Non-Empirical Calculations and Basis Set Effects on the Inversion Geometry of the Aniline Molecule*

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The geometry of the amine group and the barrier to internal conversion in aniline have been studied by single-determinant *ab initio* SCF calculations using several basis sets from minimal to double-zeta quality. The results obtained from different types and sizes of basis sets are discussed. Calculations performed with the two most flexible basis sets yield inversion barriers of 0.9–1.1 kcal/mole and angles of pyramidalization at the nitrogen atom of 38–39° which are in good agreement with the experimental results (1.3 kcal/mole and 38°). Orbital and overlap population analyses are performed and compared with the expected mesomeric and inductive effect. The calculated dipole moment 1.48–1.49 D also agrees with the experimental values (1.48–1.50 D).

Key words: Aniline molecule, inversion geometry of ~

1. Introduction

In 1966 the non-planarity of the aniline molecule was experimentally confirmed. On the basis of microwave data [1] a pyramidal bond geometry around the nitrogen atom was obtained with an angle of pyramidalization, ϕ, between the bisector of the HNH angle and the extension of the phenyl-nitrogen bond (Fig. 1) of 38°. Ultra-violet absorption studies supplied an angle of $\phi = 46°$ [2]. From resonance fluorescence investigations, Quack and Stockburger [3] calculated $\phi = 42°$ and obtained an estimate of 1.3 kcal/mole for the barrier of internal conversion. These authors used a simple harmonic oscillator model which was perturbed by a
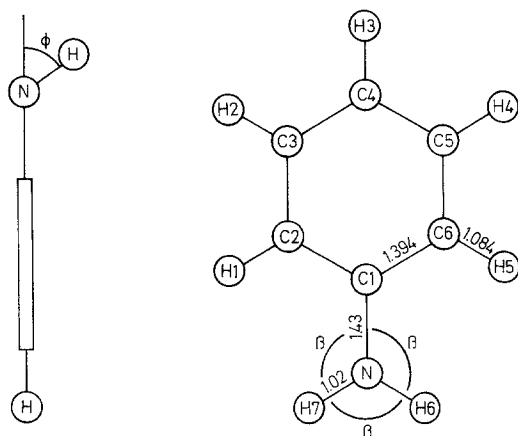

Fig. 1. Definitions of atoms and angles

Gaussian barrier potential function and calculated their results by comparing the energy levels with the assigned band peaks. More recently, the angle of pyramidalization was determined from a refined microwave study to be 37.5° [4].

Also various theoretical studies on different levels of approximation have been carried out for the purpose of determining the geometry of the amine group of aniline and of para-substituted anilines. In particular, for *p*-aminopyridines and their *N*-alkyl derivatives, *ab initio* calculations have been reported [5]. For aniline, Pople and his co-workers [6, 7] obtained from a STO-3G calculation an angle of $\phi = 47.7°$, Strametz and Schmidtke [8] calculated with the INDO method $\phi = 38°$, and Parr and Wasylishen [9] reported $\phi = 10°$ from a MINDO/3 calculation which is by far too small.

In view of the different quality of the results obtained from various methods, it was decided to look into the geometry problem of aniline by performing some non-empirical calculations improving the level of approximation to a certain extent. Since the results of *ab initio* calculations essentially depend on the choice and on the size of the basis set used, it is also intended to look into some of the interrelations between basis sets and calculated molecular properties.

2. Details of Calculation

For calculations with minimal STO-3G basis sets a CDC Cyber 76 version of GAUSSIAN 70 has been used [10]. All other calculations were performed using the PHANTOMBIG 76 system of programs which is a CDC Cyber 76 version of PHANTOM 72 [11], modified to handle generalized contraction schemes. Maximum core storage requirements were 10 K words high-speed SCM and 40 K words LCM, both 60 bits word-length.

2.1. Molecular Geometry

The phenyl ring is considered as a regular hexagon. The bond lengths are fixed at C—C: 1.394 Å, C—H: 1.084 Å, C—N: 1.43 Å, and N—H: 1.02 Å which are

average values of Sutton's interatomic distances [12, 13]. The values differ only slightly from those given by other authors; any differences are not expected to affect the results on the energy and geometry appreciably. When a pure pyramidal hybridization at the nitrogen atom (equal bond lengths and face angles) is assumed the angle of pyramidalization is interrelated to the HNH bond angle β (cf. Fig. 1) by

$$\operatorname{tg} \phi = \cos\left(\frac{\beta}{2}\right) \cdot \sqrt{\operatorname{tg}^2 \beta - \operatorname{tg}^2\left(\frac{\beta}{2}\right)}.$$

From ϕ and β the dihedral angle ϑ, which is necessary when using the Z-matrix method [14] for the geometry computation, is given by

$$\operatorname{tg} \vartheta = \operatorname{ctg}\left(\frac{\beta}{2}\right) \sin \phi.$$

In the calculation the angle ϕ was varied in the range between $0°$ and $90°$.

