Planarity of *N,N*-Dimethylacetamide, (CH$_3$)$_2$NC(O)CH$_3$

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Abstract: The molecular structure of N,N-dimethylactamide, (CH$_3$)$_2$NC(O)CH$_3$, was determined by gas electron diffraction (GED). A rigid model results in a vibrationally averaged structure with nonplanar configuration at nitrogen and with the sum of the nitrogen bond angles $\sum\alpha_N = 354.1(17)°$. The GED intensities can be fitted equally well with a dynamic model with either a quartic potential (planar equilibrium structure) or a very flat double-minimum potential (pseudoplanar structure) for the out-of-plane motion. Theoretical calculations predict either planar (HF/3-21G and B3PW91/6-311G(2d)) or slightly nonplanar equilibrium structures (HF/3-21G$^{(*)}$, MP2/6-31G*, and MP2/6-311G*). The following skeletal parameters (uncertainties are 3σ values) were derived from the GED analysis: C1=O = 1.226(3) Å, C1−C2 = 1.527(6) Å, N−C1 = 1.368(5) Å, N−C3 = N−C4 = 1.453(3) Å, N−C1=O = 121.0(7)°, N−C1−C2 = 115.9(9)°, C1−N−C3 = 123.8(13)°, C1−N−C4 = 117.8(11)° (C3 and C4 are anti and syn to oxygen, respectively, and the N−C3 and N−C4 bond lengths were assumed to be equal).

Introduction

The question whether a molecule possesses an exactly planar or slightly nonplanar equilibrium structure is often difficult to answer by experiments and/or by theory. A planar molecule is characterized by a single-minimum potential for the out-of-plane motion, a nonplanar molecule by a double-minimum potential with a certain barrier at the planar configuration. The distinction between planar and nonplanar structures is especially difficult for "pseudoplanar" molecules, where the potential barrier lies below the vibrational ground state. Two circumstances complicate the interpretation of solid-state diffraction data: (1) Intermolecular interactions may distort a slightly nonplanar structure to planarity or vice versa. (2) *Average atomic positions*, which are determined in single-crystal analyses, fake a planar structure, even if the molecule is pseudoplanar or slightly nonplanar. Thus, X-ray or neutron diffraction analyses are not well suited to answer this question. Gas electron diffraction (GED) studies determine *average interatomic distances* that fake a nonplanar configuration for a planar equilibrium structure, if a "rigid" model is applied. The resulting degree of nonplanarity depends on the amplitude of the out-of-plane vibrations. In a dynamic analysis large-amplitude vibrations can be modeled and, in principle, it is possible to obtain information about the shape of the potential function for the out-of-plane motion. Microwave spectroscopy (MW) is most likely to deliver a correct answer to this problem, provided that the relevant vibrationally excited states are included in the analysis. Beside these various experimental techniques, theoretical methods can be applied to calculate the potential function for the out-of-plane motion. However, the shape of this potential may depend strongly on the computational procedure.

A typical example that demonstrates the difficulties in answering the question about planarity or nonplanarity of a molecule by experiments and/or by theory is formamide, H$_2$NC(O)H. X-ray crystallography results in a structure that is planar within the estimated uncertainties.[1] It is known, however, that positions of the hydrogen atoms are not well determined by this method. On the other hand, a neutron diffraction investigation of

acetamide, H$_2$NC(O)CH$_3$, reports a slightly pyramidal NH$_2$ group.[2] Planarity of formamide had to be assumed in the GED analysis,[3] since nonbonded H···H distances are inaccurately determined by this method. MW data have been interpreted differently over a period of 30 years. Kurland and Wilson[4] concluded from H/D substitution effects that the molecule was planar. Costain and Dowling[5] found that the vibrational satellites in the MW spectrum are consistent only with a nonplanar equilibrium structure. Brown et al.[6] demonstrated that experimental MW and infrared data can be reproduced with a semi-rigid-bender model and a highly anharmonic single-minimum potential for the out-of-plane vibration. The importance of formamide for structural chemistry and biochemistry stimulated also a large number of theoretical calculations. The most recent theoretical investigation was reported by Fogarasi and Szalay,[7] who also give an extensive review of previous studies. The conclusion is that HF approximation and Density Functional Theory result in planar and nonplanar structures, depending on the basis sets used. Inclusion of electron correlation tends to favor nonplanarity, if the basis sets are not sufficiently large. However, electron correlation calculations (MP2, MP3, CCSD, or CCSD(T)) with a "correlation consistent" polarized valence triple-ζ basis set (including f-functions) result in an exactly planar configuration of formamide.

