

COMPARISON BETWEEN SOME SEMI-EMPIRICAL AND *AB INITIO* HARTREE-FOCK MODELS FOR THE DESCRIPTION OF AMIDES (FORMAMIDE REVISITED)

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A comparative study on the use of the MINDO/3, MNDO and AM1 semi-empirical methods for the description of formamide and aliphatic amide systems is reported. For formamide, *ab initio* Hartree-Fock calculations are also reported using both the STO-3G and 3-21G basis sets, as well as a basis set obtained by a minimal relaxation of the STO-3G contraction scheme. It is shown that both the MNDO and the STO-3G methods cannot properly reproduce the experimental results. In both cases this appears to be due to inadequacies of the basis sets used. Again in both cases only small improvements in the basis set necessary to allow for the diffuse character of the p_z orbitals lead to dramatic improvements in the calculated results. In the case of the STO-3G basis set this is demonstrated by the fact that a small relaxation in the contraction leads to results even superior to those with the 3-21G set. The conclusions reached for amide systems can be extended to other systems where planarity around or inversion with respect to nitrogen is an issue. This is demonstrated for ammonia.

INTRODUCTION

The semi-empirical quantum chemical methods MINDO/3¹ and MNDO,² based on the INDO and NDDO approximations,³ respectively, developed by Dewar and co-workers, have become important tools in the theoretical study of molecular systems. They allow full geometry optimization and the study of several molecular properties without the need for excessive computing resources even for compounds which, owing to their size, are still inaccessible to *ab initio* methods. Although in general a variety of ground-state properties of molecules are reproduced well, both methods reveal certain weaknesses.^{4,5} These are a consequence of the basic theoretical approximations or the parameterization. Recently, Dewar *et al.*⁶ reported a new method, AM1, which was stated to have overcome the major flaws of its predecessor MNDO.

In our group, we are interested in the application of quantum chemical models to the theoretical study of compounds containing amide functionalities that are of importance in both polymer and peptide chemistry. Obviously, a prerequisite is the appropriate description of the amide moiety.

At present a rigorous evaluation of the use of these semi-empirical methods applied to amides is lacking. This is unfortunate, since a survey of the literature reveals that both MINDO/3 and MNDO have already

been applied indiscriminately to amide systems (there is little point in giving a comprehensive list of references; scores of papers using one of the methods on amide systems can easily be retrieved by CAS on-line or related searches).

Remarkably, however, a comparison of the calculated data for the simplest representative, formamide (**1**) (Figure 1), obtained with MINDO/3, MNDO and AM1, respectively, shows that the semi-empirical SCF methods give ambiguous results. The minimum energy structure of **1** is predicted to be planar,⁷ non-planar² and planar,⁶ respectively. Although in the case of MINDO/3 and MNDO this has been noted before, no explanation was presented.^{8,9} In part this can be attributed to the fact that experimentally the question of planarity or non-planarity of **1** has been a contentious issue. Three microwave spectral investigations led to differing views. In the first, a planar structure was assumed.¹⁰ A subsequent investigation¹¹ favoured a non-planar structure, which was eventually challenged again.¹² The planar structure now appears to be generally accepted and is also predicted by extended basis set *ab initio* Hartree-Fock calculations with full geometry optimizations on **1**.¹³⁻¹⁷ In these studies the potential well for the out-of plane bending was found to be very small, in agreement with the most recent experimental work.¹²

The ambiguous results obtained for **1** with the semi-

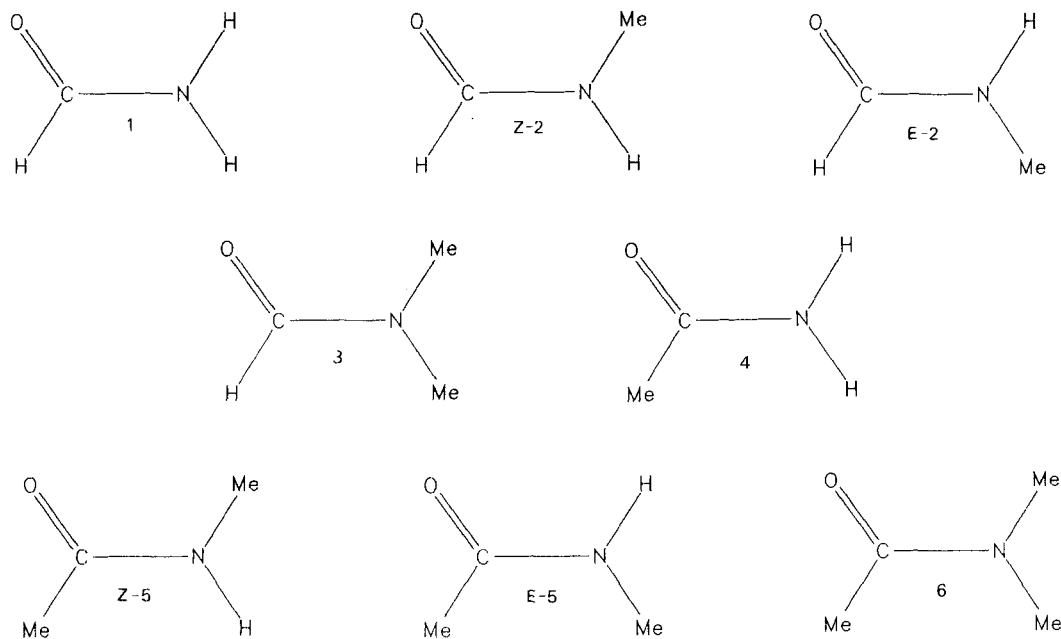


Fig. 1. Compounds considered

empirical SCF-MO method are not confined to **1** itself. Similar deviations were found by us for acetamide and *N*-methylacetamide (see below). Clearly, a systematic evaluation of the semi-empirical SCF-MO methods MINDO/3, MNDO and AM1 in their application to the theoretical study of amides is warranted.