2.2. Basis Sets

The calculation was started by using the minimal STO-3G basis set [15] which then was relaxed step by step: at first, only the coefficient of the primitive Gaussian with the smallest exponent was varied freely during the SCF procedure (STO-$(2 + 1)$G), later all primitives were allowed to vary independently (STO-$(1 + 1 + 1)$G). In addition two other minimal [2.1/1] basis sets were used, i.e. a $(9.5/6)$ set of Huzinaga [16] (from now on denoted by Huzinaga I) and a $(7.3/3)$ set of Whitman and Hornback [17]. However, it turned out that the results calculated for aniline from these two basis sets do not differ significantly. Finally also a [5.2/2] double-zeta contraction of Huzinaga's $(11.7/4)$ basis set [18] was investigated (denoted by Huzinaga II) which was the largest set used in the present study.

All six basis sets were tested by carrying out an open shell OCBSE calculation [19] on the ^3P ground state of the carbon atom. The results are listed in Table 1 and compared with the best single-zeta STO- [20], the best double-zeta STO-calculation

Table 1. Comparison of basis sets (^3P, carbon atom)

Basis set	E (a.u.)	$-V/T$
STO-3G	-37.228393	1.98085
STO-$(2 + 1)$G	-37.250708	2.02985
STO-$(1 + 1 + 1)$G	-37.268724	2.02532
Whitman + Hornback	-37.610192	2.01449
best single-zeta STO calc. [20]	-37.622389	
Huzinaga I	-37.646144	1.97986
best double-zeta STO calc. [21]	-37.686751	
Huzinaga II	-37.687240	1.99947
Hartree–Fock limit [21]	-37.688616	

[21] and also with the Hartree–Fock limit [21]. For all STO-3G contractions the total energies differ considerably from the Hartree–Fock limit. They are also by 0.35 a.u. (atomic units) higher than the best single-zeta STO result. On the other hand the energy calculated from the Huzinaga I basis set is superior to that computed with the single-zeta STO set; finally it is noticed that the Huzinaga II contraction yields a slight improvement upon the best double-zeta STO basis set and approaches the Hartree–Fock limit up to only 0.0014 a.u.

The quality of the basis sets obtained for the total energies of atoms is considered to be of comparable rank with regard to the energies of molecules. Generally it is assumed that if the basis set is flexible enough, also other molecular properties, as e.g. geometry, barriers, dipole moments, can be computed by the same standard of quality.

2.3. Integral and SCF Calculations

Integral evaluation was carried out using the BIGMOL I [22] package for generalized contractions of primitive basis functions, which was modified by incorporating the Dacre–Elder procedure [23, 24]. By this, only symmetry-unique (nonredundant) integrals were generated and processed, taking full advantage of the molecular point symmetry C_{2v}. Since the number of integrals increases roughly by the fourth power of the number of basis functions, some effort must be made in order to reduce the computational expense which is connected with large scale basis sets. This was achieved from taking two measures: 1) increasing the integral cut-off value for large basis sets (Huzinaga II and totally relaxed STO-G) from 10^{-9} to 10^{-6} a.u. by which only integrals larger than 10^{-6} a.u. in absolute value are considered in the integral file. This reduces the number of integrals to be saved by approximately 40%. Test calculations performed with cut-off values down to 10^{-12} a.u. showed that the accuracy of total energies is not affected appreciably, i.e. energies calculated from integral cut-off values of 10^{-6} a.u. are exact within 6 significant figures; 2) all two-electron integrals, which do not depend on the angle ϕ, i.e. those which contain only functions centered on the atoms $C_1, C_2, \ldots, C_6$, N, $H_1, H_2, \ldots, H_5$ (Fig. 1), are calculated only once. All integrals which involve functions on H_6 and/or H_7 have to be calculated for each point of the potential energy curve. By this procedure a substantial amount of CPU time was saved, since more than 80% of the integrals remain constant on geometry variation.

The convergence threshold for the total energy was set equal to 10^{-8} a.u. Oscillations of SCF energy were avoided by averaging corresponding elements of the first order density matrix over successive iterations until total energies differed by less than 10^{-4} a.u. The optimal convergence rate was achieved by a weighting factor of 0.6 for the new density matrix. With this averaging factor, self-consistency was reached after less than 45 iterations.

