MNDO Calculations and the Non-planarity of Arylamino Groups

David B. Adams
Department of Pharmaceutical Chemistry, Sunderland Polytechnic, Sunderland SR1 3SD

Factors determining the geometry of arylamino groups were investigated using MNDO semi-empirical molecular orbital calculations with full geometry optimization. The species studied were aniline, ring-protonated anilines, aminopyridines, and aminopyridines protonated at the ring nitrogen. The amino group is calculated to be pyramidal with its nitrogen atom displaced from the plane of the aromatic ring unless the nitrogen lone pair is conjugated with a positive centre, when the amino group becomes coplanar with the ring.

Both experimental data from the microwave spectrum of aniline[1] and *ab initio* calculations on *para*-substituted anilines and monosubstituted benzenes[2] indicate that the amino group is pyramidal. However, the *ab initio* calculations were performed with standard geometries and optimization of the angle between the NH_2 plane and the ring plane so that details of the full optimized geometry were not obtained. Semi-empirical molecular orbital methods such as MNDO[3] permit a full geometry optimization[4] to be performed without excessive computing time being required.

Full MNDO geometry optimizations on cytosine,[5,6] adenine,[5] and guanine[5] indicated that not only were the exocyclic amino groups pyramidal, but also that the nitrogens were displaced from the plane of the rings by 13—19 pm. The prediction that the amino nitrogen is out of plane, and hence that the ring carbon to which it is bonded is slightly non-planar, is in conflict with chemical intuition and there is a tendency to disregard such predictions since they may arise from a deficiency of the molecular orbital method used. However, these predictions are supported by the *X*-ray crystal structure of aniline[7] which shows that the nitrogen is out of plane by *ca.* 12 pm and an *ab initio* calculation[8] which predicts that the exocyclic nitrogen of the 4-amino-2-oxo tautomer of cytosine is out of plane by 11 pm. These deviations of the nitrogen from the ring plane, while fairly small, are interesting and the factors influencing the geometry of arylamino groups are investigated further for some molecules and ions, including heterocycles.

Calculations

The MNDO program[9] was implemented on a Harris 100 computer at the Computer Centre, Sunderland Polytechnic. Calculations with full geometry optimization were performed on two series: (i) aniline and the ring-protonated anilines, to simulate the σ-complex in electrophilic substitution and (ii) *o*-, *m*-, and *p*-aminopyridine and the cations formed by their protonation at the ring nitrogen. The ball and stick diagrams were produced using the PLUTO[10] plotting program implemented on a Harris 300 computer.

Results and Discussion

The geometry optimizations were initiated with all the atoms, except two hydrogens of the ring-protonated anilines, in the *xy*-plane. Deviations from planarity are therefore readily apparent by non-zero *z*-co-ordinates in the optimized geometry.

In all cases the ring atoms had only very minor displacements from the *xy*-plane, generally $\leqslant 1$ pm and in no case > 2 pm. The sum of the bond angles at the amino nitrogen gives a measure of the planar or pyramidal nature of the amino group: 360° for planar to 328.4° for standard tetrahedral bond angles. The amino group is considered to be a π-electron donor and the maximum electron donation would be expected if the amino group were planar and coplanar with the ring. Since the rings are planar, the sum of $2p_z$ electron densities of the six ring atoms (or the five sp^2-hybridized carbons for the protonated anilines) gives the total ring π-electron density and this may be compared with the value of 6.000 (4.000 for protonated anilines) for no π-donation by the amino group.

Aniline and Electrophilic Substitution.—The results of the MNDO calculations are shown in the Table and plots of the optimized geometries, with coplanar ring hydrogens omitted, of aniline and *meta*- and *para*-protonated aniline are shown in the Figure. The amino group of aniline is pyramidal with the