At the *ab initio* level, the effect of choice of model on the formamide geometry is well documented. Carlsen *et al.*¹³ have carried out *ab initio* calculations with full geometry optimization on **1** with a variety of basis sets. The reliability of these was estimated by their prediction of the inversion barrier of ammonia. It was concluded that the STO-3G basis set which predicted a non-planar structure for **1** was unfit. At higher levels of theory only planar or nearly planar structures were calculated. It was found, however, that the potential well is very shallow. Subsequent *ab initio* calculations on **1** have lent further support to these conclusions.^{13,14}

Although our main interest and emphasis are with the semi-empirical methods, we have nevertheless included results for formamide obtained by *ab initio* calculations. It will be seen that an interesting parallel exists between basis set inadequacies in semi-empirical and *ab initio* approaches.

ELECTRONIC STRUCTURE OF FORMAMIDE

The electronic structure of formamide is often described in terms of two major resonance forms,

forms A (neutral) and B (N^+O^-) (see Figure 2). Recently, this analysis has been challenged by Wiberg and Laidig^{15,16} and by Flegg and Harcourt.¹⁸ Wiberg and Laidig noted from the planar and non-planar structures of **1** that although the C(2)—N(3) bond is considerably shortened when planarity is enforced, there is only a very small effect on the C(2)—O(1) bond length. Obviously, a large contribution from resonance form B can explain the shortening in the first bond, but not the absence of it in the second. From an analysis of the electron populations they concluded that charge transfer is not predominantly from N to O (as is suggested by resonance form B) but from N to C. Flegg and Harcourt, in *ab initio* valence bond calculations on the six most likely resonance structures, found as the second most dominant structure the C^+O^- structure (form D) with form C (N^+C^-) as third in order of importance. The contribution of the N^+O^- form was found to be very small. However, their calculations should perhaps be viewed with care as they used STO-5G and STO-6G basis sets. It is well known that the STO-3G set performs very poorly on this system. We shall show below that this is due to the absence of any flexibility rather than to a poor convergence of the Gaussian expansion to the Slater orbital.

In an attempt to correct for this inflexible behaviour Flegg and Harcourt have also performed calculations both with all p orbital exponents and with the p_x orbital exponents only optimized for the atomic ions. Although this correction might be too extreme, it is

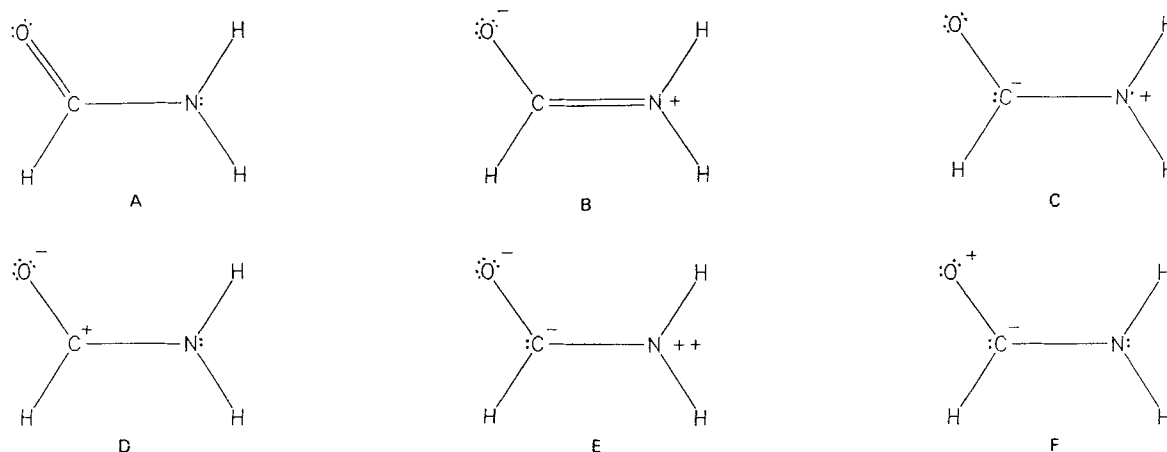


Fig. 2. The six most dominant resonance forms of formamide (taken from Ref. 18)

worth noting that the conclusions were valid for all basis sets.

All this evidence seems to indicate that one should not use the simple picture of the resonance forms A and B, but should consider several possible resonance structures, all of which nevertheless favour the planar structure.

SEMI-EMPIRICAL CALCULATIONS

Geometry and energy calculations on formamide and aliphatic amides

In Table 1 we present MINDO/3, MNDO and AM1

results for formamide. These calculations are not the first reported as they have all been included in the original papers on the methods.^{2,6,8,22,23} However, this appears to be the first systematic comparison and evaluation of the results.

