Molecular structure of tris(aziridino)methane in the gas phase and crystalline state

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Tris(aziridino)methane has the preferred *gauche–gauche–gauche* conformation of C_3 symmetry unlike the *anti–anti–anti* conformation of C_{3v} symmetry in the crystal.

Molecules possessing C_3 symmetry are attractive test objects in many areas of chemistry,[1] including the analysis of conformational equilibria, stereodynamics and stereoelectronic effects. Well-known examples related to the title compound are tris(dialkylamino)methanes,[2] trialkoxymethanes,[3] trialkylmethanes,[4] trialkylamines,[5] triarylmethanes and triarylamines.[6] Note that some of these molecules occur preferably in other symmetry forms than the C_3 symmetry.

We studied the molecular structure of tris(aziridino)methane† **1** by gas electron diffraction,‡ *ab initio* calculations§ and X-ray diffraction.¶ This compound is of interest because, in contrast to tris(dialkylamino)methanes,[2] inversion of the aziridine nitrogen in **1** is hindered, and the electron-donor ability of its lone pair is weakened. Nevertheless, it was found that the participation of stereoelectronic effects enhances the nitrogen inversion when the σ-acceptor X is placed in the α-position (>N–C– X).[8] It should be noted that the stereoelectronic (anomeric) effect was interpreted[8(a)] in terms of the $n_{(N)}$–σ^*_{CX} interaction for the first time. It was shown[8(c)] that the nitrogen inversion is facilitated only in the case of *anti*-periplanar orientation of the aziridine lone pair at the nitrogen atom relative to the CX bond. The barrier to the nitrogen inversion decreases on going from aziridinodimethylaminomethane (18.3 kcal mol^{-1})[8(c)] to **1** (17.1 kcal mol^{-1})[7(c)] and bis(aziridino)methoxymethane (16.5 kcal mol^{-1}).[7(c)] Therefore, it is reasonable to expect that the conformation of **1** is stabilised by the anomeric effect.

Conformational analysis of **1** is rather complicated because there are three rotating groups attached to a single C–H centre. The position of each of aziridine rings can be defined by the torsional angle φ between the lone pair†† and the central C–H bond, where $\varphi = 0°$ corresponds to the eclipsed position of the lone pair and the C–H bond. For each of aziridine rings, there are three likely staggered positions labeled as *a*, *g* and *g*$^-$ (Figure 1). With 3 groups, the molecule has 3×3×3 = 27 staggered conformations, which reduce to 7 since the remaining 20 are either degenerated or enantiomeric forms (Table 1). The statistical weight of the conformations varies from 6 to 1 when the symmetry decreases from C_{3v} to C_1.

According to *ab initio* calculations, *g*,*g*,*g* is the most stable conformation, as illustrated in Figure 2. The energy difference between the *g*,*g*,*g* conformation and the next *a*,*g*,*g* lower in energy is equal to 2.70, 1.93 and 2.14 kcal mol^{-1} as found by

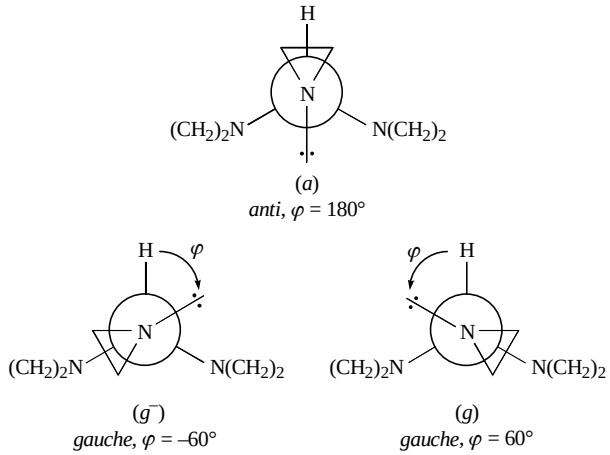

Figure 1 Staggered conformations of tris(aziridino)methane.

