Theor Chim Acta (1986) 69: 235–245

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Chimica Acta

A molecular orbital study of nitrogen inversion in aniline with extensive geometry optimization

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(Received January 3, revised June 14 and September 5/Accepted September 30, 1985)

The geometry and energy of aniline have been calculated using the 6-31G and 6-31G*(5D) basis sets for the planar structure and various pyramidal structures, assuming that the ring and the N-atom bonded to it lie in the same plane, but otherwise with full geometry optimization. With the 6-31G basis set the planar structure is predicated to be the most stable, whereas the inclusion of polarization functions in the 6-31G*(5D) basis set finds a pyramidal structure with the out-of-plane angle $\phi = 42.3°$ to be most stable and the energy barrier to inversion via the planar transition state to be 1.59 ± 0.02 kcal mol^{-1}, in close agreement with experiment. Completing the optimization, allowing the N-atom and the C- and H-atoms of the ring to take up equilibrium out-of-plane positions increases the calculated energy carrier to inversion by less than 0.1 kcal mol^{-1} to 1.66 kcal mol^{-1}. The ring adopts a very shallow inverted boat-type conformation with $\angle N_7\text{–}C_1 \cdots C_4 = 2.0°$.

Key words: Aniline — Nitrogen inversion — MO calculations — Non-planarity of ring

1. Introduction

It is well-established that the C–NH$_2$ group in aniline has a pyramidal structure, see Table 1A, with the out-of-plane angle ϕ approximately 37.5° [3], see Fig. 1a

Table 1. Experimental and calculated values for the C-NH_2 group bond angles in aniline, and the energy barrier for the nitrogen inversion, i.e. Equilibrium Pyramidal Structure → Planar Structure

Ref.	Method	Pyramidal angles (degrees)	Out-of-plane angle, ϕ (degrees)	Barrier height ($\mathrm{kcal\ mol^{-1}}$)
	A. Experimental			
1.	Vibrational analysis of first UV band system	—	≈46	—
2.	Vibrational analysis of resonance fluorescence spectra	—	42	≈1.3
3.	Substitution structure from microwave spectra	∠HNH 113.1 ± 2.0 ∠CNH 115.9 ± 2.0	37.5 ± 2	—
4.	Vibrational analysis of far IR spectra	—	—	1.50
5.	Ditto	—	—	1.50
6.	Single vibronic level analysis of fluorescence spectra	—	—	1.56
	B. Calculated			
7.	INDO calculations: optimization of pyramidal angles in C-NH_2 group assuming equal values[a]	114.8	39	1.2
8.	MINDO/3 calculations: optimization of bond lengths and pyramidal angles in C-NH_2 group[b]	∠HNH 111.4 ∠CNH 123.9	8.7	—
10.	STO-3G calculations: optimization of pyramidal angles in C-NH_2 group assuming equal values[c]	112.1	47.7	2.7
11.	STO-3G calculations: optimization of pyramidal angles in C-NH_2 group assuming equal values[a]	114.4	51	4.3
11.	STO-(2+1)G calculations, same optimization	114.8	44	1.7
11.	STO-(1+1+1)G calculations, same optimization	115.1	38	1.1
11.	Best single-zeta STO calculations,[d] same optimization	119.9	8	0.3
11.	Huzinaga basis set I calculations,[d] same optimization	119.9	12	0.6
11.	Huzinaga basis set II calculations,[d] same optimization	115.1	38	0.9
—	6-31G basis set calculations[e]	planar conformer the most stable		
	6-31G*(5D) basis set calculations[e]	∠HNH 111.1 ∠CNH 114.5	42.3 ± 0.5	1.59 ± 0.02
—	6-31G*(5D) basis set calculations[f]	∠HNH 110.7 ∠CNH 114.3	43.5	1.66

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[a] Average experimental bond lengths for ring and C-NH_2 group

[b] Standard values [9] for ring geometry

[c] Standard values [9] for ring geometry and bond lengths in the C-NH_2 group

[d] For details of the basis sets employed, see the reference

[e] This paper: assuming that the ring and the N-atom bonded to it lie in the same plane, but otherwise with full geometry optimization

[f] This paper: complete geometry optimization: ϕ has a similar connotation, but since the ring is no longer planar it is now defined with respect to the C_1-N_7 axis

and b. Inversion about the N-atom is via the planar structure, $\phi = 0°$, and not by rotation via the bifurcated amino group structure in which the H-atoms are situated equidistant on either side of the ring plane, see Fig. 1c. The inversion barrier for aniline is appreciably less than that for ammonia, which also has the planar transition state, i.e. 1.56 kcal mol^{-1} [6] compared to 5.81 kcal mol^{-1} [12].