In view of the discrepancies between the methods and since the most reliable experimental data and *ab initio* calculations indicate that the minimum structure of 1 is located in a very shallow potential well, we have done our calculations under more stringent convergence criteria than are normally applied. Special care has been taken to prevent convergence to local minima by doing cross-calculations on the geometries predicted by all methods in this study. Nevertheless, a comparison

Table 1. MINDO/3, MNDO and AM1 results for formamide

Parameter ^a	MINDO/3	MNDO	Restricted MNDO ^b	AM1	Exp. ^c
Bond lengths					
r_{CO}	1.208	1.225	1.227	1.243	1.212 ± 0.003
r_{CN}	1.334	1.409	1.389	1.367	1.368 ± 0.003
Bond angles					
θ_{NCO}	126.6	121.2	120.9	121.9	125.0 ± 0.4
θ_{HNH}	110.4	110.6	115.7	118.2	121.6 ± 1.0
Dihedral angles:					
ϕ_{HNCO}	0.0, 180.0	19.5, 153.0	— —	0.1, 180.0	
ϕ_{HNCH}	0.0, 180.0	31.4, 164.9	— —	179.9, 0.0	
Heat of formation	-51.8	-40.0	-39.2	-44.9	-44.5 ^d
Rotational barriers ^e					
	12.7, 11.9	5.4, 7.9	8.1	10.2, 15.1	18-19 ^f

^a Bond lengths are given in Å, angles in degrees of formation in kcal mol⁻¹.

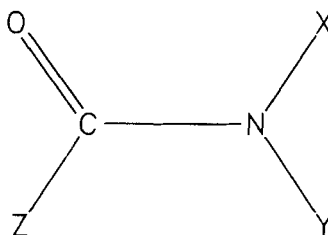
^b The molecule was forced to be planar (hence no values are given for dihedral angles).

^c Ref. 19.

^d Ref. 20.

^e The first transition state has the N-H bonds inclined towards C=O (see text). For restricted MNDO, the NH₂ group was forced to remain planar, hence there is only one transition state possible.

^f Ref. 21.

Table 2. MINDO/3, MNDO and AM1 results for methylated formamides^{a,b} (see formula for substituent sites X and Y)

Compound	Parameter	MINDO/3	MNDO	AM1	Exp. ^c
(Z)-2	r_{CO}	1.206	1.225	1.242	1.219
	r_{CN}	1.349	1.398	1.373	1.366
	θ_{NCO}	127.5	122.5	123.3	124.6
	ϕ_{XNCO}	0.0	0.4	0.2	0
	ϕ_{YNCO}	180.0	179.7	179.9	180
	ΔH_f°	-43.1	-39.9	-41.7	
(E)-2	r_{CO}	1.206	1.226	1.243	
	r_{CN}	1.351	1.399	1.373	
	θ_{NCO}	125.9	120.2	121.4	
	ϕ_{XNCO}	0.0	0.2	0.0	
	ϕ_{YNCO}	180.0	179.5	180.0	
	ΔH_f°	-42.9	-40.5	-42.1	
3	r_{CO}	1.205	1.224	1.242	
	r_{CN}	1.369	1.410	1.380	
	θ_{NCO}	127.4	122.2	122.9	
	ϕ_{XNCO}	0.0	0.6	0.9	
	ϕ_{YNCO}	179.6	179.1	178.9	
	ΔH_f°	-24.6	-36.8	-37.0	-45.8
4	r_{CO}	1.220	1.230	1.248	1.220
	r_{CN}	1.348	1.418	1.375	1.380
	θ_{NCO}	120.1	118.6	119.9	122
	ϕ_{XNCO}	180.0	149.1	180.0	180
	ϕ_{YNCO}	0.0	18.2	0.1	0
	ΔH_f°	-67.2	-48.0	-50.8	-56.9
(Z)-5	r_{CO}	1.218	1.229	1.247	1.224
	r_{CN}	1.365	1.410	1.381	1.386
	θ_{NCO}	120.7	119.6	121.2	121.8
	ϕ_{XNCO}	0.3	11.0	1.7	0
	ϕ_{YNCO}	179.7	165.5	178.3	180
	ΔH_f°	-57.8	-47.7	-47.4	
(E)-5	r_{CO}	1.219	1.231	1.248	
	r_{CN}	1.368	1.414	1.382	
	θ_{NCO}	118.6	117.2	119.0	
	ϕ_{XNCO}	0.4	6.1	1.5	
	ϕ_{YNCO}	180.0	156.0	178.0	
	ΔH_f°	-56.3	-46.7	-47.2	
6	r_{CO}	1.218	1.231	1.247	
	r_{CN}	1.391	1.420	1.390	
	θ_{NCO}	119.3	118.4	120.5	
	ϕ_{XNCO}	1.2	1.5	4.3	
	ϕ_{YNCO}	178.6	173.7	175.4	
	ΔH_f°	-35.8	-41.2	-41.5	-53.7

^a Bond lengths are given in Å, angles in degrees and heats of formation in kcal mol⁻¹.

^b See formula for definition of angles in substituted formamide.

^c Experimental data from gas electron diffraction (given where known) taken from Ref. 25, [for (Z)-2], Ref. 26 (for 4) and Ref. 27 [for (Z)-5]. The heats of formation have been taken from the on-line data file of the Design Institute for Physical Properties data (DIPPR) of the American Institute of Chemical Engineering.

between our results and those originally reported reveals only small differences.

It is clear that, whereas MINDO/3 and AM1 predict a planar structure for formamide, MNDO predicts a distinctly non-planar structure. In view of this, we have also performed a restricted MNDO geometry optimization in which the molecule was forced to remain planar. It should be noted that owing to the symmetry of the system the planar structure is necessarily an extremum and represents a saddle point on the MNDO potential energy surface. Since at that point the first derivative of the energy with respect to the out-of-plane bending coordinate vanishes, a calculation started from a planar structure in MNDO might well result in a planar structure.

Note that the MNDO results obtained for **1** with the planarity constrained applied are similar to those reported in Ref. 24. The latter workers must either have intentionally imposed the same constraint or have started from a planar initial geometry.

A survey of the calculated geometry reveals several interesting features. First, we see that the C—O bond length is almost the same in the planar and the non-planar MNDO structure, which suggests that the N^+O^- is *not* an important resonance contribution, in agreement with the findings of Wiberg and Laidig^{15,16} (see above). The C—N bond length, on the other hand, decreases markedly when the molecule is forced to remain planar, although it is still too long. These two facts strongly suggest that the C—N part of the molecule plays a dominant role in the failure of MNDO to produce the planar structure, and indeed in the whole issue of planarity.

