

# Ab Initio Calculation of Amine Out-of-Plane Angles

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Fully optimized geometries are computed at the Hartree–Fock level for formamide and methylamine with basis sets ranging up to ones that are triple-zeta plus two sets of polarization functions in the valence shell. The effect of very diffuse *s* and *p* functions is also examined. The relation of basis set size and composition to the computed amino group out-of-plane angle and to the related localized molecular orbitals is systematically investigated and compared with scattered results previously reported for other systems. It is concluded that the amino group angle is the result of a delicate balance between lone pair character of the nitrogen electrons and delocalization of these electrons into other portions of the molecule. Polarization functions in the nitrogen basis set are necessary to provide for proper description of the lone pair character, but even in methylamine the delocalization is not properly described without an extensive basis set, either polarization functions or very diffuse *s* and *p* functions, on the other heavy atoms. The effect is extreme for molecules such as formamide, aniline, and  $\text{PF}_2\text{NH}_2$ , where very large basis sets are required to obtain the correct out-of-plane angle.

## INTRODUCTION

The use of *ab initio* molecular orbital calculations at the double-zeta or larger Hartree–Fock level has become well established as a convenient and reliable method for determining molecular structures with high accuracy. The simple method has limitations, of course, including such restrictive requirements as limitation to molecules containing atoms in the upper half of the periodic chart and restriction to molecules having a stable electronic state well separated in energy from excited states so that single determinant calculations are applicable. Nevertheless, a large fraction of molecules of chemical interest falls within the scope of applicability of this technique.

As a generalization it may be said that *angles* around the few lightest elements, including the vitally important element carbon, are reproduced with a simple double-zeta basis set (or the essentially equivalent 4-21, 3-21, or 4-31 split valence sets) with an accuracy comparable to the best values normally obtainable by high-quality experiments.

Basis set convergence has been reached at this modest level, and neglect of electron correlation produces negligible effect as far as can be told by comparison with experiment. The situation with bond *lengths* is somewhat different since computed bond lengths change (normally shorten) as the basis set is enlarged beyond the double-zeta level and are slightly shorter than the experimental values when the infinite basis set Hartree–Fock limit is reached. This, of course, indicates a significant contribution of electron correlation to the bond lengths. Nevertheless, it is found that at the double-zeta level both the infinite basis set effect and the effect of neglect of electron correlation are highly reproducible for a given type of chemical bond.<sup>1,2</sup> As a practical matter, then, a predetermined corrective offset value can be added to a computed bond length for these elements to obtain a very reliable estimation of the correct equilibrium bond length.<sup>3,4</sup>

Angles around atoms having lone pairs of electrons, such as nitrogen, oxygen, and the corresponding elements in the second period, are not given accurately by calculations at the double-zeta level. Computed *bond angles* around these elements, however, may be routinely corrected with small offset values,<sup>1,2</sup> exactly as is done for bond lengths, giving

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highly accurate results. *Dihedral angles* around such atoms are less predictable and are sometimes in quite poor agreement with experiment. Until the present time, however, it has normally been observed that angles around such atoms are computed to be more nearly linear (or more nearly planar) than the observed angles, the error decreasing monotonically as the basis set is enlarged, particularly as more polarization functions are added to the central atom.<sup>5</sup> All evidence indicates that the computed angle approaches the true angle as the basis set approaches the Hartree–Fock limit.

A single case has recently been examined where the above simple generalization does not prevail.<sup>6</sup> Aniline has an angle of  $37.5^\circ \pm 2.0^\circ$  between the plane of the amino group and the ring plane, as determined by a careful microwave spectroscopic study.<sup>7</sup> As optimized with a 4-21 basis set, however, the entire molecule is planar.<sup>8</sup> This is the direction of error to be expected by omission of polarization functions in the nitrogen basis set. Addition of a single set of *d* functions to the basis set of the nitrogen atom leads to an optimized amino group out-of-plane angle of  $52.0^\circ$ .<sup>6</sup> Significantly, this value has overshoot the experimental angle rather than converging toward it. Addition of a second set of *d* functions to the nitrogen atom makes matters worse, and addition of polarization functions to the ring carbon atoms does not lead to much improvement. It was suggested<sup>6</sup> the problem arises from the very delicate balance between the effect of nitrogen atom polarization functions being required to reproduce the nonplanarity at that atom while simultaneously being capable of giving too great localization of the electrons in the lone pair rather than allowing a proper description of the degree of delocalization into the aromatic ring.

