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Molecular Structure of Aniline in the Gaseous Phase: A Concerted Study by Electron Diffraction and ab Initio Molecular Orbital Calculations

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The molecular structure of free aniline has been investigated by gas-phase electron diffraction and ab initio MO calculations at the HF and MP2 levels of theory, using the 6-31G*(6D) basis set. Least-squares refinement of a model with C_s symmetry, with constraints from MP2 calculations, has led to an accurate determination of the C—C—C angle at the *ipso* position of the benzene ring, $\alpha = 119.0 \pm 0.2^\circ$ (where the uncertainty represents total error). This parameter provides information on the extent of the interaction between the nitrogen lone pair and the π system of the benzene ring, and could not be determined accurately by microwave spectroscopy. The angles at the *ortho*, *meta*, and *para* positions of the ring are $120.3 \pm 0.1^\circ$, $120.7 \pm 0.1^\circ$, and $119.0 \pm 0.3^\circ$, respectively. Important bond distances are $\langle r_g(\text{C—C}) \rangle = 1.398 \pm 0.003 \text{ \AA}$ and $r_g(\text{C—N}) = 1.407 \pm 0.003 \text{ \AA}$. The effective dihedral angle between the H—N—H plane and the ring plane, averaged over the large-amplitude inversion motion of the amino group, is $\langle |\tau| \rangle = 44 \pm 4^\circ$. The equilibrium dihedral angle is calculated to be 41.8° at the HF level and 43.6° at the MP2 level, in agreement with far-infrared spectroscopic information. The MO calculations predict that the difference $r(\text{C}_{\text{ortho}}-\text{C}_{\text{meta}}) - r(\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}})$ is 0.008–0.009 Å. They also indicate that the nitrogen atom is displaced from the ring plane, on the side opposite to the amino hydrogens. The displacement is 0.049 Å at the HF level and 0.072 Å at the MP2 level. The two calculations, however, yield very different patterns for the minute deviations from planarity of the ring carbons.

KEY WORDS: Aniline; gas-phase electron diffraction; ab initio MO calculations; benzene ring deformation; nitrogen inversion motion.

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INTRODUCTION

The molecular structure of the simplest aromatic amine, aniline, has been the subject of several studies during the last two decades. The experimental determination of the structure of the free molecule by microwave spectroscopy [1] has been followed by a number of ab initio MO studies, involving full geometry optimization with extended basis sets at the Hartree–Fock level [2–4]. An X-ray crystallographic study has also appeared [5].

A detailed knowledge of the molecular structure of aniline is of primary importance, as it provides information on the extent of interaction between the nitrogen lone pair and the π system of the benzene ring. Both the nitrogen bond configuration and benzene ring geometry are expected to be sensitive to this interaction.

Notwithstanding the above mentioned studies [1–5], important aspects of the molecular structure of aniline have not yet been firmly established. A weakness of the microwave study [1] is that all atoms except the amino hydrogens have *very* small (<0.03 Å) *c* coordinates in the inertial reference framework. These coordinates could not be determined by the method of isotopic substitution and were deduced [1] from the relationship $\Sigma mac = 0$, under the assumption that the C_6H_5N fragment is planar. However, the MO calculations [2–4] indicated appreciable displacement, about 0.05 Å, of the nitrogen atom from the ring plane on the side opposite to the amino hydrogens. A yet greater displacement, about 0.12 Å, was reported in the X-ray diffraction study of the crystal [5], where at least some of it may be a consequence of intermolecular interactions.

Another possible source of error in the microwave study is the small *a* coordinate of atoms C2 and C6, *ca.* 0.23 Å [1] (see Fig. 1 for the numbering of atoms). Again, this coordinate could not be determined by the isotopic substitution method and was derived [1] from the first moment condition, $\Sigma ma = 0$. We have shown [6–9] for a number of monosubstituted benzene derivatives that the small *a* coordinates of atoms C1 and/or C2 (C6) have produced inaccuracies in the values of the C1–C2 bond length and C2–C1–C6 angle obtained by microwave spectroscopy [10–12]. Also, the inversion motion of the amino group may have caused inaccuracies in the substitution coordinates of the amino hy-

drogens, and hence in the dihedral angle τ between the H–N–H plane and the ring plane.

The *ab initio* MO studies [2–4] have all been carried out at the Hartree–Fock level of theory. Ignoring electron correlation may have caused systematic errors in the small changes of the C–C bond lengths and C–C–C angles induced by the amino group, and even more so in the nonplanarity of the C_6H_5N fragment and the τ angle, since the energies involved in these changes are small. The calculations at the HF/6-31G*(5D) level [3] show that the energy decrease associated with the in-plane distortion of the benzene ring is only 1.0 kJ mol^{–1}. Relaxing the planarity constraint for the C_6H_5N fragment gives rise to an even smaller decrease, 0.3 kJ mol^{–1}.

Disturbing discrepancies occur between theoretical and experimental results. The difference in the displacement of the nitrogen atom from the ring plane has already been mentioned. The C1–C2 and C2–C3 bond lengths differ by 0.003 Å from the microwave study [1] and by 0.008–0.009 Å from the MO calculations [2–4]. The *ipso* angle, C2–C1–C6, is $119.4 \pm 0.2^\circ$ from the microwave study [1] and 118.7° from the MO calculations [2–4]. Values of the dihedral angle τ range from 37.5 to 55° from various experimental techniques and *ab initio* MO calculations.

Here we present the results of a concerted study of the molecular structure of aniline by gas-phase electron diffraction and *ab initio* MO calculations, including electron correlation corrections at the MP2 level of theory. Our previous studies of nitrobenzene [7], ethynylbenzene [8], fluorobenzene [13], cyanobenzene [14], phenol [15], and *tert*-butylbenzene [16] have shown that gas-phase electron diffraction can be used successfully to obtain accurate structural information on monosubstituted benzene derivatives. In particular, the electron diffraction technique allows a reliable determination of the *ipso* angle. We have seen that this parameter is hard to determine accurately by microwave spectroscopy; it may also be difficult to determine by MO calculations, due to its sensitivity to the electronic properties of the substituent [9, 17].

