Increased π-electron withdrawal will cause the amino pyramid to flatten as the π-electron release from the amino group increases. The overwhelming experimental and theoretical evidence for the pyramidal nature of aryl amino groups and the variation with π-electron demand should be accepted and incorporated into 'text book' explanations of base strength, electrophilic aromatic substitution and other phenomena depending on their electronic properties.

Acknowledgements

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