A number of semi-empirical and *ab initio* studies of the inversion process have been carried out with partial geometry optimization, see Table 1B. In all the calculations the phenyl ring was assumed to be a regular hexagon with standard [9] or experimental values for the C–C and C–H bond lengths.

Three considerations prompted the present study. First, experimental electron diffraction and microwave techniques have reached a stage such that the extent to which the benzene ring is distorted by substitution is open to investigation, and numerous papers on this topic reflect the current interest [13–20]. Secondly, a recent *ab initio* study [21] of mono-substituted benzene derivatives has shown that changes in C–C bond length are comparable in magnitude to the change in C–N bond length, reported, for example, in the conversion of the equilibrium pyramidal form of dimethylamine into the planar structure [22] – thereby suggesting that optimization of the ring geometry in aniline is essential for a more complete appraisal of the inversion process. Thirdly, it has been shown that the inclusion of *d*-functions is almost entirely responsible for the magnitude of the inversion barrier in ammonia [23], which raises the question as to the possible importance of *d*-functions in accounting for the magnitude of the barrier in aniline.

In the microwave study [3] the very small *c*-coordinates of the atoms making up the C_6H_5N fragment could not be reliably fixed by isotopic substitution, and the

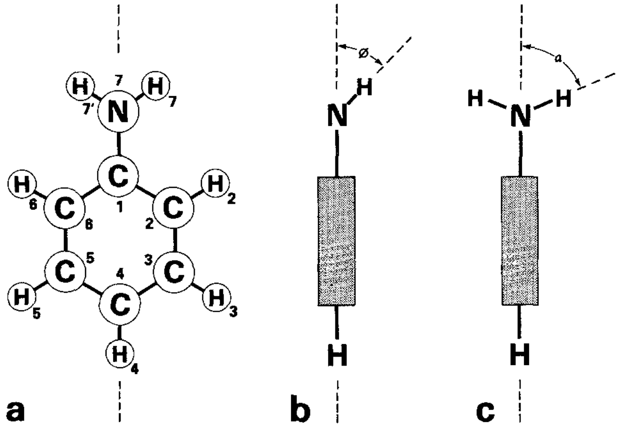

Fig. 1. a The numbering system used to identify the bond lengths and angles in aniline. **b** The structure with H_7 and $H_{7'}$ on the same side of the ring plane, ϕ is the angle between the H_7–N_7–$H_{7'}$ plane and the ring plane. **c** The bifurcated amino group structure with H_7 and H_7, situated equidistant either side of the ring plane, α is the angle between the N_7–H_7 bond axis and the ring plane, i.e. $\frac{1}{2} \cdot \angle H_7N_7H_{7'}$.

planarity condition of this fragment and the relationship $\sum mac = 0$ were invoked to establish these parameters. The main series of calculations of the geometry and energy of planar aniline and various pyramidal structures using the 6-31G and 6-31G*(5D) basis sets reported in this paper have likewise been carried out assuming that the ring and the N-atom attached to it lie in the same plane, but otherwise with full geometry optimization. The data obtained are thus strictly comparable to those obtained for the other monosubstituted benzene derivatives [21].

In view of the finding that quite large changes in the (planar) ring geometry for several of these derivatives result in only small changes in their total molecular energies, less than 1 kcal mol^{-1}, it is to be expected that relaxation of the planarity condition would not lead to any significant energy change. A calculation using the 6-31G*(5D) basis set, taking the most stable 6-31G*(5D) structure as the initial geometry, has accordingly been carried out to determine the effect of relaxing this remaining constraint.

2. Computational details

All the calculations were carried out on a VAX 11/780 computer. For the 6-31G basis set calculations [24] a modified version [25] of the Gaussian 80 program [26] was used, and for the 6-31G*(5D) basis set calculations [27] the Gaussian 82 program [28], was employed with gradient optimization for every structure.

In all cases the maximum forces in the distance and angle coordinates in the final optimization were less than 0.00045 hartree/Bohr and 0.00045 hartree/radian respectively.

3. Results

3.1. Energy

Total molecular energies, E_T, and nuclear repulsion energies, V_{nn}, for planar aniline, various pyramidal structures, see Fig. 1b, and the bifurcated structure, see Fig. 1c, calculated using the 6-31G and 6-31G*(5D) basis sets are listed in Table 2. It has been assumed that the ring and the N-atom bonded to it lie in the same plane, otherwise full geometry optimization has been carried out.