However, aniline is not an easy subject for electron diffraction. The C–N and C–C bonds have nearly equal lengths, and similarly so the C–H and N–H bonds, and also the $C1 \cdots C3$ and $N7 \cdots C2$ non-bonded interactions (see the radial distribution curve in Fig. 3). Difficulties also originate from the inversion motion of the amino group. The equilibrium value of the dihedral angle τ is of at least 40° (from resonance fluorescence spectroscopy [18], far-infrared spectro-

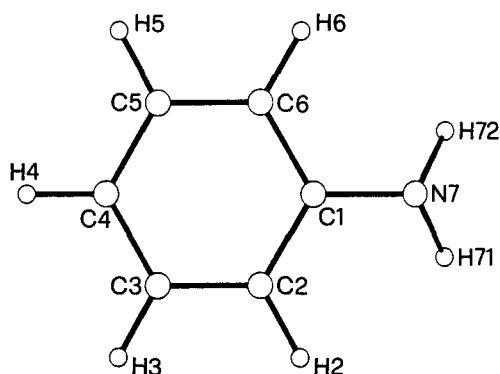


Fig. 1. Numbering of atoms in aniline.

copy [19, 20], microwave spectroscopy [21], and ab initio MO calculations [3, 4]), and the barrier to inversion is relatively low, 6.3–6.5 kJ mol⁻¹ [19, 20, 22]. This implies a large-amplitude inversion motion, governed by a double-well potential energy function, with the amino hydrogens undergoing substantial displacements from two equivalent positions on opposite sides of the ring plane. The lowest frequency associated with this mode, corresponding to the 0⁺ → 0⁻ transition [20], was observed at 40.8 cm⁻¹ [19, 22]. This large-amplitude motion is not treated adequately by standard refinement procedures of the electron diffraction analysis.

To alleviate the difficulty of closely spaced distances, we have imposed geometrical constraints from the MO calculations. Such an approach [23] has proven instrumental in the study of other monosubstituted benzene derivatives [8, 15].

In order to account for the consequences of the large-amplitude inversion motion of the amino group, we have constructed a model as a mixture of rigid conformers, differing in the value of the dihedral angle τ . The choice of the conformer populations was facilitated by the availability of spectroscopic potential functions for nitrogen inversion in aniline [19, 20, 22]. The model of multiple rigid structures is an important technique to simulate the variation in contributions to the electron diffraction intensities arising from large-amplitude motion [24].

A preliminary account of some of the results from the present study has appeared [25].

MOLECULAR ORBITAL CALCULATIONS

Ab initio MO calculations were carried out at the Hartree-Fock level and at the second order of the Møller-Plesset perturbation theory (MP2) [26], with all orbitals active. The 6-31G*(6D) basis set [27] was used throughout with gradient optimization [28]. The symmetry of the molecule was assumed to be *C_s*, with the mirror plane orthogonal to the plane of the ring; the benzene ring was not subjected to the planarity constraint. The maximum forces on the distance and angle coordinates in the final optimizations were less than 0.0005 hartree bohr⁻¹ and hartree radian⁻¹, respectively. All calculations were run on the IBM 3090/600J computer of CASPUR (Rome), using *Gaussian 90* [29].

The molecular geometry of aniline produced by our calculations is compared in Table I with that obtained from HF SCF calculations using the 6-31G** basis set [4].

ELECTRON DIFFRACTION

Experiment

The purity of the aniline sample was checked by gas chromatography and reversed-phase HPLC with photodiode array detector (Waters 991), and was found to be better than 99%. The electron diffraction photographs were taken with the Budapest EG-100A apparatus [30–32], using a so-called membrane nozzle [33] at a temperature of about 334 K. The electron wavelength, 0.04936 Å, was calibrated with a TlCl powder pattern ($a = 3.84145$ Å [34]). Nozzle-to-plate distances of about 50 and 19 cm were used; six plates for each distance were selected for analysis.

The tracing and data reduction were carried out as in Refs. 35 and 36. The ranges of the intensity data were $2.000 \leq s \leq 13.875$ Å⁻¹ and $8.25 \leq s \leq 35.75$ Å⁻¹, with data intervals of 0.125 and 0.25 Å⁻¹, respectively.

The total experimental intensities are available as supplementary material. The molecular intensities and radial distributions are presented in Figs. 2 and 3, respectively. The latter were calculated using an artificial damping factor $\exp(-0.002s^2)$; theoretical values were used in the $0.00 \leq s < 2.00$ Å⁻¹ region.

Analysis

The least-squares method was applied to the molecular intensities as in Refs. 35 and 36, using a modified version of the program by Seip and co-workers [37]. The inelastic and elastic scattering functions and phase shifts were taken from Refs. 38 and 39, respectively.

The molecule was assumed to have *C_s* symmetry and the ring *C_{2v}* symmetry. The five C–H bonds were represented by a mean bond length and each was assumed to bisect the corresponding C–C–C angle, as in our previous studies of monosubstituted benzene derivatives [7, 8, 13–16]. Under these constraints the geometry of the molecule is described by 11 independent parameters, which we have chosen as follows (see Fig. 1 for the numbering of atoms and Fig. 4 for the lettering of bond distances and angles of a benzene ring of *C_{2v}* symmetry):

(i) Two bond distances, $r(\text{C1} - \text{C2}) = a$ and $\langle r(\text{C} - \text{H}) \rangle$.

(ii) Four differences between bond distances: $\Delta_1(\text{C} - \text{C}) = r(\text{C1} - \text{C2}) - r(\text{C2} - \text{C3})$, $\Delta_2(\text{C} - \text{C}) = r(\text{C2} - \text{C3}) - r(\text{C3} - \text{C4})$, $\Delta(\text{C} - \text{N}/\text{C} - \text{C}) = r(\text{C1} - \text{N7}) - r(\text{C3} - \text{C4})$, and $\Delta(\text{C} - \text{H}/\text{N} - \text{H}) = \langle r(\text{C} - \text{H}) \rangle - r(\text{N} - \text{H})$.

Table I. Molecular Geometry of Aniline from ab Initio MO Calculations.