In the present paper we report a GED study of *N,N*-dimethylacetamide, (CH$_3$)$_2$NC(O)CH$_3$ (DMA), which is supported by theoretical calculations. The prime interest concerns the planarity or nonplanarity of the bonds around nitrogen. To our knowledge, no X-ray or neutron diffraction investigation for the parent compound has been reported and no gas-phase structure determination by MW or GED has been performed. A HF/6-31G* calculation[8] results in a pyramidal configuration

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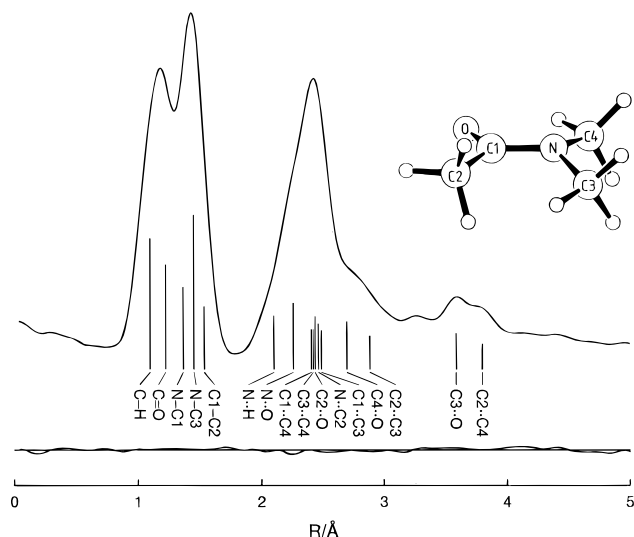
Figure 1. Experimental radial distribution function and difference curve. The positions of important interatomic distances are shown by vertical bars.

around nitrogen with the sum of the nitrogen bond angles $\sum\alpha_N$ = 358.0° and a barrier of 70 cal mol^{-1} for the planar structure. Similar calculations with slightly different basis sets[9] (HF/6-31G** and HF/DZP, DZP is a nonstandard basis set) lead to almost, but not exactly, planar structures.

Theoretical Calculations for Dimethylacetamide

The aim of these calculations is not to find a final answer to the question of planarity of DMA, but to support the analysis of the GED intensities. This implies the calculation of vibrational amplitudes and the choice of an adequate molecular model. Geometry optimizations were performed with ab initio calculations at various levels and with a density functional method (B3PW91/6-311G(2d)) with the GAUSSIAN 94 program system.[10] The HF/3-21G method predicts an exactly planar structure of $(CH_3)_2NC(O)CH_3$. This is not surprising, since HF calculations with split valence basis sets and without polarization functions at nitrogen tend to overestimate bond angles at nitrogen and, thus, favor planarity. If polarization functions are included at the nitrogen atom only, the HF approximation (HF/3-21G$^{(*)}$) leads to a nonplanar structure with dihedral angles ϕ_1(C2C1NC3) = 9.9° and ϕ_2(OC1NC4) = −6.1° (C3 and C4 are anti and syn to oxygen, respectively, see Figure 1 for atom numbering). The sum of the nitrogen bond angles $\sum\alpha_N$ decreases from 360° to 358.2°, and the barrier to inversion is predicted to be 290 cal mol^{-1}. The acetyl group deviates only very little from planarity.