We have now undertaken a further investigation of the effect of basis set size and composition on the ability of Hartree–Fock calculations to give correct values for out-of-plane angles around a nitrogen atom, using smaller molecules than aniline so that quite large basis sets can be tested. We have chosen methylamine as an illustration of a reasonable isolated amino group and formamide as typical of cases where extensive delocalization of electron density from the lone pair to

other parts of the molecule can be anticipated. We also make comparison with other published computations, although caution must be exercised with such previous results since great care must be taken to assure that the out-of-plane angle is really optimized. If the criterion for energy optimization is only that very small forces remain, those small forces may still be sufficient to produce significant alteration of the highly flexible out-of-plane angle. Changes of the magnitude and algebraic sign of those angles must also be carefully noted.

There are, of course, a number of previous computational studies of both formamide and methylamine as well as of related molecules. Unpublished evaluations of molecular geometry have been made by Pople's group at the 6-31G\* and lower levels, but there has been no systematic study of the effect of increasing the basis size with particular reference to the correct evaluation of the amine out-of-plane angle. Radom and co-workers have studied the structure of a variety of amines and have produced the best studies to date of the structure of the equilibrium state of formamide<sup>9</sup> and of its transition state.<sup>10</sup> The geometry was optimized with a double-zeta basis set augmented with *d* functions with the molecule constrained to be planar, following which the amine group angles were relaxed with no further change permitted in the remaining geometric parameters. This partial geometry optimization produced a very slightly nonplanar structure with an energy difference of only 0.03 kcal/mol from the planar conformation. It is difficult to know how much faith should be put in the exact out-of-plane angles obtained since complete geometry optimization could be significant when the energy difference is so very small.

Admittedly, the calculation of geometrical features that have only a small effect on the molecular energy, such as amino group out-of-plane angles, ring-puckering angles, and internal rotation angles, is very difficult by a procedure that is based on energy minimization. Nevertheless, the rapidly expanding use of *ab initio* calculations of molecular geometry, both for their own sake and for use as a supplement to experiment, makes it important to explore the boundaries of the region of applicability of such techniques.

## METHOD OF CALCULATION

All calculations were made with the *ab initio* gradient program TEXAS<sup>11</sup> with analytical determination of energy first derivatives using the method of Pulay<sup>12,13</sup> and geometry optimization facilitated by the GDIIS technique.<sup>14,15</sup> The basis sets used were the 4-21 set,<sup>1</sup> which is double zeta in the valence shell, the 6-311G\*\* set,<sup>16</sup> which is triple-zeta in the valence shell and includes polarization functions on all atoms, and various modifications and extensions of these as described below.

Particular attention was paid to the thoroughness of the geometry optimization since, as discussed above, appreciable changes in the amino group out-of-plane angle result in only small energy changes and consequently only small residual forces. Also, this motion is strongly coupled with the C—N bond stretching motion and with rotation around the C—N bond when this is not restricted by molecular symmetry. The problem is further complicated by the highly anharmonic character of these motions, resulting in large changes in the apparent harmonic force constant as the geometry approaches equilibrium. The result is that a simple criterion to terminate the geometry optimization at some predetermined sufficiently small value of the overall residual forces, particularly if these were examined in Cartesian coordinates, would have led to incomplete optimization unless a quite unreasonably small value were chosen for all of the acceptable residual forces.

One approach in cases such as these is to freeze the low-energy motions and optimize the remainder of the geometry. Next, the rest of the molecule is frozen, the low-energy motions are varied over a wide range, and the minimum is found from the resulting changes in energy or gradients. We have used a similar technique first achieving adequate optimization of the high-energy motions, but then permitting them to vary freely as the low-energy motions were optimized. It was considered essential, however, not only to reach a state of very small residual forces, but even more importantly to reach a structure at which these forces for the low-energy motions had changed sign, showing that the equilibrium had been passed. This sort of critical evaluation of the accuracy of geometry opti-

mization would have been very difficult if the optimization had been carried through in Cartesian coordinates and was made even more effective by choice of a particular set of internal coordinates<sup>1</sup> in which off-diagonal elements in the force constant matrix are minimized.

## RESULTS AND DISCUSSION

### Formamide

Experimental studies of the structure of formamide have led to a number of conflicting conclusions. The first microwave spectroscopic study by Kurland in 1955<sup>17</sup> found a very small positive inertial defect of 0.005 amu Å<sup>2</sup> and deduced that the molecule is entirely planar. This view was later challenged by Costain and Dowling<sup>18</sup> who made a more intensive study of the microwave spectrum and concluded that the amino group is bent by a small angle (torsional angles  $\tau(\text{HNCO})$  and  $\Delta(\text{HNCH})$  of  $7^\circ \pm 5^\circ$  and  $12^\circ \pm 5^\circ$ , respectively). Still later, Hirota et. al.<sup>19</sup> did additional microwave work with special attention to the NH<sub>2</sub> inversion vibrational satellites and decided that the inversion motion has only a single minimum and that the equilibrium configuration is strictly planar. It appears to be clear that if there is any barrier at the minimum position it must be an extremely small one and that if a double minimum exists the out-of-plane angle must be small.