To investigate whether the differences between the two models will remain in the more general case of aliphatic amides, we performed MINDO/3, MNDO and AM1 calculations on all possible methyl substituted derivatives of formamide and the results are given in Table 2. As expected from the above, we find that both MINDO/3 and AM1 predict all molecules to be in a planar or nearly planar conformation. At first sight it would appear that no clear trend evolves from the MNDO data. However, a closer scrutiny reveals that MNDO predicts a planar structure in those cases where the number of methyl groups on N exceeds that on C. An explanation of this trend will be found in the analysis of the MNDO artifacts.

On the basis of the above comparisons, it appears that MNDO is not the method of choice for the description of amides and its use in, for instance, modelling of peptide structures can lead to erroneous and misleading results. At first sight there appears to be little to choose between MINDO/3 and AM1. It is known, nevertheless, that MINDO/3 falsely predicts valence angles for amines that are too large, which leads to planar structures for secondary and tertiary amines.⁷ Note, further, that the predicted θ_{HNH} angle (110.4° ,

Table 1) is far too small. The superior description of amide structures might therefore partly be a fortunate cancellation of errors, and the use of MINDO/3 in N-containing systems should always be made with care.

Scrutinizing the energy differences between the *E* and *Z* conformers of both **2** and **5** (see Table 2), we find that for **2** both MNDO and AM1 predict the *E* conformer to be the most stable. Not only does this run counter to chemical intuition, but since only the *Z* conformer has been observed in the gas phase, there is good evidence to assume that MINDO/3 makes the superior prediction in this case. For **5**, a recent high-level quantum chemical calculation by Jørgensen and Gao²⁸ gave an energy difference between *E* and *Z* of $2.07 \text{ kcal mol}^{-1}$ at 298 K. Although all three semi-empirical models agree with the high-level *ab initio* calculation in predicting *Z* to be more stable, the energy difference predicted by MINDO/3 ($1.5 \text{ kcal mol}^{-1}$) seems to be better than the MNDO and AM1 values (1.0 and $0.2 \text{ kcal mol}^{-1}$, respectively).

Finally, looking at the predicted and available experimental heats of formation (ΔH_f°), we must conclude that AM1 seems to perform better than the other methods but the improvement, in particular that over MNDO, is small in view of the still fairly large deviations.

Resonance integrals

For a further analysis of the difference between the amide geometries as calculated by MNDO on the one hand and MINDO/3 and AM1 on the other, we have calculated the overlap and one-electron resonance integrals for the valence p_π orbitals on C and N at reference distances of 1.35 and 1.40 Å (Table 3). The importance of this resonance integral is obvious. Since there is clear evidence to suggest that the planarity around N is caused mainly by the N^+C^- resonance form (see above), the semi-empirical model should be able to give a good energy balance for two electrons in an N lone-pair type orbital against two electrons in an N—C π orbital.

It is clear from Table 3 that whereas the resonance integral values for MINDO/3 and AM1 are fairly similar, those for MNDO are significantly smaller.

Table 3. Overlap and resonance integral values for the p_π orbitals on C and N at distances of 1.35 and 1.40 Å

Parameter	MINDO/3	MNDO	AM1
at 1.35 Å:			
Overlap	0.210	0.149	0.173
Resonance	-0.0821	-0.0778	-0.0825
At 1.40 Å:			
Overlap	0.191	0.133	0.155
Resonance	-0.0746	-0.0695	-0.0742

Despite the fact that a completely unambiguous breakdown is not possible owing to the different evaluation of resonance integrals in MINDO/3 compared with MNDO and AM1, it appears that the difference in resonance integral values is due, at least in part, to the much smaller value of the overlap integrals. In this respect we note that in the parameterization of MINDO/3¹ and AM1⁶ the orbital exponent values for s and p valence orbitals on the same atom type have been optimized *separately*, whereas in the MNDO parameterization they are equal.² Since ζ_p values in MINDO/3 and AM1 are generally smaller than the ζ_s values for the same atom (indeed, this is the case for all atomic basis sets with $\zeta_s \neq \zeta_p$), the restriction inherent in the MNDO parameterization will tend to yield values for ζ_p that are too large (making the electron charge cloud due to the p orbital too contracted). In the case of π overlap, this will lead to overlap integrals and hence resonance integrals which are too small, as is demonstrated by our calculated values (Table 3).

As a result, geometry predictions will be affected because charge delocalization from N will become less favourable. From the results on the methyl-substituted formamide molecules it would appear that this artificial energy barrier to delocalization can be overcome by sufficient destabilization of the charge on the N atom. This explains why the addition of a methyl group to N leads to planarity with MNDO. Adding a methyl group to C again disfavours delocalization because of the repulsive effect on π -electrons on the amide carbon. This, in turn, can be compensated for by adding one more methyl group to nitrogen. The trend observed on going from formamide (**1**) via *N*-methylformamide (**2**) to *N*-methylacetamide (**5**) and finally to *N,N*-dimethylacetamide (**6**) is now an obvious one (see Figure 1).

To confirm our line of reasoning, in Table 1 we have listed the values for the rotational barrier for **1** as

calculated by the several methods. Note that two transition states exist. Whatever planarity the NH₂ moiety possesses in the minimum energy structure is not generally retained when the group is rotated out of plane by 90°. As a consequence, two transition states exist, one in which the H atoms incline to the side of the C=O bond, and one in which they incline to the other side. Intuitively one would expect electrostatic interaction to stabilize the former with respect to the latter. This expectation is borne out with AM1 and MNDO, but not with MINDO/3, although here the differences are small. In general we can conclude from these values that the MNDO rotational barrier is far lower than that calculated by the other methods. This, of course, is fully in keeping with the postulated lack of charge delocalization (or lesser bond order) in the MNDO case.