If electron correlation is taken into account at the MP2 approximation (MP2/6-31G*), a slighly nonplanar structure with ϕ_1(C2C1NC3) = 4.9°, ϕ_2(OC1NC4) = −3.1°, $\sum\alpha_N$ = 359.5°, and an inversion barrier of only 1.2 cal mol^{-1} is obtained. With increasing basis sets (MP2/6-311G(2d)) the optimized structure tends further toward planarity and the inversion barrier dereases to 0.13 cal/mol^{-1}. The existence of minima and maxima in the energy hyperface was checked by frequency calculations.

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The different values for ϕ_1 and ϕ_2 that are predicted for nonplanar configurations demonstrate that the out-of-plane motion is a combination of inversion at nitrogen and rotation around the N−C1 bond. An exactly planar configuration around nitrogen is predicted by the hybrid method B3PW91/6-311G(2d). The geometric parameters of selected computational methods are listed in Table 1 together with the experimental values. For the two planar structures, the lowest frequency, which corresponds primarily to the out-of-plane vibration at nitrogen, is predicted at 96 (HF/3-21G) and 72 cm^{-1} (B3PW91/6-311G(2d)). The Cartesian force constants obtained with the hybrid method were converted to symmetry force constants, and vibrational amplitudes were calculated with the program ASYM40.[11] The amplitudes are included in Table 2.

GED Analysis

The radial distribution function (RDF) was obtained by Fourier transformation of the molecular intensities (Figure 1). Preliminary geometric parameters, which were derived from the RDF, were refined by least-squares fitting of the molecular intensities. The intensities were modified with a diagonal weight matrix and known scattering factors were used.[12] Two models were applied in the structure refinements: a rigid model with small-amplitude vibrations only and a dynamic model with a large-amplitude out-of-plane vibration at nitrogen. The following constraints based on the theoretical calculations were made in the least-squares analyses: (1) Both N−CH$_3$ bond lengths were set equal. (2) Deviations from planarity are described by the dihedral angles ϕ_1(C2C1NC3) and ϕ_2(OC1NC4). Since it was impossible to refine both angles independently, the correlation was expressed as $\phi_2 = -\alpha\phi_1$. Ab initio calculations yield $\alpha \approx 0.62$ for nonplanar structures, and this value was used in the GED analysis. Variation of α by ± 0.2 had no effect on the agreement factor of the least-squares analysis. (3) C_{3v} symmetry was assumed for the three CH$_3$ groups, and all C−H bond lengths and all HCH bond angles were set equal. The tilt angles between the C_3 axes and N−CH$_3$ or C−CH$_3$ bond directions were constrained to the B3PW91 values. (4) One C−H bond of the acetyl CH$_3$ group was assumed to eclipse the C=O bond. (5) The amide CH$_3$ groups were allowed to rotate around the N−C bonds in opposite directions τ(N−C4) = -τ(N−C3). Vibrational amplitudes were collected in groups according to distances and calculated values. Amplitudes that cause high correlations or that are badly determined in the GED experiment were fixed to the theoretical values. With the above assumptions 12 geometric parameters p_i and eight vibrational amplitudes l_k were refined simultaneously for the rigid model. The following correlation coefficients had values larger than |0.7|: $p_6/p_{12} = -0.81$, $p_8/p_{12} = -0.84$, $p_3/l_2 = 0.71$, $p_6/l_3 = 0.78$, $p_8/l_3 = -0.79$, $p_8/l_6 = -0.83$, $p_{12}/l_4 = -0.72$, and $p_{12}/l_6 = 0.87$. The results for the rigid model are given in Tables 1 and 2.

This structure that represents a vibrational average deviates considerably from planarity with the sum of the angles at nitrogen, $\sum\alpha_N = 354.1(17)°$. If the skeleton is constrained to planarity, the fit of the experimental molecular intensities becomes considerably worse. The agreement factor for the intensities of the long nozzle-to-plate distance, R_{50}, increases by 75% (from 0.028 for the nonplanar to 0.049 for the planar structure). The result of this rigid analysis can be interpreted either as a planar equilibrium structure with a large-amplitude out-of-plane vibration or as a nonplanar equilibrium structure.

