

# What Is the Geometry at Trigonal Nitrogen?

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A perceptive student, after becoming acquainted with VSEPR theory (1), may well query why ammonia and alkyl amines are depicted as pyramidal in organic texts whereas anilines are always drawn as planar molecules. Following Pauling (2), the difference is generally attributed to the dispersal of nitrogen lone pair density over three polar resonance forms (3–5) in the aromatic amine that are unavailable in aliphatic amines (Fig. 1). The  $sp^3$  hybridization at nitrogen in 1 and 2 can move towards  $sp^2$  and molecular coplanarity in forms 3–5.

Supporting evidence was provided by the difference in overall dipole moments between aromatic and aliphatic amines. For example, form 5 would reinforce the amine dipole as indicated, producing aniline's higher moment (1.53 D) compared with aliphatic amines (1.22–1.33 D). Other evidence relied on the large decrease in aqueous basicity of aniline compared with alkyl amines. Only the unprotonated amine could be stabilized by the above resonance and would move equilibrium to the left (eq 1).



Indeed, Pauling equated the millionfold decrease in  $K_b$  of aniline over primary amines with an extra resonance energy ( $RT \ln 10^6$ ) of 8.2 kcal mol<sup>-1</sup>.

A number of corollaries follow. First, the amines for which lone pair dispersal over resonance forms cannot be formulated (e.g., for benzyl or cyclohexyl amines) should be stronger bases than aniline and more pyramidal at nitrogen. Second, substituents in aniline acting inductively could change the basicity and geometry at nitrogen. Electron withdrawing (-I) groups should decrease basicity and increase planarity, whereas electron donating groups (+I) should act in the opposite sense. Third, an ortho-steric effect, due to the size of ortho-substituents, could twist the amino group out of the ring plane, reducing  $p$ - $\pi$  overlap between the amino groups and ring and thus increasing basicity. Some  $pK_b$  values (3) are collected in Table 1 to show these effects. The toluidines are stronger than aniline and

the *meta*- and *para*-nitroanilines are weaker, but the expected ortho-effect is not observed.

It is interesting to see how these old premises have withstood the test of time in view of three subsequent developments—namely, measurements of gas-phase acidities and basicities, ab initio computation of structures and energies, and structural determinations by modern X-ray crystallography. Measurement of proton transfers in the gas phase enable intrinsic acidities or basicities to be derived independently of solvent interactions (4). It is

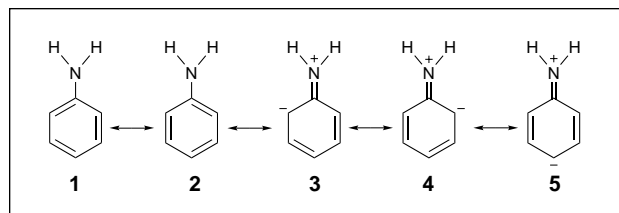


Figure 1. Main resonance structures in aniline.

now known, for example, that the increase in aqueous acidities in the  $\text{CH}_3\text{COOH}$ – $\text{CF}_3\text{COOH}$  series is not primarily a result of inductive electron withdrawal by fluorine but is mainly due to entropy contributions (5). Similarly, the increasing inductive donation of methyl groups, manifested in the gas phase basicity order



is not followed in aqueous solution where an inversion occurs to give the order (6)



This arises because the diminished hydrogen bonding of  $\text{Me}_3\text{NH}^+$  in the aqueous phase gives a lesser stabilization. Also the more effective hydrogen bonding of water to protonated aniline, as compared with aniline, will counter the resonance stabilization of the latter. In fact aniline becomes a stronger base than ammonia in the gas phase (7). The failure of the third corollary is probably due to the steric hindrance presented by ortho-substituted anilines to protonation by hydroxonium ions.

At the very least, evidence concerning geometries of anilines derived from aqueous basicities can be misleading. Also, the other type of evidence from dipole moments, derived from vector addition of bond dipoles, requires location of electron densities. This is a nonobservable, and charge distributions are to some extent arbitrary depending on the method used for partitioning electron density (8).

Advances in computational programming now enable energies and geometries of isolated molecules to be routinely calculated. The energies of isomers that are unavailable experimentally can also be estimated. Thus pyramidal and planar forms of amines can be compared and the more stable form predicted. Some energy differences and geometries calculated with the simplest ab initio basis set (STO-3G) are collected in Table 2. Although total energies become more negative with larger basis sets and with correlation corrections, energy differences between closely related isomers are reliable enough to select stable forms (9). In all instances the bent pyramidal form is the more stable. The energy difference can be regarded as the energy barrier to inversion, the planar form acting as the transition state. These ab initio calculations conform with VSEPR expectations, indicating the lone pair density in nitrogen is not fully dispersed via resonance.