Force field calculations

Force field calculations have become popular both as a tool to analyse results from a geometry calculation and as a means of predicting and interpreting IR and Raman absorption spectra.²⁹ Further, they can be used in estimating parameters for molecular mechanics or dynamics calculations. Another point of interest in force fields is the shape of the potential energy well for out-of-plane bending. This potential is shallow and therefore susceptible to deformations.^{13,17} For successful use of the present methods in geometry predictions, the correct shape of this potential well is therefore of great importance.

Although several CNDO semi-empirical SCF-MO force fields of **1** are available,^{30,31,38} we are not aware of MINDO/3, MNDO or AM1 force fields. In Table 4 we report the harmonic vibrational frequencies for formamide as calculated by MINDO/3 in the minimum energy structure, MNDO in both the minimum energy

Table 4. MINDO/3, MNDO and AM1 calculated harmonic vibrational frequencies of formamide^a

Parameter	MINDO/3	MNDO	Restricted MNDO ^b	AM1	Exp. ^c
NH asym. stretch	3688(3319)	3603(3243)	3673(3306)	3526(3173)	3545
NH sym. stretch	3713(3342)	3624(3262)	3648(3283)	3560(3204)	3451
CH stretch	3199(2879)	3292(2963)	3293(2964)	3081(2773)	2852
CO stretch	1914(1723)	2094(1885)	2081(1873)	2004(1804)	1734
NH ₂ scissor	1501(1351)	1805(1625)	1788(1609)	1710(1539)	1572
CH bend	1241(1117)	1427(1284)	1386(1247)	1325(1193)	1378
CN stretch	1393(1254)	1379(1241)	1450(1305)	1482(1334)	1255
NH ₂ rock	915(824)	1205(1085)	1150(1035)	1133(1020)	1059
NCO bend	494(445)	582(524)	591(532)	539(485)	565
CH out-of-plane	930(837)	1034(931)	1038(934)	990(891)	1030
NH ₂ twist	498(448)	363(327)	470(423)	557(501)	602
NH ₂ wagging	477(429)	641(577)	420i(378i)	331(298)	289

^a In cm⁻¹; values in parentheses have been scaled by a factor of 0.9.

^b The molecule was forced to be planar [hence the NH₂ wagging value is imaginary (i)].

^c Refs 32 and 33.

structure and the restricted planar structure and AM1 in the minimum energy structure. The values obtained by scaling the frequencies by the usual factor of 0.9 are given in parentheses.³⁴

It can be seen that in general, the AM1 results agree fairly well with the experimental numbers, with the exception of the calculated values for N-H stretching frequencies, which are too low. On the whole, MINDO/3 gives the poorest performance, in one case even reversing the order of calculated vs experimental frequencies (C-H bend and C-N stretch). The frequencies calculated by MNDO at the lowest energy (non-planar) structure agree fairly well with experimental results, with the obvious exception of the low-lying wagging, twisting and deformation modes (especially the NH₂ wagging mode).

For the constrained planar formamide the MNDO results are not very different from those for the bent structure, especially when compared with the differences between predicted and observed spectra, with the, again obvious, exception of the imaginary frequency due to the NH₂ wagging. Further, all three methods predict the asymmetric and symmetric N-H stretching frequencies in the wrong order. Note, however, that for the *constrained* geometry MNDO predicts the right ordering.

AB INITIO CALCULATIONS ON FORMAMIDE

In the above, we have seen that the artifact in the MNDO calculation of amide structures is at least partly due to the relatively poor description of the atomic p orbitals which are not diffuse enough to give sufficiently large values for p_{π} - p_{π} resonance integrals. Clearly,

there is a parallel with *ab initio* Hartree-Fock calculations where the use of minimal basis sets can lead to similar problems, especially when the same scaling factor is used for valence s and p orbitals, as is the case in the well known STO-KG basis sets.³⁵

Carlsen *et al.*¹³ have already demonstrated that the geometry calculated for formamide is very much basis set dependent: use of the STO-3G basis set resulted in a distinctly non-planar structure for formamide, whereas nearly planar structures were found using more sophisticated basis sets. Similar conclusions have been reached by other investigators.¹⁴⁻¹⁶ Carlsen *et al.* classified the problem with the poor geometry prediction as part of the general effect that STO-3G calculations tend to underestimate valence angles around N. While it is clear, therefore, that STO-3G is unfit for modelling of this kind of structure, the question of the actual deficiency in STO-3G has not been fully answered.

Although we are safe in assuming that the restricted contraction scheme of a minimal basis set will create problems similar to those described above in the analysis of the semi-empirical methods, part of the error might still be due to an inappropriate choice of Gaussians in STO-3G. Since STO-type basis sets are still being used frequently (as witnessed by the use of STO-5G and STO-6G in the valence bond calculations on formamide¹⁸), this point is not without interest.