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Table 1. Experimental and theoretical geometric parameters of DMA

	GED[a] rigid		HF/3−21G	HF/3−21G[(*)]	MP2/6−31G*	MP2/6−311G(2d)	B3PW91/6−311G(2d)
C−H	1.101(3)	p_1	1.082	1.082	1.093	1.093	1.091
C=O	1.226(3)	p_2	1.222	1.223	1.236	1.226	1.219
N−C1	1.368(5)	p_3	1.362	1.357	1.375	1.368	1.369
N−C3	1.453(3)	p_4	1.459	1.454	1.451	1.444	1.443
N−C4	1.453(3)	p_4	1.461	1.454	1.451	1.444	1.443
C1−C2	1.527(6)	p_5	1.519	1.522	1.519	1.513	1.515
N−C1=O	121.0(7)	p_6	122.0	122.2	122.0	122.0	121.8
N−C1−C2	115.9(9)	p_7	117.5	117.3	117.4	117.4	117.7
C1−N−C3	123.8(13)	p_8	126.0	124.6	125.4	125.5	125.4
C1−N−C4	117.8(11)	p_9	118.9	118.4	118.9	119.2	119.0
$\Sigma\alpha(N)$	354.1(17)		360.0	358.2	359.5	359.96	360.0
H−C−H	108.9(7)	p_{10}	108.9	109.1	108.8	108.4	108.3
tilt(C−CH$_3$)	3.4[c]		2.9	2.7	3.5	3.3	3.4
tilt(N−CH$_3$)	0.5[d]		0.1	0.4	0.3	0.3	0.5
τ_1(N−C3) [b]	19(12)	p_{11}	0.0	36.5	12.3	1.9	0.0
τ_2(N−C4)[b]	−19(12)	p_{11}	0.0	−19.9	−7.4	−1.3	0.0
ϕ_1(C2C1NC3)	18(3)	p_{12}	0.0	12.6	4.9	0.8	0.0
ϕ_2(OC1NC4)	−11(2)	p_{12}	0.0	−7.9	−3.1	−0.5	0.0

[a] r_a values in Å and deg. Uncertainties are 3σ values. For atom numbering see Figure 1. [b] Torsional angle of the CH$_3$ group around the N−C bond. For $\tau = 0°$ one C−H bond eclipses the N−C1 bond. [c] Not refined; tilt of the acetyl CH$_3$ group toward the C=O bond. [d] Not refined, tilt of the amino methyl groups away from each other.

Table 2. Interatomic Distances and Vibrational Amplitudes from GED and ab Initio Calculations

	distance	amplitudes (GED)[a]		calcd[b]
C−H	1.10	0.071(3)	l_1	0.078
C=O	1.23	0.039[c]		0.039
N−C1	1.37	0.045[c]		0.045
N−C3	1.45	0.050(4)	l_2	0.049
C1−C2	1.53	0.053[c]		0.053
N···O	2.26	0.051[c]		0.051
C1···C4	2.41 ⎤			0.061
C2···O	2.43 ⎥	0.072(4)	l_3	0.060
N···C2	2.46 ⎥			0.063
C1···C3	2.50 ⎦			0.062
O···C4	2.69 ⎤	0.094(23)	l_4	0.083
C2···C4	2.89 ⎦			0.089
O···C3	3.59 ⎤	0.075(9)	l_5	0.061
C2···C4	3.79 ⎦			0.069
(X···H)$_{gauche}$	2.41−3.00	0.23(9)	l_6	0.194
(X···H)$_{trans}$	3.06−3.38	0.12(3)	l_7	0.106
Y···H	3.30−3.96	0.26(10)	l_8	0.207
C···H	4.03−4.54	0.24[c]		0.240