The results of our geometry optimizations of formamide using a variety of basis sets are shown in Table I. A few comments may be made about accuracy and basis set effects in the remainder of the molecule before turning to the primary question of the amino group. In a previous article<sup>20</sup> we have reported the geometry calculation at the 4-21 level and have applied standard offset value corrections<sup>1</sup> to obtain the best computational estimate of the true equilibrium and  $r_0$  bond

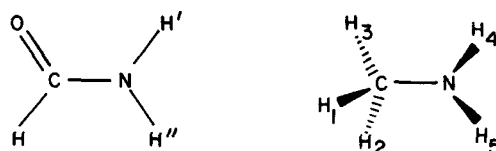


Figure 1. Labeling of atoms in formamide and methylamine.

**Table I.** Structure of formamide.<sup>a</sup>

	4-21	4-21-N*	4-21-N**	4-21-N* C*O*	4-21-N* C*O*H*	6-311- H*	6-311-N** C**O**H*	Exp <sup>b</sup>	Exp <sup>c</sup>
C=O	1.215 <sub>5</sub>	1.214 <sub>1</sub>	1.211 <sub>9</sub>	1.185 <sub>6</sub>	1.185 <sub>8</sub>	1.215 <sub>3</sub>	1.186 <sub>0</sub>	1.193(20)	1.219(12)
C-H	1.083 <sub>2</sub>	1.084 <sub>5</sub>	1.086 <sub>3</sub>	1.097 <sub>4</sub>	1.097 <sub>8</sub>	1.074 <sub>8</sub>	1.093 <sub>6</sub>	1.102(10)	1.098(10)
C-N	1.356 <sub>1</sub>	1.363 <sub>8</sub>	1.372 <sub>2</sub>	1.360 <sub>2</sub>	1.356 <sub>7</sub>	1.353 <sub>8</sub>	1.348 <sub>1</sub>	1.376(10)	1.352(12)
N-H'	0.994 <sub>9</sub>	1.005 <sub>1</sub>	1.007 <sub>5</sub>	1.003 <sub>3</sub>	0.996 <sub>4</sub>	0.992 <sub>4</sub>	0.993 <sub>5</sub>	1.014(5)	1.0016(30)
N-H''	0.992 <sub>2</sub>	1.002 <sub>6</sub>	1.005 <sub>3</sub>	1.000 <sub>8</sub>	0.994 <sub>1</sub>	0.989 <sub>9</sub>	0.990 <sub>7</sub>	1.002(5)	1.0015(30)
∠NCO	125.1	125.2	124.4	125.4	125.3	124.5	124.9	123.8(7)	124.7(3)
∠NCH	112.5	112.6	113.3	111.6	111.6	113.7	112.7	113.2(7)	112.7(2)
∠HCO	122.4	122.2	122.3	123.0	123.1	121.9	122.3	123.0	122.5(20)
∠CNH'	119.3	115.1	112.7	116.0	116.9	119.4	118.8	117.1(7)	118.5(5)
∠CNH''	121.7	116.8	113.5	118.5	119.6	121.7	120.7		120.0(5)
∠H'NH''	119.0	115.3	111.6	116.2	117.5	118.9	118.8	118.9(7)	121.6(3)
τ(H'NCO)	0	-16.5	-24.9	-14.7	-11.8	0	-6.5	-7(5)	0
τ(H'NCH)	180	165.8	158.1	167.3	169.9	180	174.4		180
τ(H''NCO)	-180	-156.6	-153.1	-160.0	-163.9	-180	-171.9		-180
τ(H''NCH)	0	25.7	30.1	22.0	17.8	0	9.0	12(5)	0
N-CHO	0	2.0	2.8	1.8	1.5	0	0.8		0
C-NH'H''	0	35.1	45.7	30.1	24.1	0	12.6		0
E + 168.	-0.5279	-0.5444	-0.5554	-0.6123	-0.6269	-0.7139	-0.7851		
E <sub>10</sub>	-0.566	-0.565	-0.567	-0.562	-0.562	-0.576	-0.576		
E <sub>11</sub>	-0.418	-0.424	-0.432	-0.418	-0.416	-0.437	-0.433		
E <sub>12</sub>	-0.402	-0.407	-0.413	-0.404	-0.404	-0.415	-0.420		
II	4.20	4.04	3.83	3.60	3.62	4.45	4.02	3.71 <sup>d</sup>	3.71 <sup>d</sup>

<sup>a</sup>Distances in Å (= 10<sup>-10</sup> m), angles in degrees, dipole moment (μ) in debye, total energy (E) and highest occupied canonical orbitals (E<sub>10</sub>, E<sub>11</sub>, and E<sub>12</sub>) in hartrees. See Figure 1 for labeling of atoms.