In order to assess the importance of flexibility in the basis set, we have for this particular purpose created a 'recontracted STO-3G' basis set which consists of the same Gaussian primitives as STO-3G but with a contraction scheme similar to that of the 3-21G basis set: for each valence orbital the two Gaussians with the

Table 5. *Ab initio* Hartree-Fock results for formamide (1)^a

Parameter	STO-3G	Recontracted STO-3G ^b	3-21G	Exp. ^c
Bond lengths:				
r_{CO}	1.216	1.205	1.212	1.212 ± 0.003
r_{CN}	1.436	1.355	1.353	1.368 ± 0.003
Bond angles:				
θ_{NCO}	123.9	125.9	125.3	125.0 ± 0.4
θ_{HNN}	109.8	118.4	118.6	121.6 ± 1.0
Dihedral angles:				
ϕ_{HNCO}	21.9, 145.8	1.5, 177.3	0.0 180.0	
ϕ_{HNCH}	161.4 37.6	178.3, 2.9	180.0 0.0	
Total energy	-166.69184	-166.86167	-167.98490	
Rotational barrier ^d				
	8.2, 9.3	15.1, 17.0	18.6, 18.6	18-19 ^e

^a Bond lengths are given in Å, angles in degrees, total energies in hartree atomic units.

^b For details refer to text.

^c Ref. 19 (gas electron diffraction).

^d For the definition of the first and second rotational barrier, see Table 1, footnote e.

^e Ref. 21.

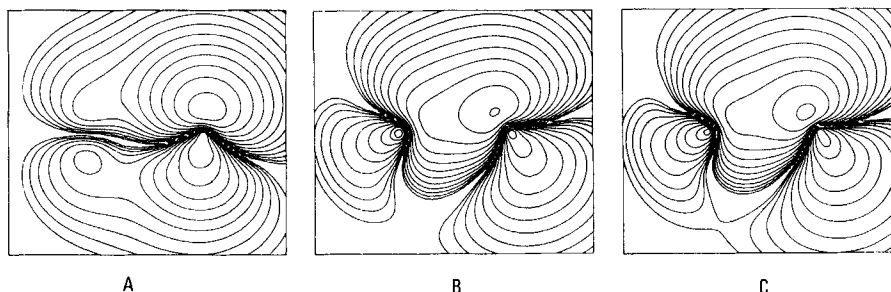


Figure 3. Electron density contour diagrams of the formamide LMO with the most nitrogen lone-pair character calculated with the STO-3G (A), recontracted STO-3G (B) and 3-21G (C) basis sets at the minimum energy structure for each basis set. The plane of intersection is defined to coincide with the C-N bond and to be either perpendicular to the plane of the molecule (B and C), or to be equidistant to the N hydrogen atoms (A). The C and N atoms are located left and right of the centre, respectively. Contour lines have been drawn at values of 2^{-1} , 2^{-2} , 2^{-3} , ..., 2^{-11} , 2^{-12}

largest orbital exponents are contracted to one orbital with the ratio between the contraction coefficients the same as in the original STO-3G contraction scheme. In this way, the STO-3G results provide a strict lower limit to the results for the recontracted basis set. Calculations performed with this basis set and with the STO-3G and 3-21G basis sets are reported in Table 5.

It is clear that the freedom allowed to the valence orbitals with the recontracted basis is sufficient to bring the results in much better agreement with 3-21G (and superior basis sets) and with experiment. As with the semi-empirical methods, this is true both for the geometry and for the rotational barriers. The only thing seriously wrong with the results of the recontracted scheme appears to be the total energy, which is not much lower than that calculated with the STO-3G basis and much more positive than that calculated with the 3-21G basis. However, much of the latter difference is due to the poor description of the core electrons (which

is no different from that with STO-3G). This has only a very small influence on the description of valence electrons. The small energy difference obtained with the normal and the recontracted STO-3G sets at different geometries again emphasizes the shallowness of the potential well for inversion around N.

At this point we should stress that we are not aiming at redeeming the STO-3G by making modifications, thereby creating yet another variety of basis sets. We feel, however, that the best case for our postulated deficiency of minimal basis sets with similar exponents for s and p orbitals is best demonstrated by showing the effect of a minimal relaxation.

To analyse the differences in chemical bonding as predicted by the models, the canonical molecular orbitals have been transformed to localized molecular orbitals (LMOs) using the method of Boys.^{36,37} For all three compounds we have plotted the orbital that has the largest density on nitrogen and therefore conforms

Table 6. STO-3G, recontracted STO-3G and 3-21G *ab initio* Hartree-Fock calculated harmonic vibrational frequencies of formamide (I)^a

Parameter	STO-3G	Recontracted STO-3G ^b	3-21G	Exp. ^c
NH asym. stretch	4161(3745)	3991(3592)	3896(3506)	3545
NH sym. stretch	3956(3560)	3843(3459)	3769(3392)	3451
CH stretch	3549(3194)	3080(2772)	3187(2868)	2852
CO stretch	2121(1909)	2043(1839)	1909(1718)	1734
NH ₂ scissor	1943(1749)	1815(1634)	1805(1625)	1572
CH bend	1616(1454)	1636(1472)	1576(1418)	1378
CN stretch	1418(1276)	1390(1251)	1355(1220)	1255
NH ₂ rock	1079(971)	1061(955)	1157(1041)	1059
NCO bend	604(544)	627(564)	616(554)	565
CH out-of-plane	1219(1097)	1192(1073)	1210(1089)	1030
NH ₂ twist	783(705)	640(576)	644(580)	602
NH ₂ wagging	421(379)	320(288)	499(449)	289

^a In cm^{-1} ; values in parentheses have been scaled by a factor of 0.9.

^b For details see text.

^c Refs 32 and 33.

most closely to an N lone-pair orbital. Figure 3 shows plots for this orbital calculated with the three basis sets at the minimum energy structure calculated for each set.