[a] Values in Å, uncertainties are 3σ values. For atom numbering see Figure 1. X = C or N, Y = C or O. [b] Calculated from the B3PW91/6-311G(2d) force field. Mean values are given for amplitudes involving hydrogen.
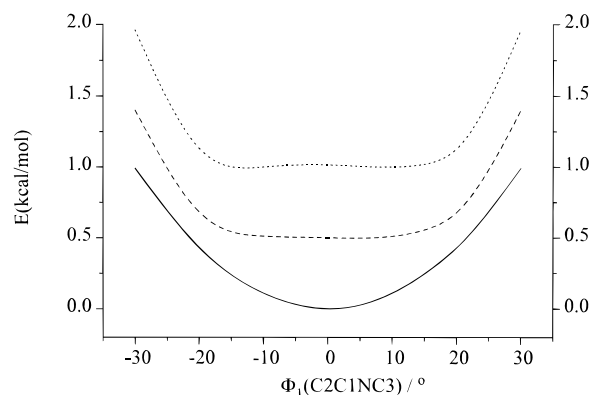

Figure 2. Potential functions for the out-of-plane motion which were used in the dynamic GED analyses: (−) $V = k_2\phi_1^2$, $k_2 = 3.6$ kcal mol^{-1} rad^{-2}; (---) $V = k_4\phi_1^4$, $k_4 = 12$ kcal mol^{-1} rad^{-4}; (···) $V = V_o[1 - (\phi_1/\phi_1^e)^2]^2$, $V_o = 15$ cal mol^{-1}, $\phi_1^e = 10°$. The curves are shifted by 0.5 kcal mol^{-1}.

The former case corresponds to a flat single-minimum potential for the out-of-plane motion, the latter to a double-minimum potential. It was attempted to distinguish between these two possibilities by applying a dynamic model with different potential functions. This motion is described by the dihedral angle ϕ_1. The dihedral angle $\phi_2 = -\alpha\phi_1$ and the torsions around the N−C bonds $\tau_1 = \beta\phi_1$ and $\tau_2 = -\beta\phi_1$ were coupled to ϕ_1. The constants α and β were set to 0.62 and 1.0, respectively. The value for β is justified by the rigid model analysis, where ϕ_1 and τ_1 are equal within their experimental uncertainties. Variation of these coupling constants α by ±0.2 and β by ±0.5 had no effect on the quality of the fit. The molecular intensities were calculated as a superposition of structures with ϕ_1 varying from 0° to 40° in steps of 10°. The intensities of the individual structures were weighted by a Boltzmann factor exp(-V/RT). Single-minimum potentials were represented by quadratic ($V = k_2\phi_1^2$) or quartic ($V = k_4\phi_1^4$) functions and double-minimum potentials by the expression $V = V_o [1 - (\phi_1/\phi_1^e)^2]^2$. V_o is the barrier at the planar configuration ($\phi_1 = 0°$) and ϕ_1^e is the out-

of-plane dihedral angle of the equilibrium structure. The various constants that describe the potential functions could not be refined in the least-squares analyses. Refinements with different fixed values were performed, and the quality of the fit was judged by the agreement factor R_{50}. With a quadratic potential function the best fit was worse ($R_{50} = 0.036$ for $k_2 = 3.6$ kcal mol^{-1} rad^{-2}) than that for the rigid model ($R_{50} = 0.028$). Equally good fit with $R_{50} = 0.029$ was obtained for a quartic potential with $k_4 = 12$ kcal mol^{-1} rad^{-4} and with a very flat double-minimum potential with $V_o = 15$ cal mol^{-1} and $\phi_1^e = 10°$. The three potential functions are shown in Figure 2. In the case of the double-minimum potential, other combinations of V_o and ϕ_1^e, such as $V_o = 0.6$ cal mol^{-1} and $\phi_1^e = 5°$, reproduce the experimental intensities as well as the two values given above. The potential curves, however, are very similar. Double-minimum potentials with $V_o > 100$ cal mol^{-1} can definitely be excluded.