Parameter	HF/6-31G**, Ref. 4	HF/6-31G*(6D), present work	MP2/6-31G*(6D), present work
Bond distances (Å)			
$r(\text{C1}-\text{C2})$ (a)	1.393	1.3926	1.4008
$r(\text{C2}-\text{C3})$ (b)	1.385	1.3835	1.3925
$r(\text{C3}-\text{C4})$ (c)	1.385	1.3855	1.3947
$r(\text{C1}-\text{N7})$	1.394	1.3973	1.4049
$r(\text{C2}-\text{H2})$	1.077	1.0766	1.0886
$r(\text{C3}-\text{H3})$	1.076	1.0759	1.0874
$r(\text{C4}-\text{H4})$	1.075	1.0748	1.0863
$r(\text{N7}-\text{H71})$	0.996	0.9974	1.0148
Angles (degrees)			
$\angle \text{C2}-\text{C1}-\text{C6}$ (α)	118.7	118.74	118.81
$\angle \text{C1}-\text{C2}-\text{C3}$ (β)	120.4	120.39	120.45
$\angle \text{C2}-\text{C3}-\text{C4}$ (γ)	120.9	120.86	120.57
$\angle \text{C3}-\text{C4}-\text{C5}$ (δ)	118.7	118.76	119.12
$\angle \text{C2}-\text{C1}-\text{N7}$	120.6	120.61	120.51
$\angle \text{C1}-\text{C2}-\text{H2}$	119.6	119.59	119.47
$\angle \text{C3}-\text{C2}-\text{H2}$	120.0	120.02	120.08
$\angle \text{C2}-\text{C3}-\text{H3}$	119.2	119.18	119.32
$\angle \text{C4}-\text{C3}-\text{H3}$	119.9	119.96	120.10
$\angle \text{C3}-\text{C4}-\text{H4}$	120.6	120.62	120.44
$\angle \text{C1}-\text{N7}-\text{H71}$	114.6	114.25	113.18
$\angle \text{H71}-\text{N7}-\text{H72}$	111.4	110.64	109.82
τ^a	— ^b	41.77	43.64
φ^c	42.3	43.80	46.79
ϑ^d	2.0	2.11	3.94
Displacements (Å) from the least-squares plane through the C atoms of the benzene ring			
C1	— ^b	-0.0007	-0.0057
C2	— ^b	0.0004	0.0041
C3	— ^b	0.0004	-0.0011
C4	— ^b	-0.0007	-0.0005
N7	— ^b	0.0487	0.0715
H2	— ^b	0.0078	0.0092
H3	— ^b	0.0005	0.0002
H4	— ^b	-0.0014	-0.0050
H71	— ^b	-0.3294	-0.3310

^a Dihedral angle between the H—N—H plane and the least-squares plane through the C atoms of the benzene ring.

^b Not given in the original paper [4].

^c Angle between the C—N bond and the H—N—H plane.

^d Angle between the C—N bond and the C2—C1—C6 plane.

(iii) Three bond angles: $\angle \text{C2}-\text{C1}-\text{C6} = \alpha$, $\angle \text{C1}-\text{C2}-\text{C3} = \beta$, and $\angle \text{H}-\text{N}-\text{H}$.

(iv) The displacement of the nitrogen atom from the ring plane, ΔN .

(v) The dihedral angle between the H—N—H plane and the ring plane, τ .

Note that the three different bond distances and four different angles of the benzene ring (Fig. 4) are linked

by two equations of geometrical constraint, expressing the conditions of planarity and ring closure [17]. Thus only five independent parameters are required to define the ring geometry.

The four differences between bond distances and the displacement of the nitrogen atom from the ring plane are too small to be determined accurately by electron diffraction and were therefore given fixed values in

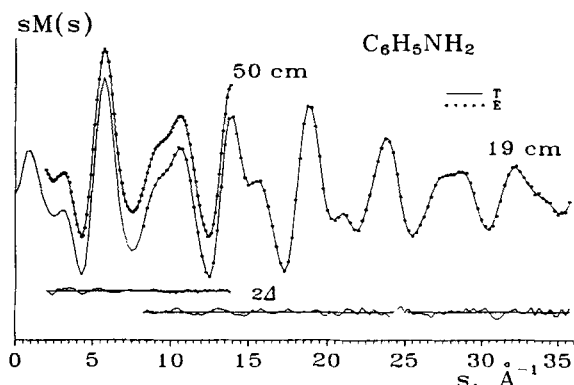


Fig. 2. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical for the model obtained from refinement B). Also shown are the difference curves (experimental - theoretical).

most refinements (see below). The angle H—N—H was also given a fixed value. The angle β was assumed to be linearly related to α , according to a well-established empirical relationship that holds for monosubstituted benzene rings, $\Delta\beta = -0.591\Delta\alpha - 0.301^\circ$ (where $\Delta\alpha$ and $\Delta\beta$ are deviations from 120°) [17].

Ten mean amplitudes of vibration were also treated as independent variables. They were coupled in groups to other amplitudes with constrained differences. These differences and other fixed amplitudes were mostly taken from spectroscopic calculations based on the MM3 force field [40]. The effect of alternative choices of the assumed differences and amplitudes on the geometrical parameters was investigated and found to be marginal. These tests were utilized to estimate total errors according to Ref. 41.

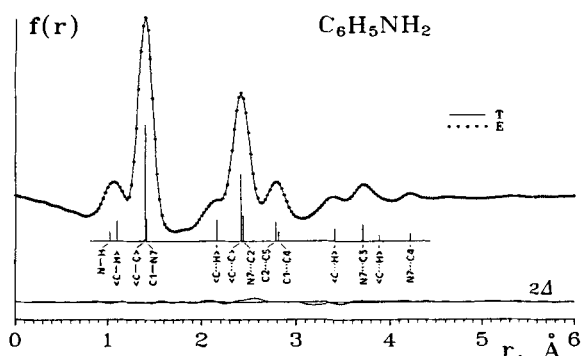


Fig. 3. Radial distribution curves (E, experimental; T, theoretical for the model obtained from refinement B). The positions of the most important distances are marked with vertical bars, the heights of which are proportional to the weights of the distances. Also shown is the difference curve (experimental - theoretical).

