The Molecular Structure and Conformational Behaviour of 1,1'-Carbonylbisaziridine

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The molecular structure and conformation of gaseous 1,1'-Carbonylbisaziridine [bis(dimethylen)urea] has been investigated by the electron diffraction method. The experimental data are in accordance with a molecular model of C_2 symmetry, in which the nitrogen lone-pair electrons are in conjugation with the π-electrons of the carbonyl group.

While changes in the structure of cyclopropane on substitution[1-3] and their chemical consequences[4] have been studied exhaustively, only little is known about the corresponding properties of saturated heterocyclic three-membered rings.[5] Recently it has been asserted that the aziridine ring structure is insensitive to substitution.[5] However, due to the similarity in the electronic structures of cyclopropane[6-8] and aziridine,[9] analogous substituent effects on the structures of both systems might be expected. On the other hand, the conformational properties of substituted cyclopropanes[1-4] and aziridines[10] are certainly different. While conjugation of the cyclopropane ring with an unsaturated substituent favours the bisected (see structure A below) conformation,[11] n/π-interaction in N-substituted aziridines might stabilize the perpendicular (B) form.[12,13] If the electron lone-pair of the aziridine nitrogen atom is in a sp^2-hybrid orbital, its donor effectiveness will be smaller than in ordinary amino groups.[14-16] Therefore, the actual conformation and, as a consequence, the structural parameters of aziridine derivatives are dependent on the relative amounts of the two possible conjugated forms.

In 1,1'-carbonylbisaziridine (1) two aziridine units are connected by a carbonyl group. Based on the vibrational spectra of 1 a conformation with C_{2v} symmetry (A) has been proposed,[17] but MNDO calculations as well as an X-ray investigation[18] and analysis of the photoelectron spectrum[19] indicated a C_2 conformation (B) similar to that of tetramethylurea.[20] We wish to report here our results obtained in an independent experimental investigation of the molecule in the gas phase by electron diffraction.

Experimental

1,1'-carbonylbisaziridine (1) was synthesized from phosgene and aziridine in toluene solution.[18] The electron-diffraction diagrams were recorded with the Oslo apparatus[12] under the following conditions: Nozzle-to-plate distances: 484.92 mm (6 plates) and 204.92 mm (6 plates). Kodak Electron Image photographic plates were used, and the temperature at the nozzle tip was 120°C during the experiments. The electron

A   B
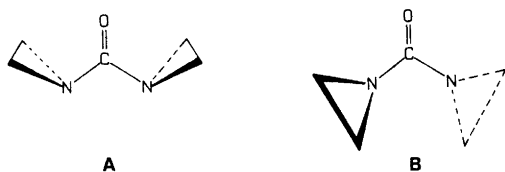
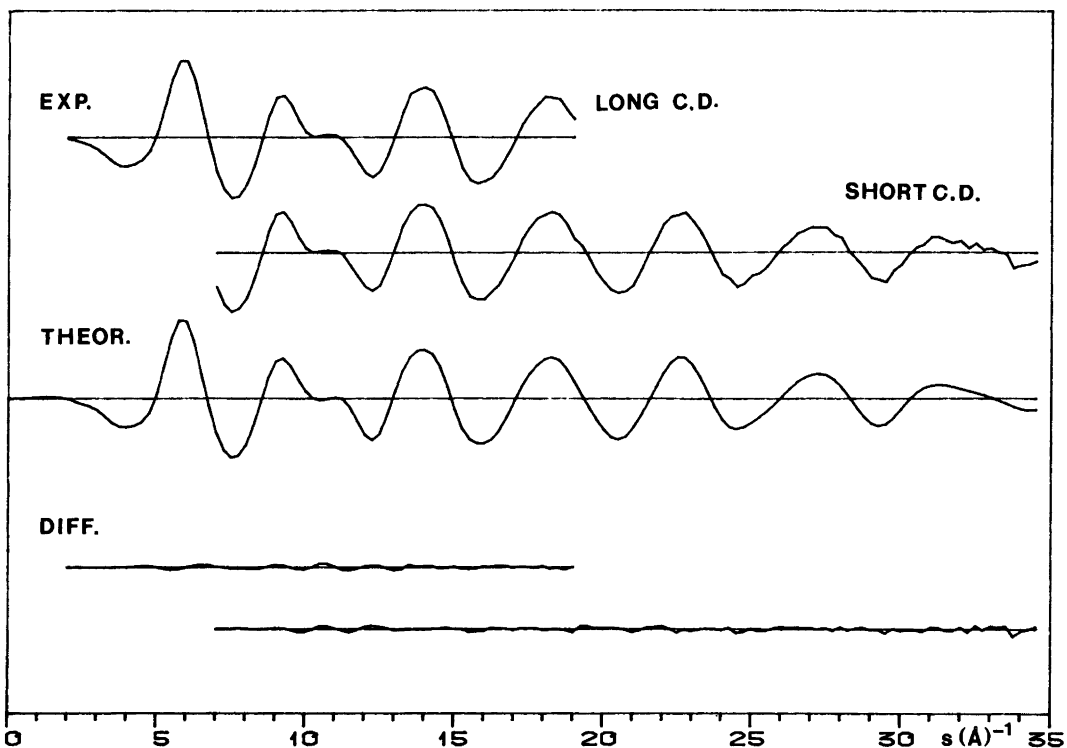*To whom correspondence should be addressed.