In the more stable bent forms the C–N distances change as expected on substitution but remain constant in the planar forms. The shortening of this bond between forms averages 0.042 Å. Unexpectedly, from the resonance viewpoint, the C–N bond in the pyramidal forms is not co-

Table 1. Values of  $pK_b$  for Aqueous Amines at 25 °C

Amine	$pK_b$
$\text{C}_6\text{H}_5\text{NH}_2$	9.37
$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	4.67
$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_2$	4.17
$3\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$	11.53
$4\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$	13.00
$2\text{-ClC}_6\text{H}_4\text{NH}_2$	11.35
$3\text{-ClC}_6\text{H}_4\text{NH}_2$	10.54
$4\text{-ClC}_6\text{H}_4\text{NH}_2$	9.85
$2\text{-MeC}_6\text{H}_4\text{NH}_2$	9.56
$3\text{-MeC}_6\text{H}_4\text{NH}_2$	9.27
$4\text{-MeC}_6\text{H}_4\text{NH}_2$	8.92
$2,6\text{-Me}_2\text{C}_2\text{H}_3\text{NH}_2$	10.11
$2\text{-Bu}_4\text{C}_6\text{H}_4\text{NH}_2$	10.11
$2,4,6\text{-(Bu)}_3\text{C}_6\text{H}_2\text{NH}_2$	>12

Table 2. Geometries at Nitrogen in Pyramidal and Planar Forms of Aromatic Amines<sup>a</sup>

Compound	C–N Distance (Å)		Sum of Angles at N (°)		C–N Inclination to Ring (°)		Inversion Barrier (kcal)
	Pyramidal	Planar	Pyramidal	Planar	Pyramidal	Planar	
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1.445	1.404	329	360	-4.9	0	4.1
2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	1.448	1.406	327	360	-1.9	0	4.6
3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	1.446	1.405	328	360	-3.3	0	5.4
3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	1.440	1.405	331	360	-4.8	0	3.5
1-Naphthylamine	1.448	1.404	326	360	-3.0	0	4.7

<sup>a</sup>Calculated with the STO 3G basis set.

planar with the ring but is slightly inclined in the opposite direction to the NH<sub>2</sub> planes. However, the calculations refer to isolated gas phase molecules free from the intermolecular forces present in the liquid or solid state. These could affect the geometry around nitrogen.

The third development has been in structural determinations on amines by single crystal X-ray diffraction—in particular, of acentric anilines, because of their desirable optoelectric properties (10). These structures are subject to the usual uncertainties (11) such as those due to thermal motions (lessened if measured at low temperatures) and the difficulty in locating hydrogen atoms. The latter have to be found indirectly after nonhydrogen atoms are positioned. The remaining small electron density is then distributed to locate hydrogens less precisely by a Fourier difference map. In earlier structures the amino-hydrogens could not be located and the C–N distance had to be diagnostic of partial double bonding. However, the most significant difference from ab initio calculations is the modification of molecules by intermolecular forces in the solid state. Weak hydrogen bonding and packing considerations (12) could be sufficient to move geometries away from ab initio predictions or even expectations based on resonance contributions. (Some crystallographers invert this process [13], apportioning resonance forms from bond distances.) An idea of the magnitude of intermolecular energies can be seen from previous STO 3G calculations on H<sub>2</sub>N–H–NH<sub>3</sub> and H<sub>3</sub>N–HOH dimers, which gave energies of 3.9 and 5.9 kcal, respectively, and hydrogen bond separations of 3.082 and 2.907 Å (14). Two hydrogen bonds per molecule would be more than enough to overcome the energy difference between planar and pyramidal forms.

A simplified picture of the bond orders expected from resonance contributions to planar and pyramidal forms of aniline is shown in Table 3. These C–N bond lengths are approached only in two extreme structures: planar 2,3,4,6-tetranitrobenzene with CN = 1.312 Å, and pyramidal 2,4,6-trinitro-*N,N*-difluoroaniline with CN = 1.461 Å. The NF<sub>2</sub> group localizes the lone pair on nitrogen in spite of the strong -I effect of three nitro groups. An almost orthogonal twist of the NF<sub>2</sub> out of the ring plane minimizes the *p*- $\pi$  overlap and hydrogen bonding is absent. Structures inter-

mediate between these extremes should exhibit on inverse relation between the C–N bond length and the average C–C lengths adjacent to the C–N bond in the above picture (15). Table 3 shows this is only roughly true. All the nitroanilines are planar and except for *m*-nitroaniline are grouped together with C–N bond orders between 1.5 and 2.