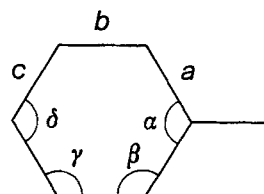


Fig. 4. Lettering of bond distances and angles in a monosubstituted benzene ring of C_{2v} symmetry.

Selected geometrical parameters from four refinements, A–D, are presented in Table II. In refinements A and B the H—N—H angle, the differences between bond distances, and the displacement of the nitrogen atom from the ring plane were assumed from the MO calculations at the HF/6-31G*(6D) and MP2/6-31G*(6D) level, respectively. In refinement C the C_6H_5N fragment was assumed to be planar; the H—N—H angle and the differences between bond distances were taken from the microwave study [1].

In refinement D the molecule was assumed to exist in the gaseous phase as a mixture of seven rigid conformers, differing *only* in the value of the dihedral angle τ (see Fig. 5). This is a rather crude approximation, because some geometrical parameters may vary appreciably with the dihedral angle τ . Ab initio MO calculations at the HF/6-31G*(5D) and 6-31G** levels [3, 4] indicate that the parameters which are most affected are $r(C1-N7)$ and $\angle H-N-H$; these vary by $+0.021$ Å and -6.7° , respectively, as the molecule goes from the planar ($\tau = 0^\circ$) to the equilibrium ($\tau = 42^\circ$) conformation. The C_6H_5N fragment was assumed to be planar; the H—N—H angle and the differences between bond distances were taken from the MP2/6-31G*(6D) calculations. The angle τ and the population of the seven conformers have been given the following values: 0° , 0.036; 11° , 0.095; 22° , 0.162; 33° , 0.245; 44° , 0.259; 55° , 0.157; and 66° , 0.045. The populations were estimated from the energies and wavefunctions of the 0^+ , 0^- , 1^+ , and 1^- states of the inversion mode, as given in Ref. 20.

It is comforting to see that the choice between the geometrical constraints from MP2/6-31G*(6D) or HF/6-31G*(6D) calculations has only marginal effects on the R factor and the molecular parameters (refinements A and B). On the other hand, adoption of constraints from the substitution structure obtained by microwave spectroscopy [1] (refinement C) causes the C3—C4—C5 angle (δ) to become unacceptably small, $118.3(1)^\circ$. The values of δ from the other refinements are close to that from the microwave study, $118.9 \pm$

Table II. Selected Geometrical Parameters^a and *R* Factors from Refinements A–D^b.

Parameter	Refinements			
	A	B	C	D
$\Delta_1(\text{C}—\text{C})^c$	0.0091 ^d	0.0083 ^d	0.0030 ^d	0.0083 ^d
$\Delta_2(\text{C}—\text{C})^c$	−0.0020 ^d	−0.0022 ^d	−0.0020 ^d	−0.0022 ^d
$\Delta(\text{C}—\text{N}/\text{C}—\text{C})^f$	0.0118 ^d	0.0102 ^d	0.0060 ^d	0.0102 ^d
$\Delta(\text{C}—\text{H}/\text{N}—\text{H})^g$	0.0786 ^d	0.0729 ^d	0.0810 ^d	0.0729 ^d
ΔN^h	0.0487 ^d	0.0715 ^d	0 ^d	0 ^d
$\angle \text{H}—\text{N}—\text{H}$	110.64 ^d	109.82 ^d	113.10 ^d	109.82 ^d
$r(\text{C1}—\text{C2})$ (α)	1.4020(1)	1.4016(1)	1.3986(1)	1.4016(1)
$r(\text{C1}—\text{N7})^i$	1.4067(1)	1.4057(1)	1.4036(1)	1.4057(1)
$\langle r(\text{C}—\text{H}) \rangle$	1.095(1)	1.094(1)	1.095(1)	1.093(1)
$\angle \text{C2}—\text{C1}—\text{C6}$ (α)	119.0(2)	119.0(2)	118.9(2)	118.9(2)
$\angle \text{C3}—\text{C4}—\text{C5}^j$ (δ)	119.2(1)	119.0(1)	118.3(1)	118.9(1)
τ^j	44(3)	44(3)	41(3)	—
R^k	0.0259	0.0260	0.0274	0.0275

^a Bond distances (r_s) are given in Å, angles in degrees. Least-squares standard deviations are given in parentheses as units in the last digit.

^b Refinements A–C differ in the assumptions on the geometry of the molecule: (A) assumptions from ab initio MO calculations, HF/6-31G*(6D); (B) assumptions from ab initio MO calculations, MP2/6-31G*(6D); (C) assumptions from the microwave study [1]. In refinement D the molecule was assumed to exist as a mixture of seven rigid conformers, differing only in the value of the dihedral angle τ (see text). In all conformers the $\text{C}_6\text{H}_5\text{N}$ fragment was assumed to be planar; other geometrical constraints were the same as in refinement B.

^c $\Delta_1(\text{C}—\text{C}) = r(\text{C1}—\text{C2}) - r(\text{C2}—\text{C3})$.

^d Assumed.

^e $\Delta_2(\text{C}—\text{C}) = r(\text{C2}—\text{C3}) - r(\text{C3}—\text{C4})$.

^f $\Delta(\text{C}—\text{N}/\text{C}—\text{C}) = r(\text{C1}—\text{N7}) - r(\text{C3}—\text{C4})$.

^g $\Delta(\text{C}—\text{H}/\text{N}—\text{H}) = \langle r(\text{C}—\text{H}) \rangle - r(\text{N}—\text{H})$.

^h Displacement of the nitrogen atom from the ring plane.

ⁱ Dependent parameter.

^j Dihedral angle between the H—N—H plane and the ring plane.

^k $R = (\sum w[I_{\text{obs}} - I_{\text{calc}}]^2 / \sum w I_{\text{obs}}^2)^{1/2}$.

0.1° [1], which we regard as particularly accurate, because the *a* and *b* substitution coordinates of atoms C3, C4, and C5 are well determined. Moreover, it agrees within $\pm 0.2^\circ$ with the values from the MO calculations of Table I.