3. Results and Discussion

Molecular equilibrium geometry, in general, is obtained by an independent and simultaneous variation of all atomic coordinates. This procedure, however, cannot

be carried out if the total energy is calculated by time-consuming non-empirical methods. Since, at present, we are primarily interested in the inversion geometry, which determines the properties connected with the non-planarity of the aniline molecule, only those internal coordinates are varied which involve the nitrogen atom. For simplicity the bond geometry at nitrogen in the non-planar molecule is assumed to form a regular pyramid. Under this condition the angle of pyramidalization, ϕ, and the HNH bond angle β are interrelated according to the formula given above. Since all other molecular parameters – as bond lengths at the nitrogen atom and all bond lengths and bond angles of the phenyl ring – are kept constant pertaining to experimental values [12, 13], the total energies for any of the present calculations are obtained as a function of ϕ only.

The results obtained for the different basis sets are compiled in Fig. 2. Since the minimal energies at the equilibrium configurations differ rather strongly for each basis set, the energy scale is plotted within various portions of ranges. In all cases the energy increases rapidly if ϕ exceeds the value of 60°. Absolute data may be compared from Table 2 in which the energies of aniline are listed as calculated from different basis sets for planar and equilibrium configuration. Due to the limited number of configurations which could be calculated and in view of the fact that the energy differences (between two large numbers) are very small $(7 \cdot 10^{-4}$ a.u.), the accuracy obtained for the equilibrium geometry is not too high. The errors estimated from the width of the curve minima are about $\pm 1°$ for the pyramidalization angle and ± 0.1 kcal/mole for the barriers to inversion. A com-
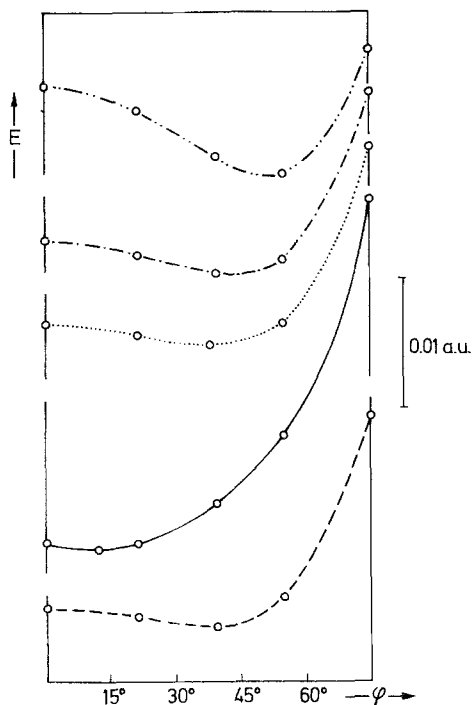

Fig. 2. Potential energies for different basis set calculations. Actually calculated geometry configurations are indicated. —··— STO-3G, —·— STO-(2 + 1)G, ··· STO-(1 + 1 + 1)G, —— Huzinaga I (and very similar Whitman and Hornback), — — Huzinaga II

Table 2. Total energies of the planar and equilibrium configuration of aniline

Basis set	E_{pl} (a.u.)	E_{eq} (a.u.)	ϕ_{eq}	β_{eq}	E(kcal/mole)
STO-3G	−282.204735	−282.211623	51	114.42	4.3
STO-(2 + 1)G	−282.481864	−282.484502	44	114.83	1.7
STO-(1 + 1 + 1)G	−282.618532	−282.620221	38	115.05	1.1
Whitman + Hornback	−284.673169	−284.673241	8	119.94	0.3
Huzinaga I	−284.991258	−284.991414	12	119.87	0.6
Huzinaga II	−285.636286	−285.637643	39	115.05	0.9
exp. [3, 4]			38	115.05	∼1.3

parison with the actual curve as derived from spectroscopical data [3] is not possible for the same reason of accuracy. The ρ-parameter, which determines the shape of the curve in the potential model, varies only very slightly with the spectroscopic constants and, therefore, is obtained from the spectrum only very inaccurately [25].