From the dynamic analysis of the GED data we can conclude that DMA possesses either a planar equilibrium structure with a large-amplitude out-of-plane vibration or a pseudoplanar structure whose potential barrier lies below the vibrational ground state. The predicted out-of-plane vibration of 96 (HF/3-21G) or 72 cm^{-1} (B3PW91/6-311G(2d)) corresponds to $h\nu_o/2 = 140$ or 100 cal mol^{-1}, and both values are higher than the

experimental barrier of 15 cal mol^{-1}. This experimental result is in agreement with most theoretical calculations, which predict either a planar equilibrium structure (HF/3-21G and B3PW91/6-311G(2d)) or a pseudoplanar structure with barriers below the vibrational ground state. Only the HF/3-21G$^{(*)}$ method, which uses polarization functions exclusively for nitrogen, predicts a higher barrier of 290 cal mol^{-1}. However, a clear-cut decision whether this molecule possesses an exactly planar equilibrium configuration or a pseudoplanar structure is not possible, neither by the GED analysis nor by the theoretical calculations.

A summary of experimental structural data for $R_1R_2NC(O)R_3$ derivatives with R_1, R_2, and $R_3 = H$ or CH_3 shows that the question of planarity or nonplanarity of these compounds cannot be answered unambiguously. As mentioned in the introduction, MW spectroscopy and high-level electron correlation calculations suggest very strongly that formamide, $H_2NC(O)H$, possesses a planar equilibrium structure. A neutron diffraction study at 23 K of acetamide, $H_2NC(O)CH_3$, results in a slightly pyramidal configuration at nitrogen.[2] In GED studies of acetamide,[13] *trans-N*-methylformamide, $CH_3HNC(O)H$,[14] and *trans-N*-methylacetamide, $CH_3HNC(O)CH_3$,[15] the question of planarity could not be answered and planar configuration at nitrogen was assumed in the analyses. The degree of nonplanarity of *N,N*-dimethylformamide, $(CH_3)_2NC(O)H$, ($\phi_1 = 11(4)°$, $\phi_2 = -16(5)°$, and $\sum\alpha_N = 357.0(8)°$ [16]), which was obtained from a GED analysis with a rigid model, is similar to that obtained for the rigid model of DMA. No dynamic analysis has been performed for this compound.

In conclusion we can state that the GED intensities for DMA can be reproduced equally well with dynamic models that correspond either to a planar or to a pseudoplanar equilibrium structure. Knowing, however, that formamide possesses most likely a planar equilibrium structure, we expect such planar structures also for the various methyl-substituted derivatives. Since substitution of the amino hydrogen atoms by methyl groups in
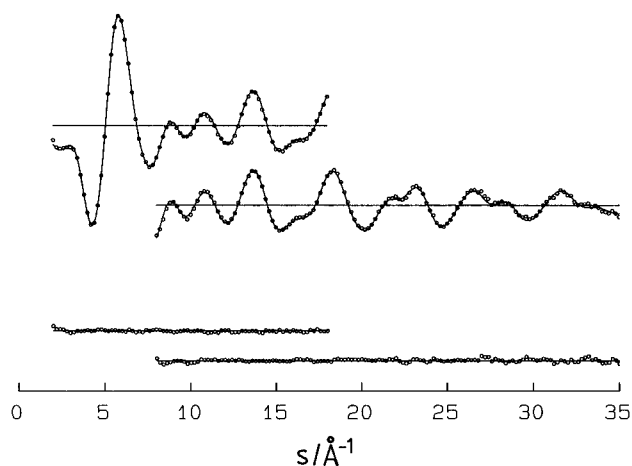

Figure 3. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and differences.

all known cases leads to an increase of the nitrogen bond angles, such a substitution in planar formamide makes planar configurations highly likely also for DMA and for the other $R_1R_2NC(O)R_3$ derivatives with R_1, R_2, and $R_3 = H$ or CH_3.

Experimental Section

A commercial sample (ALDRICH) with a purity >99% was used. The electron diffraction intensities were recorded with a Balzers Gasdiffraktograph[17] at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of ca. 60 kV. The sample was heated to 45 °C and the nozzle to 50 °C. The photographic plates (KODAK Electron Image plates 13 × 18 cm) were analyzed with the usual methods.[18] Averaged molecular intensities in the *s* ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 3.

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