Treating the present molecule as a mixture of rigid conformers (refinement D) does not cause appreciable changes in the geometrical parameters and does not improve the agreement with the experimental data. This is probably due to the fact that only some of the $\text{C} \cdots \text{H}$ and $\text{H} \cdots \text{H}$ interactions are sensitive to the conformational choice of the model.

For the above reasons we will base our discussion on refinement B. The complete list of molecular parameters from this refinement is reported in Table III, showing also the coupling of the vibrational amplitudes. Note that the least-squares standard deviations in Tables II and III should be considered merely as indicators of *pre-*

cision; they are sometimes unrealistically small due to the constraints. Correlation matrix elements having absolute values greater than 0.5 are given in Table IV; it is comforting that only few of the large number of parameters showed strong correlations among themselves.

In order to check the sensitivity of the electron diffraction intensities to the nonplanarity of the heavy-atom skeleton of the molecule, the displacement of the nitrogen atom from the ring plane, ΔN , was varied stepwise under the conditions of refinement B. It was found that the experimental data could be fitted equally well by a model with a planar heavy-atom skeleton and a model with the nitrogen atom slightly displaced from the ring plane. Displacements varying from 0 to 0.15 Å caused the angle α to decrease from 119.1 to 118.7°, δ from 119.1 to 118.9°, and τ from 46 to 41°, with virtually no effect on the *R* factor and the other molecular parameters.

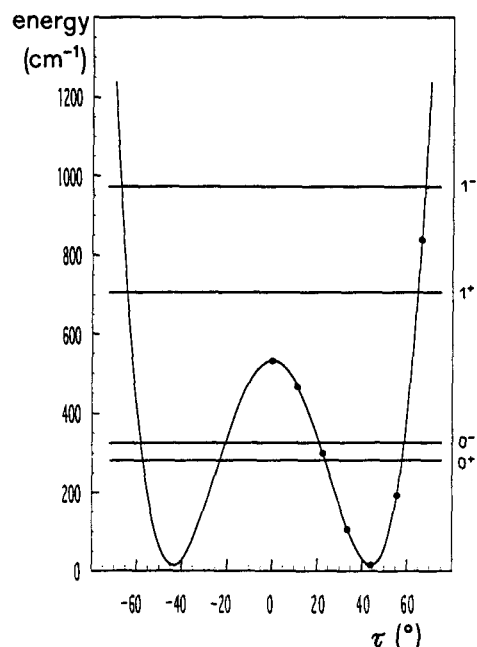


Fig. 5. A plot of the potential energy function for nitrogen inversion in aniline, after Ref. 20. Also shown are the 0^+ , 0^- , 1^+ , and 1^- inversion states. The dots mark the positions of the seven rigid conformers used in refinement D.

RESULTS AND DISCUSSION

The molecular structure of gaseous aniline obtained by electron diffraction using geometrical constraints from MP2/6-31G*(6D) ab initio MO calculations (refinement B) is compared with the structures obtained by microwave spectroscopy [1] and the same MO calculations in Table V.

In-Plane Deformation of the Benzene Ring

The in-plane deformation of the benzene ring caused by the amino group is best seen in the C—C—C angles. They undergo more extensive variation as compared with the C—C distances and are also less affected by systematic errors.

The values of α , γ , and δ from the present electron diffraction study, $119.0 \pm 0.2^\circ$, $120.7 \pm 0.1^\circ$, and $119.0 \pm 0.3^\circ$ respectively, are in excellent agreement with those from the MP2/6-31G*(6D) calculations (see Table V). The values from the microwave study [1] are the same for γ and δ , while α is slightly larger, $119.4 \pm 0.2^\circ$. (Here and throughout this paper total errors are

Table III. Molecular Parameters of Aniline from Electron Diffraction, with Geometrical Constraints from ab Initio MP2/6-31G*(6D) Calculations.^a

Atom pair	Multiplicity	r_a	l		Coupling scheme ^d
			exp.	calc. ^c	
Distances and mean amplitudes of vibration ^b (Å)					
C1—C2	2	1.4016(1)	0.0478(3)	0.045	i
C2—C3	2	1.3933(1) ^e	0.0478	0.045	i
C3—C4	2	1.3955(1) ^e	0.0478	0.045	i
C1—N7	1	1.4057(1) ^e	0.0478	0.045	i
⟨(C—H)⟩	5	1.094(1)	0.075(1)	0.077	ii
N7—H71	2	1.021(1) ^e	0.071	0.073	ii
C1⋯C3	2	2.424(1) ^e	0.0567(4)	0.057	iii
C1⋯C4	1	2.813(3) ^e	0.066(1)	0.062	iv
C2⋯C4	2	2.424(1) ^e	0.0567	0.057	iii
C2⋯C5	2	2.784(2) ^e	0.067	0.063	iv
C2⋯C6	1	2.416(2) ^e	0.0577	0.058	iii
C3⋯C5	1	2.405(1) ^e	0.0567	0.057	iii
N7⋯C2	2	2.437(1) ^e	0.0667	0.064	iii
N7⋯C3	2	3.710(1) ^e	0.068(2)	0.065	v
N7⋯C4	1	4.217(3) ^e	0.068(4)	0.067	vi
C1⋯H2	2	2.165(1) ^e	0.097(3)	0.099	vii
C1⋯H3	2	3.412(1) ^e	0.097(4)	0.097	viii
C1⋯H4	1	3.906(3) ^e	0.098(7)	0.096	ix
C2⋯H3	2	2.155(1) ^e	0.097	0.099	vii
C2⋯H4	2	3.416(1) ^e	0.097	0.097	viii

Table III. Continued.