Our result calculated for the equilibrium geometry from the minimal STO-3G basis set differs from that of Pople and co-authors [6] who obtained for the same basis, $\phi = 47.7°$; $E = -282.20892$. However, for planar aniline our total energy is identical with Pople's result within six significant figures. The disagreement for the equilibrium case is probably caused by different techniques used for the geometry optimization. Unfortunately the optimization procedure is not explained in Pople's work. If an interpolation method was used it is certainly inferior to a pointwise calculation of the potential curve as has been performed in the present work. Still, by a correct STO-3G calculation the angle ϕ is computed by a value of 13° too large. This obviously results from a basis set effect, since the error vanishes as the basis set is successively relaxed. The observation that bond angles, β, are calculated too small (i.e. the inversion angle too large) on the STO-3G level was already noticed by Bell [26], who performed a systematic study of basis set effects on small molecules. The minimal STO-3G basis set overestimates the inversion barrier by even more than 200%. On basis set relaxation by lifting the degree of contraction, the barrier height is decreased considerably. This apparently is due to the more flexible basis set which allows for a better redistribution of electron density when varying the molecular configuration. This conclusion is supported by the population analysis, which will be discussed later when comparing different basis sets.

The two minimal basis sets of Huzinaga I and Whitman and Hornback calculate the inversion angles by 30° too small, and the barrier to internal rotation is obtained 50–60% too low. These results are rather poor, they cannot be explained in a straightforward way; both basis sets have a larger number of primitive Gaussian type functions per atomic orbital than Pople's STO-3G contraction does. The latter basis set reproduces the molecular geometry better although the total energy is by far inferior to the Huzinaga I and Whitman–Hornback results. This is surprising when it is recalled that the basis sets of Huzinaga I and Whitman and Hornback in earlier calculations have proved to be rather successful for obtaining

satisfactory potential surfaces appropriate to rotations around a single bond (molecular conformations) [27]. Apparently, minimum basis sets as STO-3G, computed from least-square fits to Slater orbitals, are able to reproduce molecular equilibrium configurations more efficiently than energy-optimized orbitals, as basis sets like, e.g., Huzinaga I. The calculated angles of pyramidalization and barriers of internal conversion from the Huzinaga II double-zeta contraction and from the STO-(1 + 1 + 1)G basis set are closely similar, although the absolute values of total energies vary by more than 3 a.u., i.e. 1900 kcal/mole. From the test calculations obtained for the carbon atom it can be estimated that the Huzinaga II total energy for aniline differs from the Hartree–Fock limit by only less than 0.1 a.u.

A Mulliken orbital and overlap population analysis [28] was performed from the molecular orbital coefficients of the minimal STO-3G, STO-(1 + 1 + 1)G, and Huzinaga II basis set calculations. In these computations only contributions to overlap populations are taken into account, which result from atomic centers at distances less than 10 a.u. apart. The numbers obtained for two of these calculations are presented in Fig. 3.

For all basis sets used, the charge distributions show negative charges on carbon atoms, and in *ortho* and *para* positions they are increased compared to the benzene molecule. This is in accordance with the *ortho* and *para* directing power of the amine group for electrophilic substitution known from the experiment. The negative charges are calculated larger for the *ortho* than for the *para* position. The increased negative charges on these carbon atoms can be attributed to the mesomeric (+M)-effect due to the non-bonding electrons in the amine group. The electron density on the carbon atom attached to the amine group is lowered by the inductive (−I)-effect in such a way that a positive net charge results. Similar shifts of electron density are observed for the two hydrogen atoms bonded to the amine group which in fact can be understood in terms of electronegativity differences between nitrogen and hydrogen or carbon. The magnitude of these effects depends on the degree of pyramidalization: comparing the results for planar and equilibrium configuration it is noticed that the mesomeric effect becomes smaller for all calculations when the inversion angle, ϕ, is increased. Contrary to what is expected for the inductive effect, a decreased induction is calculated from all contractions of the STO-3G basis set if the molecule is varied to non-planar geometry. Only the Huzinaga II set supplies the correct description of a simultaneous increase of the inductive and decrease of the mesomeric effect. For the choice of the basis set it must be concluded that, apart from the degree of relaxation, also the number of primitive Gaussians contained in the basis set is important for computing electron redistribution effects correctly. In this respect, the Huzinaga II set is superior to the totally relaxed STO-(1 + 1 + 1)G basis set. It is further noticed that the gross atomic populations on H_1, H_2, . . ., H_5 and C_3, C_5 are only subject to smaller changes.