† The sample of **1** was synthesised using the published procedure[7(a)] and distilled in a vacuum, bp 50 °C (1 mmHg), mp 28.0–28.5 °C. ^{1}H NMR (C_6D_6, 40 °C) δ: 1.40 (br. s, 6H, *cis*-H_a of the ring relative to N–CH), 1.56 (br. s, 6H, *trans*-H_b of the ring relative to N–CH), 2.56 (s, 1H, HC). ^{13}C NMR (C_6D_6, 40 °C) δ: 22.80 (ddm, CH_2N, $^1J_{CH_a}$ 165.5 Hz, $^1J_{CH_b}$ 176.0 Hz), 99.30 (ddm, CH, ^1J 155.3 Hz).[7(c)] A sample of **1** was placed in a sealed evacuated (1 Torr) NMR tube; next, the sample was sublimed to the opposite cold end of the tube. Then the tube 50 mm long was cut off and used in electron diffraction experiment. An ampoule containing well-formed crystals was cooled with liquid nitrogen, then opened and a single crystal suitable for X-ray study was chosen.

‡ The electron-diffraction photographs were obtained on an EG-100M unit with an accelerating voltage of 50 kV for two nozzle–photoplate distances (169.5 and 375.0 mm) at 20 °C. The electron wavelength was calibrated by the internal gas standard method[9] using the data for benzene.[10] According to our estimations, the scale error did not exceed 0.07%. The tracing of the plates and the data reduction are described elsewhere.[11] Total scattering intensities were obtained in the ranges s = 2.25–16.875 and 8.25–40.0 Å^{-1}.

§ *Ab initio* quantum-chemical calculations for **1** were carried out by the following methods: HF/6-31G**, B3PW91/6-31G* and MP2/6-31G** using the programs SPARTAN 5.1[12(a)] and GAUSSIAN 98.[12(b)]

¶ *Crystallographic data for* **1** at 110 K: crystals of $C_7H_{13}N_3$ are hexagonal, space group $P6_3$, $a = b$ = 13.249(3) Å, c = 7.846(3) Å, V = = 1192.8(5) Å^3, Z = 6, M = 139.20, d_{calc} = 1.163 g cm^{-3}, μ(MoKα) = = 0.074 mm^{-1}, F(000) = 456. Intensities of 4904 reflections were measured with a Smart 1000 CCD diffractometer at 110 K [λ(MoKα) = = 0.71072 Å, ω-scans with a 0.4° step in ω and 20 s per frame exposure, $2\theta < 55°$] and 1799 independent reflections (R_{int} = 0.0598) were used in further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.2135 and GOF = 1.031 for all independent reflections [R_1 = 0.0784 was calculated against F for 1165 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2000. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/66.

†† We assumed that the C–N(CH_2)$_2$ unit and the lone pair have the C_S local symmetry with a common plane of symmetry. Therefore, here and below the torsional angles involving the lone pair were calculated with respect to this plane of symmetry.

Table 1 Conformations of tris(aziridino)methane; the *R*-factors and energy differences (ΔE) were found by the HF/6-31G** calculations.

No.	Definition	Statistical weight	Torsional angle[a]/°			Symmetry	*R*-factor[b] (%)	$\Delta E^{b,c}$/kcal mol^{-1}
			φ_1	φ_2	φ_3			
1	*a*,*a*,*a*	1	180	180	180	C_{3v}	21.2	7.0
2	*g*,*g*,*g*	2	60	60	60	C_3	5.6	0.0
3	*a*,*g*$^-$,*g*	3	180	–60	60	C_S	12.4	17.6
4	*a*,*g*,*g*$^-$	3	180	60	–60	C_S	10.6	6.4
5	*a*,*g*,*g*	6	180	60	60	C_1	7.3	2.7
6	*g*,*g*,*g*$^-$	6	60	60	–60	C_1	8.8	14.5
7	*a*,*a*,*g*	6	180	180	60	C_1	9.8	3.9

[a]For the tetrahedral configuration of bonds at the central C atom. [b]For the optimised geometry of each conformation. [c]The zero-point energy corrections were not included.

the HF/6-31G**, B3PW91/6-31G* and MP2/6-31G** calculations, respectively.

In the structural analysis based on the electron diffraction data, all seven models were investigated. To describe the molecular geometry of **1**, we used the following assumptions based on the *ab initio* results: (1) all aziridine rings exhibit local C_{2v} symmetry, and their structural parameters are identical; (2) three $HC_{meth}N$ fragments have local C_{3v} symmetry. Accordingly, 12 geometrical parameters were used to describe the molecular geometry of **1**: the C_{meth}–N, C_{ring}–N, C–C, C–H_{meth} and C–H_{ring} bond lengths, the $HC_{meth}N$, $C_{meth}NC_{ring}$, CCH and NCH_{ring} valence angles and the φ_1, φ_2 and φ_3 rotational angles for each ring. The amplitudes of vibrations and the perpendicular vibrational corrections were calculated from the scaled force field obtained from the HF/6-31G** calculations.