Table 2. Values of E_T and V_{nn} (a.u.) for various aniline structures, see Fig. 1b and c, calculated using the 6-31G and 6-31G*(5D) basis sets

		6-31G				6-31G*(5D)	
Structure		$-E_T$	V_{nn}	Structure		$-E_T$	V_{nn}
$\phi = 0$	planar	285.63306	272.93692	$\phi = 0$	planar	285.72716	273.27677
$\phi = 20°$	pyr.	285.63250	272.90559	$\phi = 34.1°$	pyr.	285.72926	273.15395
$\phi = 40°$	pyr.	285.62999	272.74971	$\phi = 42.8°$	pyr.	285.72969	273.05942
$\alpha = 57.2°$	bifur.	285.62375	271.94052	$\phi = 51.2°$	pyr.	285.72919	272.97739

E_T relative to the values for the planar structure is plotted as a function of ϕ in the lower part of Fig. 2, where it can be seen that without polarization functions the planar structure is the more stable. However inclusion of *d*-functions on the carbon and nitrogen finds a pyramidal structure, $\phi = 42.3°$, to be the most stable with the planar structure less stable by 1.59 ± 0.02 kcal mol^{-1} serving as the barrier to inversion, in close agreement with the experimental values, see Table 1.

Inversion by rotation about the C-N bond via the bifurcated amino group structure is a much less favored process. At the 6.-31G level, the optimized bifurcated structure with $\alpha = 57.2°$, see Fig. 1c, has an energy 5.84 kcal mol^{-1} less negative than that for the planar structure.

In recent studies [21, 29] using the 6-31G basis set it was found that the energy change accompanying the distortion of the benzene ring,

i.e., [Benzene geometry] $- X \rightarrow$ [Phenyl geometry] $- X$

in monosubstituted benzene derivatives such as fluorobenzene, nitrobenzene, phenol, cyanobenzene and styrene was remarkably small, less than 1 kcal mol^{-1}, and further calculations on fluorobenzene using the 6-31G*(5D) basis set gave a similar value. The corresponding calculation for the 6-31G*(5D) 42.8° pyramidal structure of aniline likewise gives a very small distortion energy, namely 0.23 kcal-mol^{-1}. The optimized structure for aniline, like that for the other derivatives, is evidently at the bottom of broad minima with little change in energy accompanying fairly sizeable geometrical distortions. This raises the possibility that in the condensed phase, in which intermolecular forces possibly amount to a few

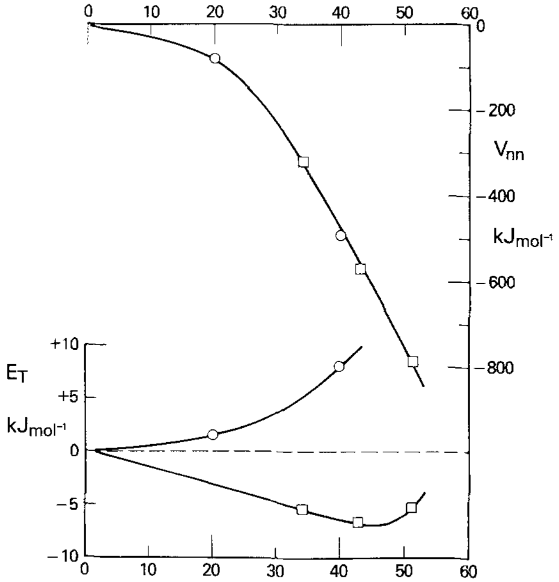

Fig. 2. The variation of E_T and V_{nn} in kJ mol^{-1} for pyramidal structures of aniline as a function of the out-of-plane angle ϕ, see Fig. 1b, relative to the values for the planar structure, calculated using the 6-31G and 6-31G* basis sets, circles and squares respectively

kcal mol^{-1}, significantly different structures might be stabilized with some C–C bonds shorter, some longer, by about 0.005 Å.

3.2. Geometry

The geometrical parameters for the ring in the various aniline structures calculated using the 6-31G and 6-31G*(5D) basis sets are listed in Table 3, and the corresponding data for the amino group bonding in Table 4. Since the value of ϕ interpolated for the minimum in the E_T curve in Fig. 2 is so close to 42.8° no serious error will be introduced by taking the geometrical parameters obtained with this out-of-plane angle for comparison with experiment (column two in Tables 3 and 4).