<sup>b</sup>Reference 18.

<sup>c</sup>Reference 19.

<sup>d</sup>R. J. Kurland and E. B. Wilson, *J. Chem. Phys.*, **27**, 585 (1957).

lengths. It was shown there that these computed values (with the standard corrections taken entirely from previous data) reproduced the observed molecular moments of inertia and their isotopic shifts at least as well as did the structures obtained from empirical fitting of those experimental inertial moments. Except for the investigation of the amino group, the modest 4-21 basis set provides more meaningful structural information than do the larger basis sets, the largest of which requires 64 times the computational time, because the appropriate offset values are reliably known from wide experience with the smaller set. These comments are relevant for computed *absolute* values of bond lengths; bond angles and relative values of bond lengths are comparatively invariant to changes in the basis set provided it is of 4-21 quality or better. As an illustration, note that the difference between the two nonequivalent N—H distances varies only from 0.002<sub>2</sub> to 0.002<sub>8</sub> for all the basis sets used. The various angles around the carbon atom show only

minor variations with basis set and these angles as computed with the 4-21 basis differ by 0.2° or less from those found with the largest basis. It is a different story, of course for the angles around the nitrogen atom.

Our earlier article<sup>20</sup> presented a critical comparison of the corrected computed structure with those obtained from the two microwave studies and from a study by Kitano and Kuchitsu,<sup>21</sup> which combined results from an electron diffraction experiment with the measured microwave moments of inertia. The conclusions reached there remain unchanged, but a few further points can be made on the basis of the information in Table I. The difference between the NCO and NCH angles is 12.0° according to Hirota et. al.<sup>19</sup> and 10.6° according to Costain and Dowling.<sup>18</sup> The calculations consistently favor the larger value. On the other hand, the calculations consistently predict that the HNH angle should be less than 120°, as expected on a qualitative basis<sup>20</sup> and as found by Costain and Dowling.<sup>18</sup> Similarly, the largest basis set

calculation gives good agreement with the torsional angles found by Costain and Dowling around the nitrogen atom, although both the experiment and the computation are quite uncertain on this point.

The main point of the present work, however, is concerned with the effect of basis set size on the computation of the geometry around the nitrogen atom, particularly the out-of-plane angle of the amino group. Both the 4-21 basis and the much larger 6-311-H\* basis converged to a completely planar structure. Only with polarization functions on the nitrogen atom is the molecule predicted to be nonplanar. As was the case with aniline,<sup>6</sup> addition of a set of *d* functions to the nitrogen atom in the 4-21-N\* set causes the amino group to become excessively nonplanar. (While the experimental evidence is not definitive concerning whether the molecule is perfectly planar or not, it is certainly not as nonplanar as this basis set predicts.) Addition of a second set of *d* functions to the nitrogen atoms, the 4-21-N\*\* set, exaggerates the error. In order to provide a more balanced basis set and give the electron density an opportunity to redistribute into the remainder of the molecule, *d* functions were added to the carbon and oxygen atoms as well as to nitrogen, reducing the out-of-plane angle to 30.1°. As was observed with aniline,<sup>6</sup> this effect is in the correct direction, but the reduction from 35° to 30° is only a small part of the needed correction. In fact, the addition of polarization functions to the hydrogen atoms as well has a larger effect, decreasing the out-of-plane angle to 24.1°. The final basis set was triple-zeta plus two sets of polarization functions on the heavy atoms and *p* functions on the hydrogens. With this basis, the fully optimized geometry gave an out-of-plane angle in reasonable agreement with one interpretation of the experimental data. It must be emphasized, however, that there is no evidence that the angle has converged to a final value even with this basis. In fact, a calculation<sup>22</sup> with a 9s5p basis contracted to 4s2p with the addition of *d* functions to N, C, and O, gave an out-of-plane angle of 9.9°, indicating that even at this level the angle remains sensitive to the details of the basis set composition. All that can be said with certainty is that a basis of at least the largest size

that has been used up to this time is required before the amino group angle is properly reproduced.