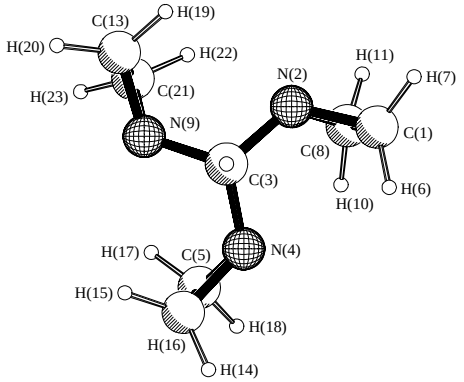

Figure 2 The *g*,*g*,*g* conformation of tris(aziridino)methane in the gas phase.

For each of models 1–7, bond lengths and valence and torsional angles were refined with the initial values taken from *ab initio* calculations. As can be seen in Table 1 and Figure 3, the best agreement with the experiment is achieved for models 2 and 5 having *g*,*g*,*g* and *a*,*g*,*g* conformations. Based on the theoretical and experimental results, the *g*,*g*,*g*$^-$ conformer (model 6) seems to be less favourable. Apparently, this is the result of repulsive ring hydrogen–hydrogen interactions. The H···H nonbonded distances between the neighbouring aziridine rings of less than 0.8 Å support this way of rationalization. That is significantly less than the sum of van der Waals radii (2.40 Å). Therefore, model 6 was excluded from analysis, and only models 2 and 5 were refined using the standard procedure of structural analysis,[13] which includes the background correction and refinement of mean-square amplitudes. At the final stage of structural analysis, model 2 was found to agree with the experimental data appreciably better than model 5. Note that a simultaneous refinement of the C_{meth}–N, C_{ring}–N and C–C bond lengths led to correlation coefficients up to 95%. Accordingly, they were varied using fixed differences between them obtained from *ab initio* calculations.

Table 2 Geometry parameters of the *g*,*g*,*g* conformation of tris(aziridino)-methane (*r*/Å, ∠/°) obtained by gas electron diffraction (GED) and the HF/6-31G** calculations.

Parameter[a]	GED (r_a)		Calculated (r_e)
r(C_{meth}–N)	1.471	(2)	1.449
r(C_{ring}–N)	1.464		1.442_{av}
r(C–C)	1.497		1.475
∠H–C–N	104.4(14)		106.1
∠C_{meth}–N– C_{ring}	115.9(14)		120.1
φ_1	59.3	(17)	78
φ_2	59.3		78
φ_3	59.3		78
∠N–C–N [b]	114.0(11)		112.6
∠lone pair–N–C– N[b]	172.6(51)		166.3
R-factor	5.63%		

[a]The error limits are 3σ, the parameters in braces were refined with fixed differences taken from *ab initio* calculations. [b]Calculated from independent geometrical parameters.

The structural results obtained by electron diffraction analysis are compared with the calculated data in Table 2. Note that the valence angles around the central carbon atom of **1** differ considerably from the tetrahedral value 109.5°: ∠HCN 104.4(14)° and ∠NCN 114.0(11)°. The difference between the experimental (r_a) and theoretical (r_e) φ values is obviously due to the effect of torsional vibrations around C–N bonds. The experimental and theoretical values of the remaining geometrical parameters agree fairly good. Depending on the *ab initio* method, the deviations in bond lengths and bond angles vary in the ranges 0.008–0.02 Å and 2–3°, respectively. The aziridine ring geometry obtained for **1** indicates shortening of the C_{ring}–N bond and elongation of the ring C–C bond by 0.010–0.015 Å as compared with the aziridine molecule where r_s(C–N) = 1.475(3) Å and r_s(C–C) = 1.481(3) Å [14]