Table. Results from MNDO calculations

Molecule or Ion	Calculated heat of formation (kJ mol^{-1})	*z*-co-ordinates of amino group (pm) N	H	H	Sum of amino group bond angles (°)	C–N bond distance (pm)	π-electrons donated to ring
Aniline	90.5	11	−34	−32	329.9	142	0.072
Aniline *ortho*-protonated	792.9	0	0	0	360.0	134	0.477
Aniline *meta*-protonated	876.8	17	−30	−9	337.1	141	0.230
Aniline *para*-protonated	781.9	0	0	0	360.0	134	0.482
Planar aniline	108.0	0	0	0	360.0	139	0.145
o-Aminopyridine	107.7	13	−50	−4	332.5	142	0.088
o-Aminopyridinium	761.3	4	0	1	359.7	136	0.270
m-Aminopyridine	122.4	12	−30	−34	329.5	142	0.070
m-Aminopyridinium	781.1	15	−16	−13	344.4	139	0.170
p-Aminopyridine	118.3	12	−30	−30	332.5	142	0.088
p-Aminopyridinium	745.5	0	0	0	360.0	135	0.319

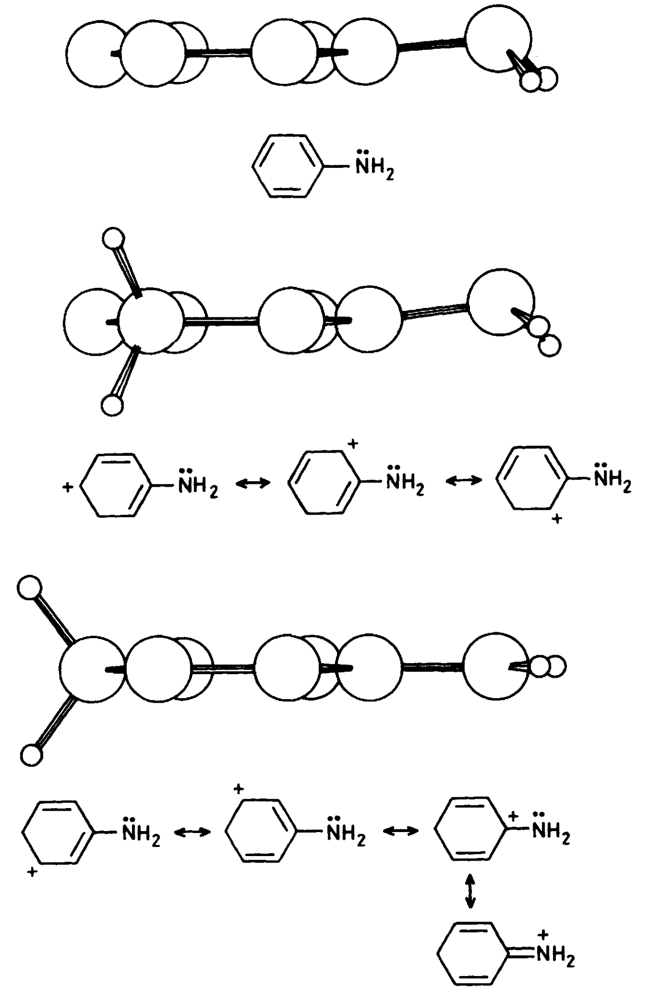

Figure. Optimized geometries of aniline and *meta-* and *para-*protonated aniline

nitrogen displaced from the plane of the ring by 11 pm and with the hydrogens displaced to the opposite side of the ring as observed by *X*-ray diffraction.[7] The sum of the amino group bond angles, 329.9°, is typical of that for sp^3 hybridization compared with the values of 338(11) and 346(11)°, intermediate between sp^3 and sp^2, observed for the two crystallographically independent molecules in the crystal.[7] However, the MNDO calculations refer to the free molecule but in the crystal the amino group is involved in hydrogen bonding. The calculated C–N bond distance, 142 pm, is quite close to the values of 140 and 139 pm observed in the crystal.[7] As expected for a pyramidal amino group, the π-electron density donated to the ring is quite small, 0.072e. A calculation in which the amino group is constrained to be coplanar with the ring indicates that planar aniline is less stable by 17.5 kJ mol^{-1}. However, the π-electron density donated to the ring has doubled. The heats of formation clearly show that the *ortho-* and *para-*σ-complexes are significantly more stable than the *meta*, in agreement with the experimentally observed *ortho/para* directing influence of the amino group. The geometry of the amino group changes dramatically on *ortho-* or *para-*protonation, becoming coplanar with the ring. There is also a substantial release of π-electron density to the sp^2 carbons, although a small amount (*ca.* 0.06e) of the 0.48e is released from the ring methylene group. In contrast, *meta-*protonation leaves the amino group pyramidal, although there is a flattening of the pyramid and an increased electron release to about half that observed for *ortho-* or *para-*protonation. Thus, when the lone pair of the amino group is conjugated with the positive charge of the hexadienyl cation it exerts its maximum electron-releasing effect by becoming planar and maximizing the N(2*p*)–C(2*p*) overlap.