In a search for a more economical way to compute an out-of-plane angle that is at least approximately correct, we have examined the use of diffuse functions as recommended for anions by Clark et al.<sup>23</sup> Our attention was directed by a referee to the suggestion by these authors that addition of such diffuse functions to a nitrogen or oxygen atom should give a better description of the lone pair. The actual situation turns out to be a bit more complicated. We have repeated the geometry optimization of formamide using the 4-21 basis set with the addition of very diffuse *s* and *p* functions having the orbital exponents given by Clark et al.<sup>23</sup> for the N, C, and O atoms. The molecule was predicted to be strictly planar. It appears that functions with a higher angular momentum are required on the nitrogen atom to give the proper flexibility for description of the out-of-plane angle. We next optimized the geometry with the 4-21-N\* basis (*d* functions on nitrogen only) with the addition of diffuse *s* and *p* functions to nitrogen only. This resulted in an optimized out-of-plane angle of 30.3°, only 4.8° less than obtained with the 4-21-N\* basis alone and still far from the correct value.

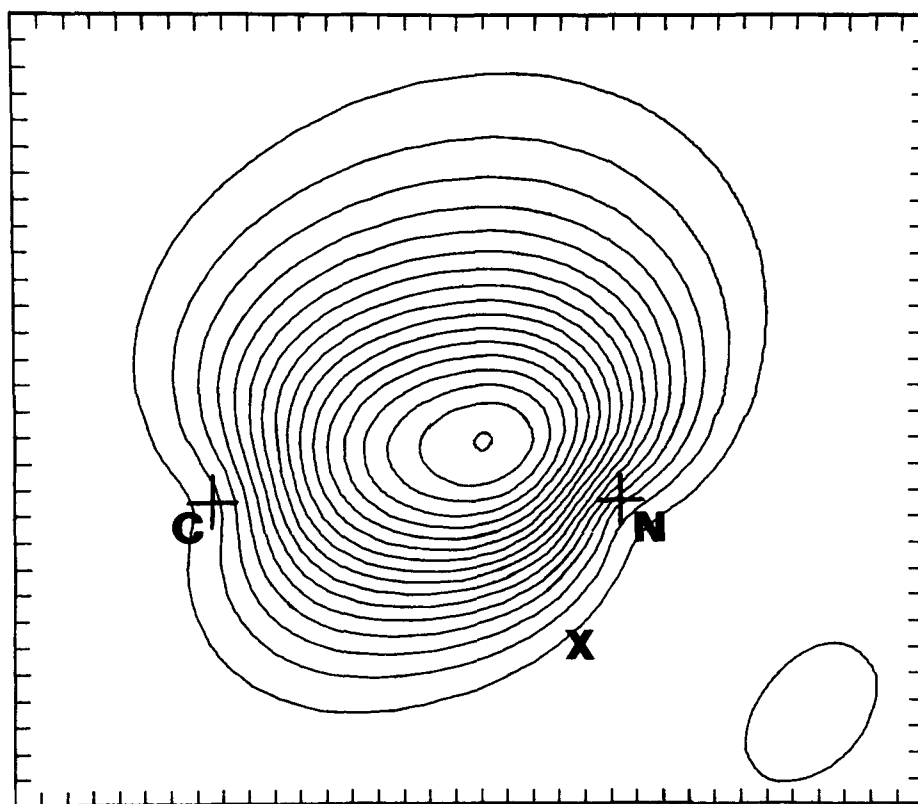
As concluded above, it appears that polarization functions are needed on the nitrogen atom, but a sufficiently large basis set is also needed in the rest of the molecule to describe the delocalization of the lone pair. Accordingly, we next optimized the geometry using the 4-21-N\* basis with diffuse *s* and *p* functions added to all three heavy atoms. This resulted in prediction of a completely planar geometry. Thus it appears that while diffuse functions added to the nitrogen atom may not be adequate to give a proper description, they provide an economical means of permitting effective delocalization when they are added to the basis in the remainder of the molecule. Bond distances were, of course, different since they are far from the Hartree-Fock limit with this rather distorted basis.

While all methods for partitioning the molecular wave function contain a degree of arbitrariness, it is informative to examine the localized orbitals, derived according to the Boys definition,<sup>24</sup> that result from the various

calculations. With the 4-21 basis set, the highest two occupied localized orbitals correspond to lone pair electrons on the oxygen atom. There is no nitrogen atom lone pair, but rather a nearly identical pair of orbitals that describe a highly polarized double bond with the centers of charge located at 0.28 Å away from the C—N axis and 26% of the distance away from the nitrogen atom. When polarization functions are added to the nitrogen atom giving the 4-21-N\* basis, the C=N localized orbitals split, producing a lower energy orbital that corresponds to a C—N single bond and a new HOMO that is a slightly distorted lone pair on the nitrogen atom.