Atom pair	Multiplicity	r_a	l		Coupling scheme ^d
			exp.	calc. ^c	
C2...H5	2	3.878(2) ^e	0.098	0.096	ix
C2...H6	2	3.409(2) ^e	0.097	0.097	viii
C3...H2	2	2.157(1) ^e	0.097	0.099	vii
C3...H4	2	2.166(1) ^e	0.097	0.099	vii
C3...H5	2	3.398(1) ^e	0.097	0.097	viii
C3...H6	2	3.878(2) ^e	0.098	0.096	ix
C4...H2	2	3.412(1) ^e	0.097	0.097	viii
C4...H3	2	2.157(1) ^e	0.097	0.099	vii
N7...H2	2	2.672(1) ^e	0.131 ^f	0.131	
N7...H3	2	4.589(1) ^e	0.126(18)	0.110	x
N7...H4	1	5.311(3) ^e	0.098 ^g	0.098	
C1...H71	2	2.038(15) ^e	0.108	0.110	vii
C2...H71	2	2.589(18) ^e	0.144 ^f	0.144	
C3...H71	2	3.964(19) ^e	0.147	0.145	ix
C4...H71	2	4.727(20) ^e	0.154	0.138	x
C5...H71	2	4.442(17) ^e	0.144	0.128	x
C6...H71	2	3.276(14) ^e	0.117	0.117	viii

Angles (degrees)

$\angle C2-C1-C6$ (α)	119.01(16)
$\angle C1-C2-C3$ (β)	120.28(10) ^e
$\angle C2-C3-C4$ (γ)	120.69(4) ^e
$\angle C3-C4-C5$ (δ)	119.03(11) ^e
$\angle C2-C1-N7$	120.45(8) ^e
$\angle H71-N7-H72$	109.82 ^g
τ^h	43.6(29)

Differences between bond distances and displacement of the nitrogen atom from the ring plane (\AA)

$\Delta_1(C-C)^i$	0.0083 ^g
$\Delta_2(C-C)^j$	-0.0022 ^g
$\Delta(C-N/C-C)^k$	0.0102 ^g
$\Delta(C-H/N-H)^l$	0.0729 ^g
ΔN^m	0.0715 ^g

^aRefinement B. Least-squares standard deviations are given in parentheses as units in the last digit.

^bThe H...H distances are not shown; they have been given fixed amplitudes of 0.120–0.201 \AA .

^cFrom molecular mechanics calculations (MM3 force field [40]). These were carried out with the 1992 version of the program.

^dThe roman numerals indicate the groups within which the amplitudes were refined with constant differences between them.

^eDependent parameter.

^fAssumed from molecular mechanics calculations.

^gAssumed from ab initio MP2/6-31G*(6D) calculations.

^hDihedral angle between the H–N–H plane and the ring plane.

ⁱ $\Delta_1(C-C) = r(C1-C2) - r(C2-C3)$.

^j $\Delta_2(C-C) = r(C2-C3) - r(C3-C4)$.

^k $\Delta(C-N/C-C) = r(C1-N7) - r(C3-C4)$.

^l $\Delta(C-H/N-H) = \langle r(C-H) \rangle - r(N-H)$.

^mDisplacement of the nitrogen atom from the ring plane.

Table IV. Correlation Matrix Elements with Absolute Values Greater than 0.5.^a

<i>i</i>	<i>j</i>	x_{ij} ($i \neq j$)
r^b	$l(C1 \cdots H2)$	-0.81
r^b	$l(C1 \cdots H3)$	-0.58
$l(N7 \cdots C3)$	$l(C1 \cdots H4)$	0.53
$l(C-C)$	S_{19}^c	0.79

^aFrom refinement B.^bDihedral angle between the H-N-H plane and the ring plane.^cScale factor for the 19-cm data set.

given as error limits. Least-squares standard deviations are given in parentheses as units in the last digit.)

The MP2/6-31G*(6D) calculations indicate that *a* is 0.008 Å longer than *b*, which, in turn, is 0.002 Å

shorter than *c*. These differences are virtually the same as those obtained at the Hartree-Fock level (see Table I). The corresponding differences from the microwave study are 0.003 and 0.002 Å, respectively [1]. These bond length changes are too small to be determined reliably by electron diffraction. Nevertheless, refining $\Delta_1(C-C) = r(C1-C2) - r(C2-C3)$ as an independent variable under the conditions of refinement B leads to a value of 0.011(2) Å, close to the result of the MO calculations.

In conclusion, the results from the present study strongly support the idea that the values of α and $a - b$ obtained for aniline by microwave spectroscopy [1] are not very accurate, due to the small *a* coordinates of atoms C2 and C6.

A comparison of the benzene ring deformation occurring in gaseous and crystalline aniline would be of

Table V. Molecular Geometry of Aniline: Comparison of Experimental and Theoretical Results.^a

Parameter	Microwave spectroscopy [1] ^b	Ab initio MO calculations [MP2/6-31G*(6D) level], present work ^c	Electron diffraction [with constraints from MP2 MO calculations], present work ^d
$r(C1-C2)$ (<i>a</i>)	1.397 ± 0.003	1.401	1.403 ± 0.003
$r(C2-C3)$ (<i>b</i>)	1.394 ± 0.004	1.393	1.395 ^e
$r(C3-C4)$ (<i>c</i>)	1.396 ± 0.002	1.395	1.397 ^e
$r(C-N)$	1.402 ± 0.002	1.405	1.407 ^e
$\langle r(C-H) \rangle$	1.082 ± 0.002	1.088	1.099 ± 0.003
$r(N-H)$	1.001 ± 0.010	1.015	1.026 ^e
$\angle C2-C1-C6$ (α)	119.4 ± 0.2	118.8	119.0 ± 0.2
$\angle C1-C2-C3$ (β)	120.1 ± 0.2	120.5	120.3 ± 0.1
$\angle C2-C3-C4$ (γ)	120.7 ± 0.1	120.6	120.7 ± 0.1
$\angle C3-C4-C5$ (δ)	118.9 ± 0.1	119.1	119.0 ± 0.3
$\angle H-N-H$	113.1 ± 2	109.8	109.8 ^f
τ^g	37.5 ± 2	43.6	44 ± 4
ΔN^h	0 ⁱ	0.072	0.072 ^j