In the case of the STO-3G set, we find the orbital to best resemble an N hybrid lone-pair orbital, which is not surprising in view of the non-planar structure. The plots of the orbitals calculated with the other two basis sets however, are rather different. Apart from small contributions of O atomic orbitals (not represented in the plots) we find these to have the character of 'banana bonds' between C and N, indicating the increased C—N bond order to be expected with the relatively large weight of the N^+C^- structure [see Figure 2(C)] as proposed by others.^{15,16,18}

As with the semi-empirical models, we have calculated the force fields and harmonic frequencies. Table 6 gives the calculated harmonic frequencies for all three methods with the molecule in the calculated minimum energy geometry. As before, we have also given the numbers used by scaling with a factor of 0.9. Not surprisingly, the regular STO-3G basis set gives the poorest rendering. The best overall results are obtained from calculations with the recontracted STO-3G basis set, especially with respect to the NH_2 wagging. Apparently, the potential well is best described by this basis set.

CALCULATIONS ON AMMONIA

As Carlsen *et al.*¹³ pointed out, there is an interesting parallel between the question of planarity of the amide unit and the inversion barrier of ammonia. In his terms,

the tendency of some basis sets to underestimate valence angles around N tends to carry over from the one system to the other. At first sight this might seem surprising. In the above we have discussed the inefficacy of several computational models in terms of the nitrogen p_x orbital and its overlap. Obviously, there can be no effective overlap between this orbital and any other in ammonia (interaction with virtual p_x orbitals on the hydrogen atoms being more of a formal possibility). However, one can intuitively understand the tendency of the electron lone-pair density in the planar state of ammonia to move away from the electrostatic repulsion of the sigma orbital hybrids.

This being true, the freedom allowed by the basis set in *ab initio* calculations will have an importance in describing the process of inversion around N in ammonia similar to that in determining the structure of the amide unit. Where in the case of formamide the energy difference between an N sp^3 lone pair and a 'polarized' p_x lone-pair orbital was important, we now are dealing with an sp^3 N lone pair in the minimum energy geometry and a diffuse p_x orbital (polarized away from the plane of the σ -hybrids in a sense) in the transition state. Therefore, we can again expect potential problems with a restricted basis to be reflected in the results of the semi-empirical methods. Here the MNDO method will keep the electron too close to the repulsive field of the σ -electrons, thereby raising the energy of the planar transition state and, consequently, the inversion barrier for ammonia.

With this in mind, Table 7 gives the results of the semi-empirical models for both unconstrained (C_{3v}

Table 7. MINDO/3, MNDO and AM1 results for ammonia^{a,b}

	MINDO/3		MNDO		AM1		Exp. ^c C_{3v}
	C_{3v}	D_{3h}	C_{3v}	D_{3h}	C_{3v}	D_{3h}	
Geometry:							
r_{HH}	1.627	1.724	1.601	1.701	1.626	1.691	1.624
r_{NH}	1.031	0.996	1.007	0.982	0.998	0.977	1.012
Vibrational spectrum: ^d							
a deform.	1116(1004)	—	1474(1327)	—	1141(1027)	—	950
e deform.	1518(1366)	1432(1289)	1849(1664)	1730(1557)	1765(1589)	1691(1522)	1627
a stretch	3554(3199)	3886(3497)	3634(3271)	3719(3347)	3535(3182)	3663(3297)	3337
e stretch	3577(3219)	3886(3497)	3573(3216)	3764(3388)	3465(3119)	3641(3277)	3444
Negative force constant (for D_{3h})	—	-0.2859	—	-0.6901	—	-0.3360	
Heat of formation	-9.14	-3.03	-6.05	5.54	-7.28	-3.02	
Difference between C_{3v} and D_{3h}	6.11		11.59		4.26		5.8 ^e

^a Distances are given in Å, vibrational frequencies in cm^{-1} , force constants in $mdyn \text{ \AA}^{-1}$ and heats of formation in $kcal \text{ mol}^{-1}$.

^b C_{3v} refers to the unconstrained ammonia molecule, D_{3h} implies the restriction of planarity.

^c Taken from Ref. 35.

^d In cm^{-1} ; values in parentheses have been scaled by a factor of 0.9.

^e Taken from Ref. 13.

Table 8. *Ab initio* Hartree-Fock results for ammonia with three different basis sets^{a,b}

Parameter	STO-3G		Recontracted STO-3G		3-21G		Exp. ^c C _{3v}
	C _{3v}	D _{3h}	C _{3v}	D _{3h}	C _{3v}	D _{3h}	
Geometry:							
r _{HH}	1.629	1.724	1.646	1.722	1.666	1.717	1.624
r _{NH}	1.033	1.006	1.016	0.994	1.003	0.991	1.012
Vibrational spectrum: ^d							
a deform.	1423(1281)	—	1113(1002)	—	868(781)	—	950
e deform.	2078(1870)	1868(1681)	1876(1689)	1773(1596)	1860(1674)	1771(1594)	1627
a stretch	3812(3431)	3994(3595)	3588(3229)	3794(3415)	3618(3256)	3724(3352)	3337
e stretch	4090(3681)	4338(3904)	3774(3397)	4044(3639)	3777(3399)	3938(3543)	3444
Negative force constant (for D _{3h})							
	—	-0.1467	—	-0.0861	—	-0.0476	
Total energy	-55.45542	-55.43767	-55.50531	-55.49802	-55.87220	-55.86964	
Difference between C _{3v} and D _{3h} ^e							
	0.01775(11.14)		0.00729(4.57)		0.00256(1.61)		(5.8) ^f

^a Distances are given in Å, vibrational frequencies in cm⁻¹, total energies in hartree atomic units and force constants in atomic units.

^b C_{3v} refers to the unconstrained ammonia molecule, D_{3h} implies the restriction of planarity.

^c Taken from Ref. 35.

^d In cm⁻¹; values in parentheses have been scaled by a factor of 0.9.

^e For comparison, the difference is also given in kcal mol⁻¹ in parentheses.