In terms of predicting the amino group out-of-plane angle, the 4-21 and the 4-21-N\* basis sets erred in opposite directions, while the largest basis set used in the present calculations gave an intermediate result which appears to be in more reasonable agreement with experiment. The nature of the localized orbitals follows the same pattern. The highest

occupied localized molecular orbital calculated from the 6-311-N\*\*C\*\*O\*\*H\* basis is qualitatively similar to that from the 4-21-N\* basis, but because of the near planarity of the entire molecule it is located nearly perpendicular to that plane, maintaining reasonably normal angles between the N—H bonds and the lone pair. The lower energy C—N bond is plotted in Figure 2 which gives the electron density contours in a plane perpendicular to the CHO group and containing the C and N atoms. The center of charge of the lone pair orbital (orbital 12) is located at the point marked with an X. It can be seen that the C—N bond orbital is essentially a strongly distorted single bond with its center of charge drawn toward the nitrogen atom and repelled by the lone pair. Alternatively, the combination of the lone pair and the C—N bond orbitals could be considered as the two components of an even more strongly distorted  $\pi$  bond, as found with the basis sets omitting polarization functions on the nitrogen atom.



**Figure 2.** Electron density contour map of localized orbital corresponding to C—N single bond. Plotted in plane containing C, N, and O atoms. Wave function from 6-311-N\*\*C\*\*O\*\*H\* basis set. Area covered is  $3.0 \times 2.7$  Å. Contour interval = 0.04 electrons bohr<sup>-3</sup>.

It needs to be repeated that localized orbitals result from an arbitrary partitioning of the molecular wave function, but they do permit description of the bonding in the equally artificial language of lone pairs, double bonds, etc. In these terms, the bonding in formamide results from a pair of bonds which is intermediate between the two components of a  $\pi$  bond and a single bond plus nitrogen lone pair. Calculations with basis sets that do not contain nitrogen  $d$  functions do not give sufficient emphasis to the lone pair contribution while small basis sets containing nitrogen  $d$  functions overemphasize that contribution. Proper description of the complex shape of the true wave function requires a large, flexible basis set evenly distributed on all of the atoms, although it would appear that the correct description can be found within the Hartree-Fock approximation, omitting any consideration of dynamical electron correlation.

## METHYLAMINE

It was anticipated that the computational results for methylamine would differ from

those obtained with formamide because of the expected lack of interaction between the lone pair of the amino group and other portions of the molecule. There have been numerous previous *ab initio* calculations on methylamine, of course, as there have on formamide. None of these have involved geometry optimization with large basis sets, however, so the requirements for accurate calculation of the amino group out-of-plane angle have not been investigated.

The results of the methylamine calculations are shown in Table II along with the experimental structure derived by Takagi and Kojima<sup>25</sup> from an extensive microwave spectroscopic study. The spectra of methylamine and its isotopically substituted forms are complicated by splitting resulting from internal rotation coupled with inversion, but the analysis has been very carefully done and it is expected that the results are accurate within the uncertainties shown in the table and the usual restrictions involving effects of vibration on bond parameters obtained from microwave spectroscopy. There is no essential disagreement with the results of earlier microwave studies.<sup>26</sup> It should be pointed out,

Table II. Structure of methylamine.<sup>a</sup>

	4-21 <sup>b</sup>	4-21-N*	4-21-N**	5-31-N*C*O* <sup>b</sup>	6-311-N**C**O**H*	Exp. <sup>c</sup>
C-H <sub>1</sub>	1.089	1.088 <sub>5</sub>	1.087 <sub>8</sub>	1.091	1.090 <sub>0</sub>	1.0987(50) <sup>d</sup>
C-H <sub>2</sub>	1.081	1.082 <sub>8</sub>	1.082 <sub>5</sub>	1.084	1.084 <sub>1</sub>	1.0987(50) <sup>d</sup>
C-N	1.474	1.475 <sub>8</sub>	1.476 <sub>0</sub>	1.453	1.454 <sub>0</sub>	1.4714(20)
N-H	1.000	1.011 <sub>3</sub>	1.011 <sub>0</sub>	1.002	1.000 <sub>0</sub>	1.0096(50)
$\angle$ NCH <sub>1</sub>	114.6	114.7	114.0	114.8	114.5	113.8 <sup>e</sup>
$\angle$ NCH <sub>2</sub>	108.9	108.9	109.0	109.2	109.4	108.8 <sup>e</sup>
$\angle$ H <sub>1</sub> CH <sub>2</sub>		108.2	108.3		108.0	108.0(5) <sup>d</sup>
$\angle$ H <sub>2</sub> CH <sub>3</sub>		107.7	107.8		107.3	108.0(5) <sup>d</sup>
$\angle$ CNH <sub>4</sub>		108.0	107.3		110.3	110.3(5) <sup>f</sup>
$\angle$ H <sub>4</sub> NH <sub>5</sub>	110.9	104.9	103.6	106.8	106.5	107.1(5)
C-NH <sub>2</sub>	45.0	59.5	61.2	53.8	54.5	54.3 <sup>e</sup>
E + 95.	+0.0030	-.0200	-.0298	-.1903	-.2455	
E <sub>7</sub>		-0.540	-0.543		-0.556	
E <sub>8</sub>		-0.509	-0.510		-0.516	
E <sub>9</sub>		-0.381	-0.388		-0.387	
$\nu$	1.48	1.58	1.54	1.53	1.34	1.29