First it may be noted that in general the calculated bond lengths are less than experiment, as in the comparison of 6-31G calculated values and experimental values for fluorobenzene, phenol, cyanobenzene and toluene [21]. Yet both theory and experiment find the same inter-relationship among the bond lengths around the ring,

i.e., C_1–C_2 & C_6–$C_1 > C_3$–C_4 & C_4–$C_5 > C_2$–C_3 & C_5–C_6.

However the calculated values accentuate the difference between C_1–C_2 & C_6–C_1 and the rest. C_1–N_7 is 0.006 Å shorter than experiment, the C–H bonds shorter on average by 0.006 Å, and the N–H bonds shorter by 0.004 Å.
Although the 6-31G*(5D) calculations underestimate the ipso angle $\angle C_6C_1C_2$, by 0.7°, the opposite angle $\angle C_3C_4C_5$ is the same within the experimental uncertainty of 0.2°. Moreover the calculations correctly predict the type of ring distortion. There is an elongation with respect to the $C_1 \cdots C_4$ axis. The ipso angle and the angle opposite are less than 120°, whilst the angles at the sides of the ring are all greater than 120°. Further comparisons with the 6-31G*(5D) data for benzene serve to emphasize this feature.

The trends in bond lengths, bond angles, nonbonded distances and ring area as pyramidal structures are converted into the planar structure, and the extent to which these trends are sensitive to the inclusion of polarization functions, can be established by comparing the increments in going from $\phi = 40°$ to zero using the 6-31G basis set data and from $\phi = 42.8°$ to zero using the 6-31G*(5D) basis set data. The magnitude of the variation of the parameters with ϕ is such that the small difference in these initial values makes no perceptible difference to the increments.

The trends are in general remarkably insensitive to the inclusion of polarization functions on the carbon and nitrogen at this level of calculation. In only two instances do the increments differ in sign, namely for $\angle C_1C_2C_3$ and for the nonbonded distance $C_2 \cdots C_5$. But in both cases the increments are some of the smallest, and hence the least significant.

As would be expected the biggest changes are in the parameters for the amino group bonding. C–N decreases by about 0.022 Å in going to the planar structure, and N–H by about 0.006 Å. The changes in the C–C bonds in the ring get

Table 3. Geometrical parameters[a] of the phenyl group in aniline for the planar structure, structures with pyramidal nitrogen having various values for the out-of-plane angle ϕ, and for the bifurcated amino group structure[b], see Fig. 1b and c. calculated using the 6-31G and 6-31G*(5D) basis sets

		6-31G				6-31G*(5D)			
Geometrical parameter[c]	Expt.[d]	Planar, $\phi = 0$	$\phi = 20°$	$\phi = 40°$	Bifurcated NH_2 group	Planar, $\phi = 0°$	$\phi = 34.1°$	$\phi = 42.8°$	$\phi = 51.2°$
C_1-C_2, C_6-C_1	1.397(3)	1.397_0	1.396_2	1.394_3	1.391_7, 1.389_8	1.395_8	1.394_0	1.393_1	1.391_9
C_2-C_3, C_5-C_6	1.394(4)	1.384_7	1.384_9	1.385_4	1.387_5, 1.387_7	1.382_7	1.383_3	1.383_8	1.384_0
C_3-C_4, C_4-C_5	1.396(2)	1.388_0	1.387_9	1.387_8	1.387_7, 1.387_8	1.386_1	1.385_8	1.385_8	1.385_7
H_2-C_2, H_6-C_6	1.082(4)	1.074_2	1.074_2	1.074_3	1.074_1, 1.071_9	1.076_4	1.076_6	1.076_7	1.076_6
H_3-C_3, H_5-C_5	1.083(2)	1.073_7	1.073_7	1.073_5	1.073_4, 1.073_3	1.076_1	1.075_8	1.075_8	1.075_7
H_4-C_4	1.080(2)	1.072_6	1.072_4	1.072_6	1.073_2	1.074_3	1.074_6	1.074_8	1.075_0
$\angle C_6C_1C_2$ (ipso)	119.4(2)	118.5_8	118.6_8	118.7_6	119.4_2	118.5_6	118.6_6	118.6_8	118.7_4
$\angle C_1C_2C_3$, $\angle C_5C_6C_1$	120.1(2)	120.4_2	120.4_0	120.4_1	119.7_3, 120.5_7	120.3_7	120.3_8	120.4_1	120.4_2
$\angle C_2C_3C_4$, $\angle C_4C_5C_6$	120.7(2)	120.9_4	120.8_7	120.7_7	120.0_6, 120.1_1	121.0_6	120.9_6	120.9_0	120.8_3
$\angle C_3C_4C_5$	118.9(2)	118.7_0	118.7_8	118.8_8	119.7_1	118.5_8	118.6_6	118.7_0	118.7_6
$\angle H_2C_2C_1$, $\angle H_6C_6C_1$	119.8(2)	119.5_3	119.5_5	119.5_7	119.2_6, 118.4_0	119.5_7	119.6_0	119.5_9	119.5_9
$\angle H_3C_3C_4$, $\angle H_5C_5C_4$	119.1(1)	119.9_1	119.9_4	119.9_7	120.0_7, 120.0_5	119.9_2	119.9_3	119.9_5	119.9_8
$\angle H_4C_4C_3$, $\angle H_4C_4C_5$	120.5(1)	120.6_5	120.6_1	120.5_6	120.1_2, 120.1_7	120.7_1	120.6_7	120.6_5	120.6_2