The asymmetric unit in aniline, determined at 252 K, contains two independent molecules (16) with different C–N distances of 1.399(6) and 1.385(6) Å and angle sums around nitrogen of 346(11) and 338(11)°. The average C–C distances are constant at 1.385(6) Å with the ortho C–C's at 1.396(6) Å. The C–N bond is tilted 4.5° to the ring. The ab initio calculation (Table 2) reproduces the C–C distances and the tilt, but the C–N distance is 0.04–0.05 Å longer and the pyramidal angle closed down by 9–17°, indicating the presence of intermolecular forces in the solid. These are supplied by two kinds of weak N–H–N bonds with distances of 3.180 and 3.373 Å, comparable with the 3.082 Å in the H<sub>2</sub>N–H–NH<sub>3</sub> dimer mentioned earlier. There is only one hydrogen bond per molecule. In nitroanilines the amount of hydrogen bonding doubles, both of the amino hydrogens together with oxygens on the nitro groups involved giving stronger NH–O bonds. It is reasonable to assume that the extra hydrogen bond energy tilts the balance away from the pyramidal form favored in the ab initio calculations to the planar form in the solid state.

Similarly, the planarity around nitrogen in protein structures can be ascribed primarily to the linear H-bonding, intramolecularly in the  $\alpha$ -helix and intermolecularly in the  $\beta$  sheets. The usual explanation based on restricted rotation around a partially doubly bonded C–N link could be a consequence rather than a cause of planarity.

Planar geometry can also be induced if the nitrogen lone pair density can be efficiently delocalized. This is possible in planar N(SiH<sub>3</sub>)<sub>3</sub> by donation into *d*-orbitals available to silicon but not to carbon. Alternatively, very electronegative groups allow dispersal of lone pair density. Thus (CF<sub>3</sub>)<sub>2</sub>–N–N–(CF<sub>3</sub>)<sub>2</sub> has *D*<sub>2d</sub> symmetry and planarity at nitrogen, unlike F<sub>2</sub>N–NF<sub>2</sub>. Recent structure determinations of *p*-MeC<sub>6</sub>H<sub>4</sub>N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (17) and *N*-bis-sulfonyl fluorides –N(SO<sub>2</sub>F)<sub>2</sub> (18) also showed nitrogen planarity.

In answer to an enquiring student, the VSEPR theory seems valid unless hydrogen bonding is strong enough or dispersal of nitrogen lone pair density is possible over receptive groups.

Table 3. Idealized Resonance Contributions to Planar and Pyramidal Forms of Aniline

Structure	Bond Order		Bond Length (C–N) (Å)
	C–N	ortho C–C	
	2	1	1.28
	1	1.5	1.47

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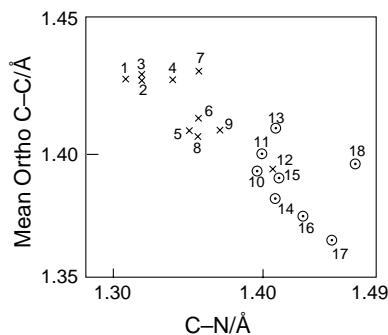


Figure 2. Relation of C-N with mean of the ortho C-C bond lengths in substituted anilines (see appendix). x = planar nitrogen;  $\odot$  = pyramidal nitrogen. Number 10 is aniline (see appendix for others).

## Appendix

Benzene-substituent groups in the numbered structures (Fig. 2) are:

1	1-NH <sub>2</sub> ; 2,3,4,6-NO <sub>2</sub>	10	1-NH <sub>2</sub>
2	1,3-NH <sub>2</sub> ; 2,4,6-NO <sub>2</sub>	11	1-NH <sub>2</sub> ; 4-Cl
3	1,3,5-NH <sub>2</sub> ; 2,4,6-NO <sub>2</sub>	12	1-NH <sub>2</sub> ; 3-NO <sub>2</sub>
4	1-NH <sub>2</sub> ; 2,4,6-NO <sub>2</sub>	13	1-NH <sub>2</sub> ; 2,5-Cl
5	1-NH <sub>2</sub> ; 4-NO <sub>2</sub>	14	1-NH <sub>2</sub> ; 4,6-Me
6	1-NHMe; 4-NO <sub>2</sub>	15	1-NMe <sub>2</sub> ; 2,6-Cl
7	1-NMe <sub>2</sub> ; 4-NO <sub>2</sub>	16	1-NH <sub>2</sub> ; 2,4,6-Br
8	1-NH <sub>2</sub> ; 2,6-Cl; 4-NO <sub>2</sub>	17	PhNH <sub>2</sub> ; SbCl <sub>3</sub>
9	1-NMe <sub>2</sub> ; 3-NO <sub>2</sub>	18	1-NF <sub>2</sub> ; 2,4,6-NO <sub>2</sub>

Details of these structure can be accessed in the Cambridge Crystallographic Data Base (19).