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Molecular structure of *N*-azidomethyl-*N*,*N*-dimethylamine according to gas-phase electron diffraction data and quantum-chemical calculations

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As found experimentally (gas-phase electron diffraction) and theoretically, the equilibrium conformers of *N*-azidomethyl-*N*,*N*-dimethylamine are stabilized by anomeric effects.

Organic azides can be used for the preparation of various materials, including potentially explosive substances.[1–6] They are also of interest for click chemistry.[7,8]

The molecular conformation of *N*-azidomethyl-*N*,*N*-dimethylamine (AMDMA) is considerably affected by an anomeric effect. The stabilizing interaction between the lone pair of N_{amino} and the antibonding σ* orbital of the $C_{methylene}$–N_{azido} bond leads to a strong preference for the *anti* orientation of the $C_{methylene}$–N_{azido} bond relative to the lone pair due to the maximum orbital interaction lone pair of N_{amino} → σ* $C_{methylene}$–N_{azido}, and this corresponds to a *gauche* orientation of the $C_{methylene}$–N_{azido} bond relative to C_{Me}–N_{amino}.[9] In addition to the stabilization of the *gauche* conformer, this orbital interaction also has an impact on bond lengths.[10] Compared to molecules without an anomeric effect, a shortening of the $C_{methylene}$–N_{amino} bond and a lengthening of the $C_{methylene}$–N_{azido} bond are expected.

AMDMA of 98% purity was obtained by a reaction between *N*-methoxymethyl-*N*,*N*-dimethylamine and commercial trimethylsilyl azide as an azide group donor:[11]

$$\mathrm{Me_2NCH_2OMe + Me_3SiN_3 \rightarrow Me_2NCH_2N_3 + Me_3SiOMe.}$$

The theoretical calculations were performed using the GAUSSIAN 03 program package running under the Linux operating system.[12]

The rotations around the N(1)–C(2) and C(2)–N(3) bonds were considered (Figure 1). The search for low-energy conformers was first performed with the two-dimensional scan of the φ_1[C(6)N(1)C(2)N(3)] and φ_2[N(1)C(2)N(3)N(4)] torsion angles with 10° steps. The potential energy surface derived with the MP2 method and 6-311+G(d,p) basis set (Figure 2) shows the presence of three conformers (*gauche-gauche*, *gauche-anti* and *anti-anti*, Figure 1), one of which possesses C_s symmetry, and the others, C_1. The calculated molecular force fields confirmed that the optimal structures obtained correspond to minima on the potential energy surface.

At the second step, we searched for all possible stable conformers by a series of one-dimensional potential energy scans. The three optimized minima (*gauche-gauche*, *gauche-anti* and *anti-anti*) were used as starting points for these scans. The energy profiles as functions of the torsional angles φ_1[C(6)N(1)C(2)N(3)] and φ_2[N(1)C(2)N(3)N(4)] were determined by the one-dimensional scanning of angles from 0° to 360° with 10° steps, while the remaining molecular structure parameters were optimized. From the calculated torsional profiles, the two new stable conformers (*anti-gauche* and *anti-gauche*-2, Figure 1) were detected. Calculated vibrational frequencies for these structures were plausible, confirming that these conformers corresponded to stationary points. The positions of the determined minima corresponding to the higher energy conformers (*anti-gauche* and *anti-gauche*-2) are displayed in Figure 2.

The conformational vapour composition was estimated from the relative Gibbs free energies. Thus, the *gauche-gauche* conformer

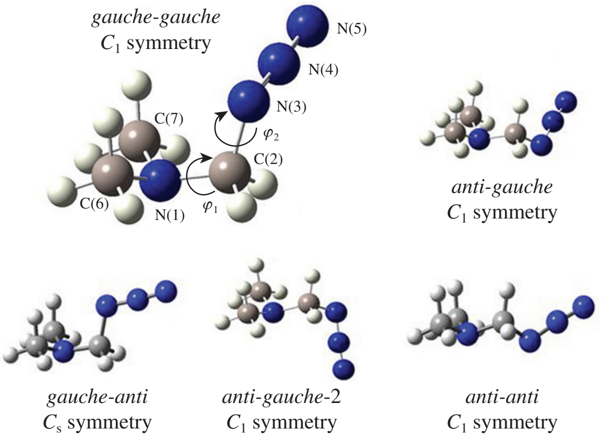

Figure 1 Five stable conformers of AMDMA.

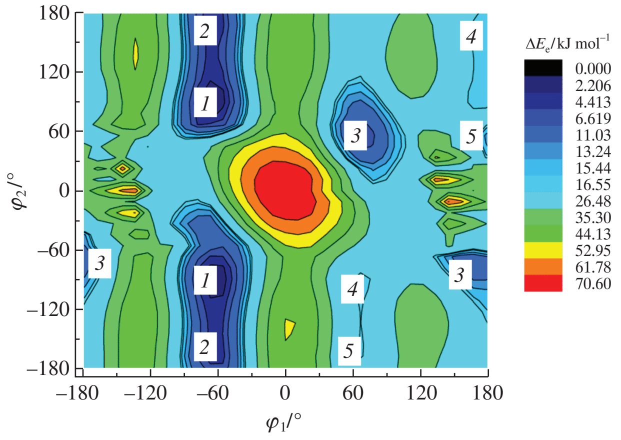

Figure 2 MP2/6-311+G(d,p) potential energy surface as a function of torsional angles φ_1[C(6)N(1)C(2)N(3)] and φ_2[N(1)C(2)N(3)N(4)]. Five minima *(1)*–*(5)* are located on this surface. The minima correspond to *(1)* *gauche-gauche*, *(2)* *gauche-anti*, *(3)* *anti-anti*, *(4)* *anti-gauche*-2 and *(5)* *anti-gauche* conformers. ΔE_e (kJ mol^{-1}) is the relative electronic energy.