<sup>a</sup>See Table I for units and Figure 1 for labeling.

<sup>b</sup>Reference 1.

<sup>c</sup>Reference 25. Uncertainties taken from J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote (with the assistance of I. Buck and B. Starck), *Landolt-Börnstein, Numerical Data and Functional Relations in Science and Technology, Vol. 7, Structure Data of Free Molecules*, K.-H. Hellwege and A. M. Hellwege, Eds., Springer-Verlag, Berlin, 1976.

<sup>d</sup>Symmetry assumed in experimental analysis.

<sup>e</sup>Calculated from other parameters given.

<sup>f</sup>This number is printed erroneously as  $\angle$ NCH in original reference (K. Takagi, private communication).

however, that an electron diffraction investigation<sup>27</sup> has yielded an  $r_g(0)$  bond length for C—N of 1.467 Å which the authors thought to be more accurate and outside the quoted error limit of the corresponding parameter obtained from the microwave study.

Turning to the computational results, there is seen to be a strikingly accurate agreement between the angular structure obtained from the largest basis set and the experimental angles. In fact, the agreement within 0.2° for the amino out-of-plane angle is probably deceptive since the calculated value is an equilibrium angle and the experimental value retains some degree of vibrational averaging. As discussed above, the most accurate computed absolute values for bond distances could be found from a calculation with a basis set, such as the 4-21 set, for which reproducible offset values are known from previous work.

The effects of basis set size and composition on structural parameters other than the amino group angle are totally in accord with expectation. Again, the invariance of *differences* between related bond angles or bond lengths is notable.

The general effects of basis set composition on the amino group out-of-plane angle observed with formamide are also seen with methylamine, although the magnitudes of the errors are considerably less. Rather than predicting a planar molecule, the 4-21 basis gives an angle too small by 9°. It might be mentioned that a previous calculation<sup>28</sup> with a 4-31 basis gave an angle of 41°, too small by 13°. This may be another indication that between these two nearly equivalent basis sets, the simpler one is a bit better balanced and occasionally gives slightly superior geometry predictions. Alternatively, it may indicate inadequate geometry optimization with the 4-31 basis.

Addition of a set of  $d$  functions to only the nitrogen atom gives an amino group angle that is too large by 5°, overcorrecting the error from the original  $sp$  basis. Note that in formamide the corresponding error, compared with the largest basis set calculation was 22.5°. Exaggeration of the basis set imbalance by adding a second set of  $d$  functions to the nitrogen atom produces a very slight increase in this overestimation. Calculation with a moderate-sized basis with polarization functions on both nitrogen and carbon

(5-31-N\*C\*) gave results that are essentially indistinguishable from either the experimental ones or those computed with the largest basis set.

## OTHER MOLECULES

*NH<sub>3</sub>*. It has long been known that the out-of-plane angle in ammonia is predicted to be too small if polarization functions are not included in the nitrogen basis. The angle is computed to be 14° less than observed with the 4-21 basis<sup>1</sup> (or 26° too small with the 4-31 basis<sup>29</sup>), while the 5-31-N\* basis<sup>1</sup> gives an angle within experimental uncertainty of the experimental value<sup>30,31</sup> or with that obtained from a near Hartree–Fock calculation.<sup>32</sup> There is no report that the angle has ever been calculated too large by a significant amount. Ammonia, of course, presents an extreme example of a situation in which the nitrogen atom lone pair has no place for delocalization except to the attached hydrogen atoms.

*Ethylamine*. Ethylamine gives predicted out-of-plane amine angles that have nearly identical basis set dependence as does methylamine.<sup>33</sup> The *trans* conformer yields an angle of 46.0° with the 4-21 basis, 59.5° with the 4-21-N\* basis, and 60.8° with 4-21-N\*\*. The corresponding parameters for the *gauche* conformer, calculated with those basis sets, are 46.2°, 59.2°, and 60.8°. No accurate experimental value is known, but the parallelism with methylamine is striking.