In the case of *meta-*protonation this conjugation cannot occur and the overall π-electron release and stabilization of the cation are less. There is also a noticable shortening of the C–N bond distance when the optimized geometry of amino group is planar, but only a very slight shortening when the amino group of aniline is constrained to be coplanar with the ring.

Aminopyridines.—The results of the calculations for the aminopyridines and aminopyridinium ions are also shown in the Table. Many of the features of the aminopyridines are similar to those of aniline. The amino groups are pyramidal and the nitrogen is displaced slightly from the plane of the ring with the hydrogens being displaced to the opposite side of the plane. There is, however, a slight flattening of the amino groups of *o-* and *p-*aminopyridine compared with *m-*aminopyridine and aniline. The π-electron density donated to the ring is quite small, but slightly greater for the *ortho-* and *para-*compound than for the *meta-*compound and aniline.

Protonation of the ring nitrogen of *o-* and *p-*aminopyridine results in the amino group becoming planar and a significant release of π-electron density to the ring, while for *m-*aminopyridine the pyramid is only flattened and the release of π-electron density is much less. A noticeable C–N bond-shortening is again associated with a coplanar amino group.

When the amino group releases electrons to the ring π-system it does so to the *ortho-* and *para-*positions and only if the positive centre is in one of these positions does the amino group exert its maximum π-electron-releasing ability by becoming coplanar with the ring. The electron-withdrawing effect of an unprotonated ring nitrogen is not sufficient to produce co-planarity of the amino group. *Ab initio* calculations, optimizing only the angle between the NH_2 plane and the ring, also indicate that *para-*electron-withdrawing groups flatten the amino pyramid.[2a]

Conclusions.—Arylamino groups are pyramidal but with the nitrogen displaced from the plane of the aromatic ring. Unless there is a nearby positive centre pulling electrons away from the amino group the release of electrons to the π-system is small, and would still be fairly small even for a coplanar amino group. A nearby positive centre will increase the electron release from the amino group and flatten the amino pyramid. However only if the nitrogen lone pair is conjugated with the positive centre will the C–N bond shorten significantly, the nitrogen become sp^2-hybridized, and the amino group become coplanar with the ring to exert its maximum π-electron-releasing ability.

References

1 D. G. Lister and J. K. Tyler, *Chem. Commun.*, 1966, 152; D. G. Lister, J. K. Tyler, J. H. Hogg, and W. Larsen, *J. Mol. Struct.*, 1974, **23**, 253.
2 W. H. Hehre, L. Radom, and J. A. Pople, (*a*) *J. Chem. Soc., Chem. Commun.*, 1972, 669; (*b*) *J. Am. Chem. Soc.*, 1972, **94**, 1496.
3 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4898, 4907.
4 R. Fletcher and M. J. D. Powell, *Comput. J.*, 1963, **6**, 163; W. C. Davidon, *ibid.*, 1968, **10**, 406.
5 D. B. Adams, unpublished results.
6 A. Sygula and A. Buda, *J. Mol. Struct.* (*Theochem.*), 1985, **121**, 133.
7 M. Fukuyo, K. Hirotsu, and T. Higuchi, *Acta Crystallogr.*, 1982, **B38**, 640.
8 M. H. Palmer, J. R. Wheeler, H. Kwiatkowski, and B. Lesyng, *J. Mol. Struct.* (*Theochem.*), 1983, **92**, 283.
9 W. Thiel, MNDO, QCPE program No. 353.
10 W. D. S. Motherwell, '1978 PLUTO. A Program for Plotting Molecular and Crystal Structure,' University of Cambridge, Cambridge.

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