Table 1 Molecular structure of the *gauche-gauche* conformer of AMDMA obtained by gas-phase electron diffraction and quantum-chemical calculations.

Parameter	GED mixture of conformers $r_{h1}(\angle_{h1})^a$	MP2(full)/aug-cc-pVTZ $r_e(\angle_e)$
r[N(1)–C(2)]	1.426(2) Å^{a1}	1.419 Å
r[C(2)–N(3)]	1.511(2) Å^{a1}	1.502 Å
r[N(3)–N(4)]	1.232(2) Å^{a2}	1.226 Å
r[N(4)–N(5)]	1.154(2) Å^{a2}	1.149 Å
∠[N(3)C(2)N(1)]	115.1°^{b}	114.2°
∠[N(4)N(3)C(2)]	116.2(13)°	114.8°
∠[N(5)N(4)N(3)]	179.5(28)°	174.5°
φ_1[C(6)N(1)C(2)N(3)]	–63.0°^{b}	–62.0°
φ_2[N(4)N(3)C(2)N(1)]	–89.3°^{b}	–92.8°
φ[C(7)N(1)C(2)N(3)]	64.5°^{b}	–63.4°
φ[N(5)N(4)N(3)C(2)]	–170.6°^{b}	–172.6°
Conformer	Mole fraction (%)	
gauche-gauche	70	
gauche-anti	12	
anti-gauche	18	
R_{total}	5.5	

^{a}Values in parentheses are three times the standard deviations. The same numeric superscripts indicate that these parameters were refined in one group; differences between parameters in the group were assumed at the values from MP2(fc)/6-311+G(d,p) calculation. ^{b}Assumed at the value from MP2(fc)/6-311+G(d,p) calculation.

should be prevailing with 42.9–50.2% (B3LYP) or 59.2–62.8% (MP2). The concentration of the *gauche-anti* conformer is significant with 46.0–54.9% (B3LYP) and 30.3–31.7% (MP2). The *anti-anti* conformer is predicted to possess an abundance of 1.9–3.8% (B3LYP) or 3.9–9.2% (MP2). The predicted total abundance of *anti-gauche* and *anti-gauche*-2 conformers was about 1%. The fitting of gas-phase electron diffraction (GED) intensities was carried out using the UNEX program.[13]

Thus, in the first instance of GED study, we assumed that the vapour consisted of only one species – a *gauche-gauche* conformer, *gauche-anti* conformer, or *anti-anti* conformer. The theoretical intensities were calculated separately for each conformer. The reasonable agreement between experimental and theoretical data was achieved just for the *gauche-gauche* conformer.

At the second step, the model of the mixture of three conformers was tested. The coefficients corresponding to conformer mole fractions were changed discretely in the ranges of 0.40–1.00, 0.00–0.60 and 0.00–0.20 (for *gauche-gauche*, *gauche-anti* and *anti-anti* conformers, respectively). The minima were achieved for the mole fractions of 0.70, 0.12 and 0.18, respectively.

Then, we carried out the GED structural analysis with a fixed conformer composition (70, 12 and 18% for *gauche-gauche*, *gauche-anti* and *anti-anti* conformers, respectively). Differences in the bond lengths, bond angles and vibrational amplitudes of the conformers were set to the MP2(fc)/6-311+G(d,p) values. The experimental and calculated geometric parameters of the *gauche-gauche* conformer are given in Table 1. The anomeric effect is reflected in a shorter C_{Me}–N_{amino} bond in AMDMA [1.426(2) Å], as compared to that in $MeNH_2$[14] [1.471(3) Å], $NH_2CH_2CH_2NH_2$[15] [1.474(5) Å] or $Me_2CHNHCHMe_2$[16] [1.470(4) Å]. The $C_{methylene}$–N_{azido} bond in AMDMA [1.511(2) Å] is longer than that in MeN_3[17] [1.468(5) Å], $H_2C{=}CHCH_2N_3$[18] [1.475(15) Å] or $MeC{\equiv}CCH_2N_3$[19] [1.474(15) Å]. Figure 3 shows the experimental and theoretical radial distribution curves with difference curves.

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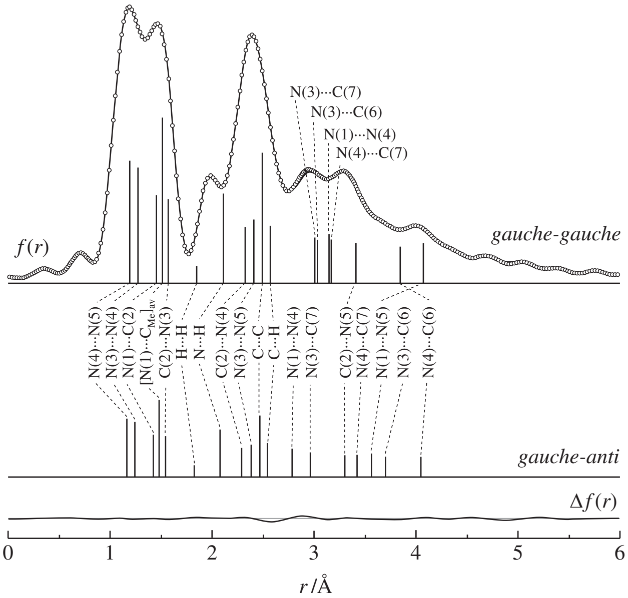

Figure 3 Experimental (open circles) and theoretical (solid line) radial distribution curves $f(r)$ with difference curves $\Delta f(r)$ for a model with $R_f = 5.5\%$. Distance distribution for these conformers is indicated by vertical bars. The lengths of these bars are proportional to the distance weights.

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