*Aniline*. Aniline presents a case similar to formamide in that polarization functions are required on nitrogen to reproduce the lone pair, but the possibility of delocalization into the ring must be allowed for properly or the molecule is predicted to be too planar. With the 4-21 basis, the amino group is predicted to be planar, with 4-21-N\* the out-of-plane angle becomes 52.0°, and with 4-21-N\*\* it is 55.6°, all compared with an experimental angle of  $37.5^\circ \pm 2^\circ$ .<sup>6</sup> Comparison with formamide suggests that a very large balanced basis set would be required to describe this angle correctly.

*Vinylamine*,  $CH_2=CHNH_2$ . Vinylamine is another molecule in which one would expect to have strong delocalization of the nitrogen lone pair into the  $\pi$  system of the group to which it is attached. Computation at the 3-21 level<sup>34</sup> predicted that the entire molecule



should be planar, while the 6-31-N\*C\* basis set led to a structure having CCNH torsional angles of 16.5° and 37.8°. Analysis of the microwave spectrum of this molecule is very complicated,<sup>35,36</sup> but further fitting of the 6-31-N\*C\* structure to the observed moments of inertia<sup>34</sup> produced torsional angles of 22.5° and 31.1°, radically different from those obtained from the calculation alone. It would appear that for this molecule where delocalization should be extreme, a still larger basis set would be required to assure geometry convergence of the out-of-plane angles at nitrogen.

*PH<sub>2</sub>NH<sub>2</sub> and PF<sub>2</sub>NH<sub>2</sub>.* In these molecules, there can be delocalization of the nitrogen lone pair to the phosphorus atom or, as a still more extreme case, also into the fluorine atoms. Calculation at the 4-21-N\*P\* level<sup>37</sup> for PH<sub>2</sub>NH<sub>2</sub> gave a P-out-of-NH<sub>2</sub>-plane angle of 38.7° and addition of a second set of *d* functions on nitrogen (4-21-N\*\*P\*) increased the angle to 50.5°. The corresponding results for PF<sub>2</sub>NH<sub>2</sub> were 14.1° and 44.5°. For the latter molecule, a microwave spectroscopic study<sup>38</sup> led to the conclusion that the structure around the amino group is completely planar. An electron diffraction study of the same molecule<sup>39</sup> concluded that the phosphorus atom is 34° out of the NH<sub>2</sub> plane. Whatever the true situation, it is evident that the out-of-plane angle is at least small and that its evaluation by *ab initio* methods is strongly basis set dependent.

*Aminoheterocycles.* Geometry optimization of 4-amino-1,2,3-diazaphosphole at the 4-21 level<sup>40</sup> predicts a completely planar amino group. At the 4-21-N\* level, the out-of-plane angle becomes 51.0° and at the 4-21-N\*\* level it is 56.3°. These results are very similar to those for aniline, again reflecting inadequate description of the balance between lone-pair and delocalized  $\pi$ -bond character. The true angle may be appreciably smaller than 51° (for aniline it is 37.5°). Quite similar results have been obtained in some preliminary calculations on cytosine.<sup>37</sup>

## CONCLUSIONS

Aside from the information obtained about individual molecules, the results presented here lead to three basic conclusions about the evaluation of molecular geometries around a nitrogen atom:

(1) As known previously, polarization functions on the nitrogen atom are essential to reproduce the electron distribution in the nitrogen lone pair and generate sufficient nonplanarity around the nitrogen atom. A larger *sp* basis set does not serve the same function since it lacks the geometric flexibility introduced by the *d* functions.

(2) Polarization functions on nitrogen alone overemphasize the contribution of the lone pair so that the resulting geometry optimization predicts excessively large nonplanarity unless the basis set used in the rest of the molecule has sufficient flexibility to describe the delocalization of the lone pair.

(3) The requirement for a large and balanced basis set is especially severe in molecular environments where the amino group is attached to a conjugated system or to an element, such as phosphorus, with vacant *d* orbitals. Although there is no evidence that the correct geometry for such substances cannot be found within the Hartree-Fock approximation, the quality of the basis set required may place some of them beyond the reach of present computational possibility. There may be hope in the use of very diffuse *s* and *p* functions *on the atom centers into which the nitrogen lone pair is delocalizing*. The results reported here suggest that extreme care should be taken in computing the structures of a number of biologically important pyrimidine and purine derivatives such as cytosine, adenine, and guanidine if it is desired to properly describe the geometry at the amine nitrogen.

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