[a] Units: internuclear distances in Å, bond angles in degrees, and ring areas in $Å^2$

[b] H_7 and $H_{7'}$ lie above and below the ring plane at the right-hand side of the plane through $C_4 \cdots C_1$-N_7 perpendicular to the ring plane: $\alpha = \frac{1}{2}\angle H_7N_7H_{7'} = 57.1°_7$

[c] Values for benzene: C-C 1.388_3 & 1.386_3, H-C 1.073_3 & 1.075_5, $C_1 \cdots C_4$ 2.776_5 & 2.772_6, $C_2 \cdots C_6$ 2.404_5 & 2.401_1, $H_2 \cdots H_3$ 2.461_6 & 2.461_7, and the ring area 5.007472 & 4.993055, using the 6-31G and 6-31G*(5D) basis sets respectively

[d] $\phi = 37.5 \pm 2.0°$. In parentheses, the uncertainty in the last figure [3]

Table 4. Geometrical parameters[a] of the C–NH_2 group in aniline for the structures listed in Table 3

		6-31G				6-31G*(5D)			
Geometrical parameter	Expt.[b]	Planar, $\phi = 0°$	$\phi = 20°$	$\phi = 40°$	Bifurc. Str.	Planar, $\phi = 0$	$\phi = 34.1°$	$\phi = 42.8°$	$\phi = 51.2°$
C_1–N_7	1.402(2)	1.380_5	1.385_4	1.401_5	1.426_9	1.374_1	1.387_5	1.395_6	1.405_0
N_7–H_7, N_7–$H_{7'}$	1.001(10)	0.989_0	0.990_4	0.994_6	0.994_2	0.991_4	0.994_8	0.997_0	1.000_1
$H_7 \cdots H_{7'}$	1.670	1.694_4	1.685_2	1.662_5	1.670_8	1.697_8	1.668_4	1.644_4	1.607_4
$C_1 \cdots H_7$, $C_1 \cdots H_{7'}$	2.048	2.072_0	2.062_9	2.031_2	2.080_9	2.068_3	2.039_8	2.023_8	2.005_3
$\angle H_7N_7H_{7'}$	113.1	117.8_8	116.6_0	113.4_0	114.3_4	117.8_0	113.9_8	111.1_2	106.9_6
$\angle C_1N_7H_7$, $\angle C_1N_7H_{7'}$	115.9	121.0_6	119.6_0	114.8_7	117.4_0	121.1_0	116.8_3	114.5_0	111.8_8
$\sum$ angles	344.9	360	355.8_0	343.1_4	349.1_4	360	347.6_4	340.1_2	330.7_2

[a] Bond lengths in Å, bond angles in degrees

[b] $\phi = 37.5 \pm 2.0°$[3].

progressively smaller the farther away the bond is from the amino group. There would appear, however, to be a small but perceptible alternation, with C_1–C_2 increasing in length, C_2–C_3 decreasing, and C_3–C_4 increasing. The bond angles characterizing the ring are very little affected, ∠CCC by less than 0.2° and ∠HCC by less than 0.1°.

The amino group bond angles increase in going to the planar structure since their sum must become 360°. The inclusion of polarization functions has relatively little effect on ∠CNH, the increments being $+6.1_9$ and $+6.6_0$ at the 6-31G and 6-31G*(5D) levels. But the effect on ∠HNH is much more pronounced. The increments are $+4.4^\circ_8$ and $+6.6^\circ_8$ respectively, i.e. a difference of 2.2°_0 compared to 0.4°_1.