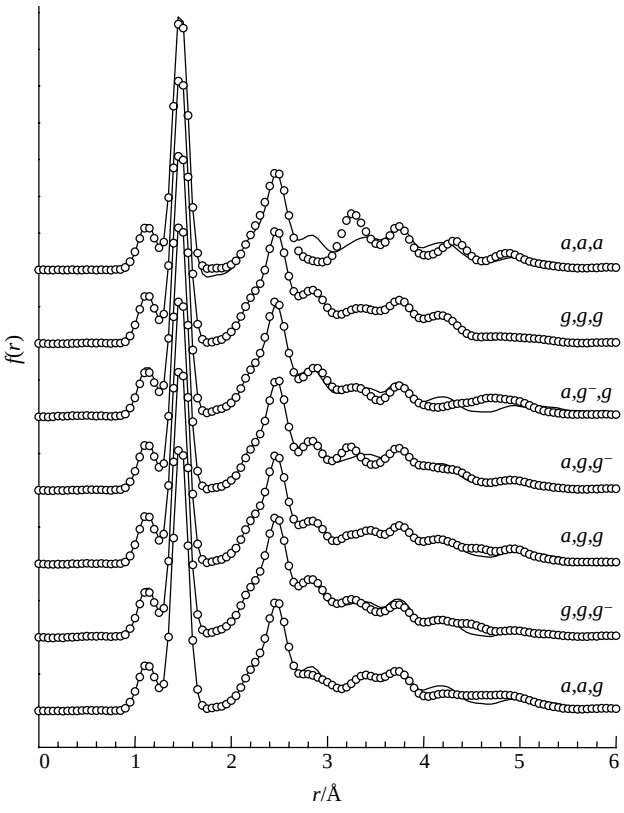

Figure 3 Experimental (—) and theoretical (○) radial distribution curves for models 1–7 (Table 1).

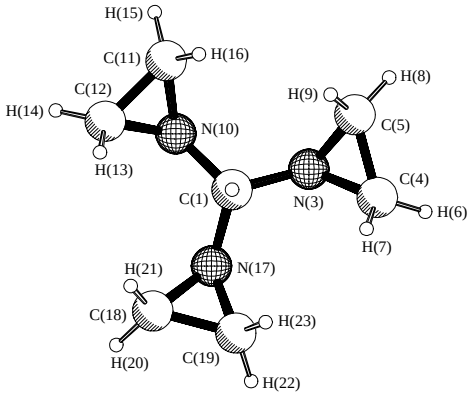

Figure 4 The *a*,*a*,*a* conformation of tris(aziridino)methane in a crystal. The average bond lengths and angles for three independent molecules are $r(C_{meth}–N)$ = 1.461(4) Å, $r(C_{ring}–N)$ = 1.476(6) Å, r(C–C) = 1.485(7) Å, $\angle C_{meth}–N– C_{ring}$ = 114.2(4)°, ∠H–C –N = 112.0°, ∠N–C–N = 106.8° and φ = 176°.

We can conclude that the *g*,*g*,*g* conformation is preferable for **1** in the gas phase. This result is consistent with the NMR data for tris(dialkylamino)methanes.[2(*a*)] Based on these data, less crowded triple rotors prefer a *g*,*g*,*g* conformation, while more crowded ones adopt an *a*,*g*,*g* arrangement. The predominance of the conformation obtained for **1** is consistent with the occurrence of the anomeric effect $n_{(N)}–\sigma^*_{CN}$. This result is supported by the orientation of lone pair relative to the (H)C–N bond, which is close to *anti*-periplanar: the lone pair–N –C–N dihedral angle is equal to 172.6±5.1° (exp.) or 166.3° (HF/6-31G** calculations).

The X-ray study revealed that three independent molecules of **1** lie on the crystallographic C_3 axis, and each of them has the *a*,*a*,*a* conformation of approximately C_{3v} symmetry, as shown in Figure 4. This conformation is characterised by a much higher energy than the *g*,*g*,*g* conformation found in the gas phase (Table 1) and is evidently stabilised by the intermolecular $C_{ring}–H\cdots N$ bonding in a crystal [$r(C_{ring}–H\cdots N)$ = = 2.54 Å, $\angle C_{ring}–H\cdots N$ = 145°]. The remarkable difference between the NCN bond angles in the crystal and gas phase, 106.8° and 114.0°, respectively, should also be noted.

With φ = 176°, as determined in the crystal, the nitrogen lone pair orientation clearly indicates that only the $n_{(N)}–\sigma^*_{CH}$ interaction is possible in the crystal unlike the anomeric effect $n_{(N)}–\sigma^*_{CN}$ in the gas. Thus, the packing and stereoelectronic effects can dramatically change the conformation of **1** in the crystalline state as compared with the gas phase.

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