^aBond distances are given in Å, angles in degrees.^bBond distances are r_s values.^cTo facilitate comparison, calculated geometrical parameters are given with the same number of digits as the experimental ones.^dFrom refinement B; bond distances are r_g values. Total errors are given as error limits; they have been calculated according to the expressions [41, 42] $\sigma_T = [2\sigma_{LS}^2 + (0.002r)^2 + (\Delta/2)^2]^{1/2}$ (for bond distances) and $\sigma_T = [2\sigma_{LS}^2 + (\Delta/2)^2]^{1/2}$ (for angles), where σ_{LS} is the least-squares standard deviation, and $\Delta/2$ is the effect of the constraints adopted in the refinement, estimated according to Ref. 41.^eThe differences $r(C1-C2) - r(C2-C3)$, $r(C2-C3) - r(C3-C4)$, $r(C1-N7) - r(C3-C4)$, and $\langle r(C-H) \rangle - r(N-H)$ have been constrained from the ab initio MP2/6-31G*(6D) calculations.^fAssumed from the ab initio MP2/6-31G*(6D) calculations.^gDihedral angle between the H-N-H plane and the ring plane.^hDisplacement of the nitrogen atom from the ring plane.ⁱAssumed.

considerable interest, since the electronic properties of a polar substituent may vary appreciably due to intermolecular hydrogen bonding or dipole-dipole interactions in the solid state [9, 43]. In *p*-diaminobenzene the internal ring angle at the *ipso* position was found to decrease by 2° in going from the free molecule to the crystal molecule [36]. Unfortunately the X-ray crystallographic study of aniline [5] is not accurate enough to allow a reliable comparison with the present results. The experiment was carried out at 252 K, which is only 15 K below the melting point of aniline. This has resulted in a low observations-to-parameters ratio ($834/183 = 4.56$), a relatively high *R* factor (0.063), and high standard deviations for the C—C bond distances (0.006–0.007 Å) and C—C—C angles (0.4–0.5°). Nevertheless, the values of α for the two crystallographically independent molecules in the asymmetric unit are both 117.9(4)°, which is about 1° less than the value obtained here for the free molecule. Although the difference is hardly significant, it may reflect an increase in π donation from the substituent to the ring [44] in going from the free molecule to the crystal molecule. This could be a consequence of intermolecular hydrogen bonding in the solid state [9, 43], as in the cases of *p*-diaminobenzene [36], phenol [15], and other hydroxybenzenes [45].

Accurate structural information from solid-state studies is available for a molecular fragment closely related to aniline, C_6H_5-NHX ($X = C, N$). A survey of several molecules containing this fragment, all studied by X-ray crystallography, yields the following mean angles: $\langle\alpha\rangle = 119.1(2)^\circ$, $\langle\beta\rangle = 120.0(1)^\circ$, $\langle\gamma\rangle = 120.9(1)^\circ$, and $\langle\delta\rangle = 119.1(1)^\circ$ [44]. They are similar to the present experimental results. Hydrogen bonding patterns in the crystals of these molecules are, of course, different from those occurring in crystalline aniline [5] and *p*-diaminobenzene [36].

The mean length of the ring C—C bonds from electron diffraction, $\langle r_g(C-C) \rangle = 1.398 \pm 0.003$ Å, is virtually the same as in unsubstituted benzene, 1.399 ± 0.003 Å [46]. The difference from the value obtained by MO calculations at the Hartree-Fock level of theory, 1.387 Å [6-31G*(6D) basis set], may originate from several sources, such as the inherent difference in physical meaning (r_g versus r_e), basis set limitations, and neglect of electron correlation. Correction for the latter at the MP2 level yields $\langle r_e(C-C) \rangle = 1.396$ Å; this coincides with the value of $\langle r_s(C-C) \rangle$ from the microwave study [1]. The distance type r_s obtained by the substitution method [47] of microwave spectroscopy is considered to be very close to r_e . Differences

$\langle r_g(C-C) \rangle - \langle r_s(C-C) \rangle$ ranging from 0.004 to 0.008 Å have been obtained for fluorobenzene [13], cyanobenzene [14], nitrobenzene [7], phenol [15], and ethynylbenzene [8]; the value for aniline is 0.002 Å. Such differences are reasonable for a relatively rigid system like benzene.

The MO calculations indicate a 0.001 Å decrease of $r(C-H)$ at each step in going from C2—H2 to C3—H3 and to C4—H4, see Table I. These are much smaller changes than the experimental errors from the microwave study, 0.002–0.004 Å [1]. The MO calculations also show that the C2—H2 and C3—H3 bonds are bent toward the substituent by *ca.* 0.5 and 0.8°, respectively. This finding is consistent with the corresponding angular differences from the microwave study [1].

Out-of-Plane Deformation of the Benzene Ring

The benzene ring of aniline is expected to show some deviation from planarity, due to the shape and symmetry of the amino group in its equilibrium geometry. This deviation, however, is too small to be detected by electron diffraction or even by microwave spectroscopy, though it shows up in the MO calculations. Relaxation of the planarity constraint for the C_6H_5N fragment at the HF/6-31G*(5D) level [3] causes the total energy to decrease by only 0.3 kJ mol^{−1}, and gives rise to minute deviations from planarity of the ring atoms, of the same type as those reported [48] for the orthogonal conformers of toluene, ethylbenzene, styrene, nitrosobenzene, benzaldehyde, and phenol, with the benzene ring adopting a very shallow boat-type conformation. A similar distortion is obtained here from the MO calculations at the HF/6-31G*(6D) level (see Table I). Note that the displacement of the nitrogen atom from the least-squares plane of the ring is much more pronounced than those of the ring carbons.

However, correction for electron correlation at the MP2 level of theory gives rise to a totally different pattern of deviations from planarity of the ring carbons, while increasing the nitrogen displacement from the ring plane (see Table I). This casts serious doubts on the suitability of *ab initio* MO calculations, at the accessible levels of theory, to provide information on the out-of-plane deformation of the ring in benzene derivatives. As no experimental support is attainable from gas-phase studies, and the available X-ray diffraction results [5] are inadequate for this purpose, an accurate, low-temperature neutron crystallographic study of aniline would be highly desirable. The results of such a study, how-

ever, would suffer from possible intermolecular interactions, as the intramolecular driving forces leading to deviations from planarity are weak.