These results, which vary only slightly with each of the basis sets investigated, reflect the usual concept of charge distribution rearrangement in substituted
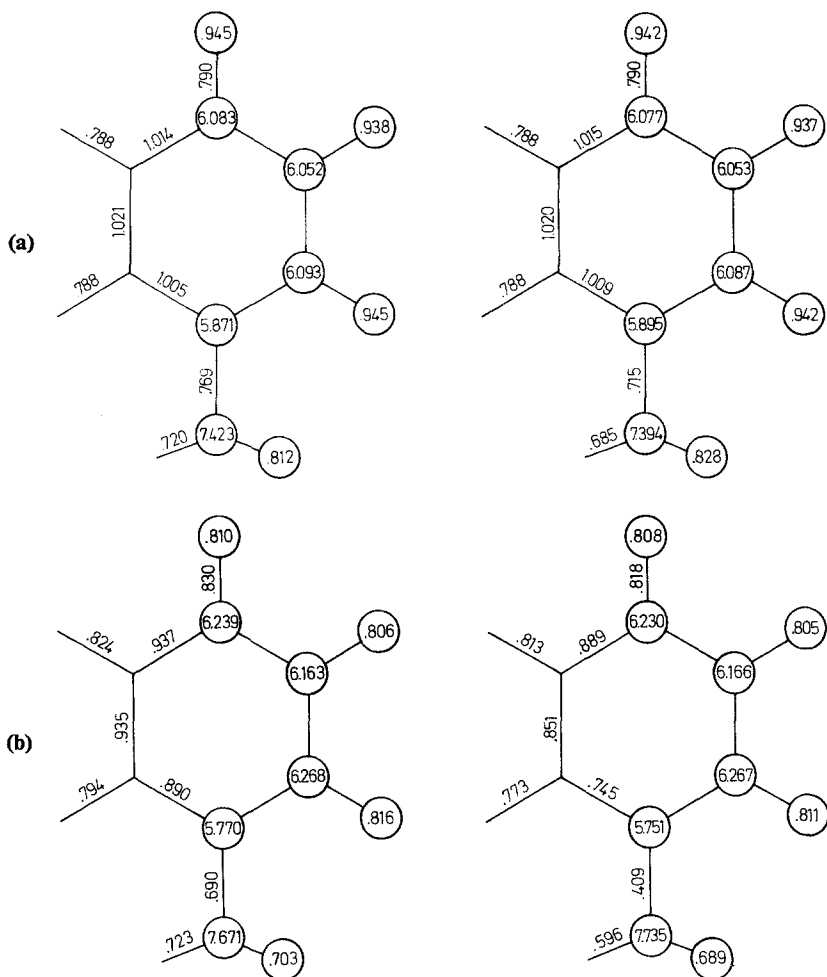
Fig. 3. Mulliken orbital and overlap population analysis from (a) STO-(1 + 1 + 1)G and (b) Huzinaga II basis set calculations

aromatic molecules. If the data obtained for different basis sets are compared with atomic charges calculated for benzene, it is noticed that both the mesomeric and inductive effects are more pronounced in the Huzinaga II basis set, they are decreased for the STO-(1 + 1 + 1)G set and have the smallest effect in the STO-3G basis set calculation. These findings confirm the statement made above that molecular properties can only be expected to be calculated well enough if the basis set of a certain size has sufficient flexibility.

Finally, expectation values for dipole moments are calculated from wave functions as obtained from the STO-3G, STO-(1 + 1 + 1)G, and Huzinaga II basis sets. Table 3 shows that good agreement with the experiment is obtained for all basis sets. The experimental results in inert solvents differ from 1.48 to 1.50 D [29]. The negative pole of the moment is calculated to be located on the amine group. This

Table 3. Dipole moments of aniline in Debye

Basis set	Planar $|\mu|[D]$	Pyramidal configuration				
		μ_x	μ_y	μ_z	$|\mu|[D]$	ϕ
STO-3G	1.15	0.0	0.244	1.456	1.48	51°
STO-(1 + 1 + 1)G	1.34	0.0	0.829	1.221	1.48	38°
Huzinaga II	1.35	0.0	0.726	1.301	1.49	39°
exp. [29]					1.48–1.50	

is in accordance with the population analysis which supplies a negative charge on the amine group of approximately $0.1e$ (elementary charge units). The absolute value of dipole moment increases from planar to pyramidal configuration, the corresponding vector moving out of plane (Table 3).

Other expectation values, e.g. quadrupole moments, electric field gradients, $\langle 1/r \rangle$, etc., have not been calculated since reliable results for these one-electron properties can only be expected if polarization functions are included in the basis set [30]. This would increase the number of basis functions for a molecule of the present size to an extent which cannot be handled with a reasonable amount of computer-time. Due to the lack of experimental results a comparison of these data would not be possible anyway. However, it should be stated that from *ab initio* calculations such close agreements, for a variety of experimental details, have not been obtained yet for molecules of the present size.

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