^f Taken from Ref. 13.

symmetry) and planar NH₃ (D_{3h} symmetry). It is immediately clear that the above predictions are borne out, as it is MNDO that gives the poorest rendering of the energy barrier with a value (11.6 kcal mol⁻¹) that is almost twice the experimental value (5.8 kcal mol⁻¹; Ref. 13). MINDO/3, on the other hand, comes very close with a value of 6.11 kcal mol⁻¹, while that calculated by AM1 is too small (4.26 kcal mol⁻¹). In keeping with this, the MNDO value for the one negative force constant in the force field of the transition state (-0.6901 mdyne Å⁻¹) is much more negative than the values of -0.2859 and -0.3360 mdyne Å⁻¹ for MINDO/3 and AM1, respectively.

With respect to the good results obtained with MINDO/3, we should again take care not to over-emphasize this fact since, as stated above, MINDO/3 is known to perform poorly with alkyl-substituted amines.^{7,8}

Regarding the *ab initio* calculations (Table 8), as expected we find an STO-3G-calculated value for the inversion barrier that is much too high (11.14 kcal mol⁻¹). The 3-21G model, on the other hand, grossly underestimates this value (1.61 kcal mol⁻¹), similarly to what has already been observed for the comparable 4-31G basis set [with a value of 0.4 kcal mol⁻¹ (Ref. 13)]. In contrast, we find that the recontracted STO-3G model gives a fair account of the barrier with a value of 4.57 kcal mol⁻¹. This may be a fortuitous result based on a coincidental cancellation of errors (note that a poorer basis set overestimates and an in principle better basis set under-

estimates the energy value). Nevertheless, the results indicate the enormous improvement obtained over STO-3G by a simple relaxation of the contraction scheme.

Obviously, these results agree with those of force field calculations on formamide with the same basis where a very good rendering of the harmonic frequency for inversion around N was also obtained. The harmonic frequencies resulting from force field calculations are also presented in Tables 7 (semi-empirical) and 8 (*ab initio*). Neither of the semi-empirically calculated vibrational spectra corresponds exceptionally well with the experimental data for the C_{3v} structure, but MINDO/3 at least predicts the correct order in which the several modes should appear. MNDO and AM1 reverse the order for the a and e stretching modes. For MNDO we further find a value for the symmetric deformation mode that is far too large, in keeping with the far too negative corresponding force constant for the D_{3h} structure and the related value for the inversion barrier that is too large.

Ab Initio calculations using the 3-21G and recontracted STO-3G basis sets give a fair rendering of the C_{3v} vibrational spectrum, whereas that obtained with the STO-3G basis set compares poorly, although the ordering is still correct.

COMPUTATIONAL DETAILS

All semi-empirical calculations were carried out with the program MOPAC 2.0,³⁹ modified to include the

AM1 method. Instead of the incorrect expressions from Ref. 6, those from Ref. 40 were taken. The program was run on an IBM 3090-200 computer. In all calculations the 'precise' option of the program was used.³⁹ Failure to do so was in many cases found to result in improper convergence often far from the actual geometric minimum owing to the shallowness of the potential well, depending on the starting geometry used.

The *ab initio* calculations were carried out using both the HONDO/5 program on the IBM 3090-200⁴¹ and the Gaussian 80 USCF program of Chandra Singh and Kollman taken from the TRIBBLE program set,⁴² running on a DEC microVAX 2000 workstation. Localized molecular orbitals were generated by a modified version of the Boys program,³⁵ and orbital contour plots were made from a numerical grid prepared by the MOPLOT program.⁴³

Force field analyses on all minima have shown these to be genuine. In order to ensure as much as possible the global character of the minima in the case of the formamide molecule, results from one model were always used as input geometry in the others and were found to lead the same model-dependent results upon convergence.

CONCLUSIONS

With respect to the use of Hartree-Fock models for the description of formamide and related systems, we can draw the following conclusions. Regarding the semi-empirical models, MNDO does not appear to be the method of choice for amide systems. It apparently produces artifacts in the prediction of molecular geometries and may well have problems with other properties in view of the rather poor description of π -overlap. These problems are caused, at least partly, by the definition of the atomic orbital basis set used. Both MINDO/3 and AM1 appear to be better model choices. Of these, one should probably prefer the AM1 model, as it is in general a better model than the relatively outdated MINDO/3, which is known to produce artifacts in amine systems. However, calculations with both MINDO/3 and AM1 on more aromatic amide systems are now under way. Preliminary results indeed seem to indicate that AM1 is better for routine modelling of a wide range of amide systems.

Unfortunately, a number of MNDO calculations on amide (peptide) systems have appeared in the literature. It is obvious that conclusions reached in these studies about, e.g. pyrimidalization angles, should be viewed with care, as they may very well be of an artificial nature.

Our *ab initio* results obviously agree with those obtained by others. It is striking, however, that the poor quality of the STO-3G results can be fully ascribed to the inflexibility in the basis set, as the smallest relaxation possible already gives dramatic improvements,

yielding results which, in some cases, even excel that of the 3-21G basis. This again indicates the dangers inherent in using STO-KG orbitals, which should only be used, if ever, when storage limits for the two-electron integrals are an issue and after careful analysis of parent molecules. From these data, they at least appear unfit for amide systems. It is worth noting that the reasons for the failure of both STO-3G and MNDO in these systems are rather similar, as both use an orbital exponent for the valence p orbital which is too contracted as it has been given the same value as the orbital exponent for the valence s orbital in N, C and O.

Conclusions reached for formamide are mostly valid for the ammonia systems also. In particular we can conclude that for inversions around N, AM1 should be used rather than MNDO for the same reasons as for the amides.

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