In both the 6–31G and 6–31G*(5D) calculations the ring areas in the aniline structures are invariably greater than that for benzene: the areas decrease as ϕ increases: and the increments in going from the 40° and 42.8° pyramidal structures respectively to the planar structures are about 0.1% of the benzene value.

3.3. *The effect of relaxing the remaining geometrical constraint*

Taking the $\phi = 42.8°$ 6-31G*(5D) structure as the initial geometry, and allowing the N-atom and the C- and H-atoms of the ring to move out-of-plane, E_T is further decreased from −285.72969 to −285.72981 a.u. The increase in the calculated energy barrier to inversion is consequently less than 0.1 kcal mol^{-1}.

As might be expected the N-atom is most affected. Taking the $C_1 \cdots C_4$ axis in the plane passing through C_1 and C_4 perpendicular to the $C_2 \cdots C_6$ and $C_3 \cdots C_5$ axes as reference, N_7 lies 0.0495 Å above this axis with $\angle N_7C_1 \cdots C_4 = 2.03°$. The $C_2 \cdots C_6$ and $C_3 \cdots C_5$ axes pass through the $C_1 \cdots C_4$ plane 0.0004 Å and 0.0005 Å above this reference axis respectively. The ring thus adopts a very shallow inverted boat-type conformation. The hydrogens, however, are disposed differently. The $H_2 \cdots H_6$ axis passes through the $C_1 \cdots C_4$ plane 0.0068 Å above the $C_1 \cdots C_4$ axis, whereas the $H_3 \cdots H_5$ axis passes through 0.0002 Å below this axis, and H_4 likewise lies below it, by 0.0006 Å.

With regard to the ring geometry the carbon-carbon bond lengths all decrease a little, C_1–C_2 and C_2–C_3 by 0.0003 Å, and C_3–C_4 by 0.0001 Å. The ipso angle, $\angle C_6C_1C_2$, and the opposite angle $\angle C_3C_4C_5$, increase by 0.02°, whereas the two angles at the side of the ring each decrease by 0.01°.

In the bonding of the amino group C_1–N_7 and N_7–H_7 both increase, from 1.3956 to 1.3964 Å and from 0.9970 to 0.9974 Å respectively: $\angle C_1N_7H_7$ decreases from 114.50 to 114.33°, and $\angle H_7N_7H_7$, from 111.12 to 110.73°: ϕ, now defined with respect to the C_1–N_7 axis, is a little bigger, 43.5° compared to 42.3°.

4. Discussion

Previous calculations on aniline using several *sp* basis sets [11], assuming that the phenyl ring is a regular hexagon, experimental values for the bond lengths, and optimizing the amino group angles with the further assumption that $\angle CNH = \angle HNH$, predicated pyramidal structures to be the most stable, see Table 1B; and good agreement was obtained with experiment for the inversion barrier and the out-of-plane angle ϕ in the case of the two most flexible basis sets. However the present calculations, assuming that the ring and the nitrogen atom attached to it lie in the same plane but otherwise with full geometry optimization, find the planar structure to be the most stable at the 6-31G level, and a pyramidal structure to be the most stable only if d-functions on the carbon and nitrogen are included in 6-31G*(5D) calculations - equally good agreement with experiment then being obtained. Completion of the optimization, allowing the N-atom and the C- and H-atoms of the ring to take up their equilibrium out-of-plane positions, increases the calculated inversion barrier by less than 0.1 kcal mol^{-1}.

These results on aniline thus fall into line with the corpus of results on ammonia [10, 23, 30–34] in which it is well-established that the inclusion of d-functions on the nitrogen is essential to get close agreement for the barrier height. But, the barrier height being greater in ammonia, i.e. 5.81 compared to 1.56 kcal mol^{-1} [6, 12], calculations with optimized geometries, even without the inclusion of d-functions, find a pyramidal structure to be the more stable [30].

Sigma, pi and total atomic charges and sigma, pi and total overlap populations in the various aniline structures calculated using Mulliken population analysis and a comparison with results reported in the literature for ammonia, and a comparison of expectation energy differences characterizing the barrier to inversion in aniline and in ammonia, can be obtained by writing to the authors.

Acknowledgement. The authors gratefully acknowledge the generous grant of computer time provided by the computer center of the Philadelphia College of Textiles and Science.

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