The C—N Bond

Some uncertainty remains as to the actual extent of the bend of the C—N bond from the ring plane. The MO calculations at the HF/6-31G*(6D) level of theory indicate that the nitrogen displacement from the ring plane amounts to 0.0487 Å; this increases to 0.0715 Å upon correction for electron correlation (MP2 level). Both values are considerably smaller than those reported for crystalline aniline, 0.113(4) and 0.122(3) Å for the two crystallographically independent molecules in the asymmetric unit [5]. Note, however, that displacements of 0.066–0.086 Å have been found in crystalline *p*-diaminobenzene from an accurate X-ray diffraction study [36]. This points to the fact that the nitrogen displacement is a relatively “soft” parameter, which may easily be perturbed by weak intermolecular hydrogen bonds and/or van der Waals interactions in the solid state.

The difference $\Delta(\text{C—N/C—C}) = r(\text{C1—N7}) - r(\text{C3—C4})$ is 0.006 Å from the microwave study [1] and 0.010 Å from the MP2/6-31G*(6D) calculations. As the microwave study assumed a planar $\text{C}_6\text{H}_5\text{N}$ fragment, but the *a* and *b* substitution coordinates of atoms N7, C1, C3, and C4 are otherwise well determined, the former value is felt to be slightly underestimated. The C—N bond length from the present electron diffraction study, $r_g(\text{C—N}) = 1.407 \pm 0.003$ Å, was obtained by fixing $\Delta(\text{C—N/C—C})$ at 0.010 Å. The same result was obtained when $\Delta(\text{C—N/C—C})$ was refined as an independent variable under the conditions of refinement B. The corresponding bond length from the microwave study, $r_s(\text{C—N}) = 1.402 \pm 0.002$ Å [1], is slightly smaller, as expected.

The C—N bond length (r_g) obtained by gas-phase electron diffraction in aliphatic amines is substantially larger than in aniline. For instance, it is 1.472 ± 0.003 Å in methylamine [49] and $1.470/1.475 \pm 0.010$ Å in the *trans* and *gauche* conformers of ethylamine [50]. This points to the importance of π donation from the substituent to the ring in determining the molecular structure of aniline.

In gaseous *p*-diaminobenzene $r_g(\text{C—N})$ is 1.424 ± 0.005 Å [36]. The difference from aniline is significant, and reflects a less pronounced interaction between the nitrogen lone pair and the π system of the ring in the *para*-disubstituted derivative. This is consistent with the fact that the *ipso* angle is practically undistorted in

p-diaminobenzene, $119.8 \pm 0.2^\circ$ [36]. Simple additivity of the structural impacts of the two amino groups would predict a 118.0° *ipso* angle; the larger experimental value denotes a less pronounced π donation from the substituent to the ring [44].

Pyramidalization of the Amino Group

The microwave study yielded $37.5 \pm 2^\circ$ for the dihedral angle τ , which was only a rough estimate of the equilibrium angle [1]. It is difficult to locate hydrogen atoms involved in large-amplitude, highly anharmonic internal motions, such as the inversion of the amino group in aniline. The assumption that deuterium atoms adopt the same positions in the amino group as do hydrogen atoms is a rather crude approximation. Moreover, the *c* coordinates of these atoms are small, *ca.* 0.3 Å, and thus inherently difficult to determine by the substitution method. Roussy and Nonat [21] reanalyzed the microwave data of Ref. 1, by explicitly treating the anharmonicity of the inversion motion and including the effective rotational constants for the first two inversion states, 0^+ and 0^- . They obtained $\tau_e = 42.4 \pm 0.3^\circ$, in agreement with the values obtained by resonance fluorescence spectroscopy, 42° [18], and far-infrared spectroscopy, $42 \pm 1^\circ$ [19]. A slightly larger value, $44.30(16)^\circ$, was obtained [20] from a semirigid bender analysis of the far-infrared data of Ref. 22. In this analysis the C—N bond was assumed to lengthen with increasing τ according to a quadratic law. Inclusion of nonrigidity for the C—N bond has been found important for a correct description of the nitrogen inversion motion in vinylamine [51], cyanamide [52], and formamide [53].

The present MO calculations yield $\tau_e = 41.8^\circ$ at the HF/6-31G*(6D) level of theory, and 43.6° upon correction for electron correlation (MP2 level). This is very close to the result from the semirigid bender analysis mentioned above [20].

The dihedral angle determined by electron diffraction, $44 \pm 4^\circ$ from refinement B, is an effective angle, $\langle |\tau| \rangle$, averaged over the large-amplitude inversion motion of the amino group at the temperature of the electron diffraction experiment. It is different, in principle, from the equilibrium dihedral angle τ_e .

CONCLUSIONS

The present study provides conclusive evidence on the in-plane deformation of the benzene ring caused by

the amino group in free aniline. Considering also the results of previous investigations [1, 3–5, 19–21], the following features appear characteristic:

(i) The C1–C2 bond is 0.008–0.009 Å longer than the C2–C3 bond.

(ii) The C2–C3 bond is about 0.002 Å shorter than the C3–C4 bond.

(iii) The $\langle r_g(\text{C}—\text{C}) \rangle$ and $r_g(\text{C}—\text{N})$ distances are 1.398 ± 0.003 Å and 1.407 ± 0.003 Å, respectively.

(iv) The C2–C1–C6 and C2–C3–C4 angles are $119.0 \pm 0.2^\circ$ and $120.7 \pm 0.1^\circ$, respectively.

(v) The C3–C4–C5 angle is unlikely to differ from 118.9° by more than 0.2° .

(vi) The equilibrium dihedral angle between the plane of the amino group and the ring plane is close to 44° .

With regard to the out-of-plane deformation of the heavy-atom skeleton, the nitrogen atom is displaced from the ring plane, on the side opposite to the amino hydrogens. The extent of the displacement is estimated to be in the range 0.07–0.11 Å.

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SUPPLEMENTARY MATERIAL AVAILABLE

A listing of total electron diffraction intensities of aniline for two camera distances (four pages) is available from the authors upon request.

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