Fig. 1. Experimental and theoretical molecular intensities for **1** together with the difference curves.

wavelength was 0.06472 Å, as determined by calibration against diffraction patterns of gaseous benzene using $r_a(C-C) = 1.397$ Å as standard. The estimated standard deviation in the determination of the electron wavelength is 0.1 %. The ranges of the scattering data were 1.25–19.25 and 6.25–43.0 ($\Delta s = 0.25$) Å^{-1}. The experimental data were processed in the usual way.[22] The in-

tensities were modified by $s \cdot f_C'^{-1} \cdot f_N'^{-1}$, and the scattering amplitudes (f') were calculated by the partial wave method,[23] using Hartree-Fock atomic potentials.[24] The inelastic scattering factors used were those of Tavard *et al.*[25] The experimental molecular intensity functions for the two sets of data are shown in Fig. 1.
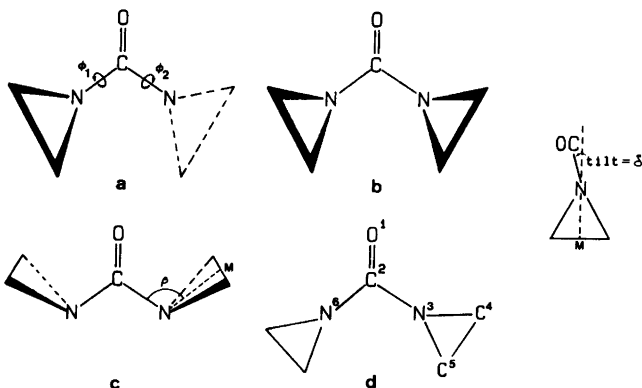

Fig. 2. Molecular models of **1** that have been studied in the present investigation.

Table 1. Valence force constants (in mdyn Å^{-1} or mdyn Å rad^{-2}) used in normal coordinate calculations for 1.

Type	Valence coordinate	Value	Type	Valence coordinate	Value
Stretch	C=O	10.000	Str./str.	O=C; C^2−N	0.574
	C^2−N	4.939		N^3−C^4; N^3−C^5	0.400
	N−C_{ring}	4.152		C^2−N^3; C^2−N^6	1.659
	C−C_{ring}	4.152		C^2−N^3; N^3−C^4	0.490
	C−H	5.100			
Bend	O=C−N	1.000	Str./bend	N−C^4; N−C^4−H	0.331
	N−C−N	1.031		N−C^4; C^2−N−C^4	0.575
	C^2−N−C	1.000		C^2−N; C^2−N−C	0.842
	N−C−H	0.650		C^2−N; N−C−N	0.627
	C−C−H	0.650		C^2−N^3; O=C−N^3	0.938
	H−C−H	0.423		C^2−N^3; O=C−N^6	0.312
				O=C; N−C−N	0.114
Torsion	−C^2−N−	0.150		O=C; O=C−N	0.435
	−N−C−$_{ring}$	0.226			
	−C−C−$_{ring}$	0.226			
O.o. plane	O=C	0.210			

Structure analysis

Fig. 2 shows the four conformers of **1** that have been considered in the present study. Some structural parameters are also defined in this figure.

The following ten structural parameters were chosen to describe the molecular geometry of one conformer of **1**:r(C=O), r(OC−N), r(N−C)$_{ring}$, r(C−C)$_{ring}$, r(C−H), $\angle$O=C−N, $\angle\beta$, $\angle$HCH, $\angle\Phi$, $\angle\delta$(tilt). The aziridyl rings were assumed to have local C_{2v} symmetry. Two dihedral angles of type Φ (see Fig. 2) are of course necessary to define one conformer of **1**. The various conformers were, however, restricted at follows: **1a**: $\Phi_1 = \Phi_2$, **1b**: $\Phi_1 = -\Phi_2$, **1c**: $\Phi_1 = \Phi_2 = 0°$. In conformer **1d** all atoms except the hydrogen atoms were assumed to be coplanar.

The present study employed interactive least-squares intensity refinements, combined with information obtained from radial distribution (RD) curves. The geometries were calculated on the basis of r_a parameters, which include corrections for shrinkage effects.[26] The vibrational amplitudes (u) and perpendicular amplitude correction coefficients (K) were calculated by normal coordinate analyses. The applied valence force field is shown in Table 1 and is based on relevant data

published for tetramethylurea[20] and cyclopropane.[27]

The four molecular models **1a–d** were at first studied separately. Fig. 3 shows theoretical RD curves for the four models, together with the experimental RD curve and the difference curves. The average R-factors for models **1a–d** are 0.067, 0.091, 0.172 and 0.405, respectively. Models **1c** and **1d** are both unacceptable, and model **1a** is clearly better than **1b**. It was therefore decided first to concentrate the further study on model **1a** and thereafter consider a conformational mixture of models **1a** and **1b**.

In the final stages of the study it was possible to refine all geometrical parameters of model **1a** simultaneously in the least-squares intensity refinements, and excellent correspondence between experimental and theoretical data was achieved.

Model **1b**, which was introduced in the final conformational mixture, was assumed to have the same bond distances and bond angles as model **1a**. Because of the repulsion between the closest inter-ring methylene groups in **1b** this is probably not a good approximation for some of the valence angles. The contribution from model **1b** was, however, found to be so small that this kind of
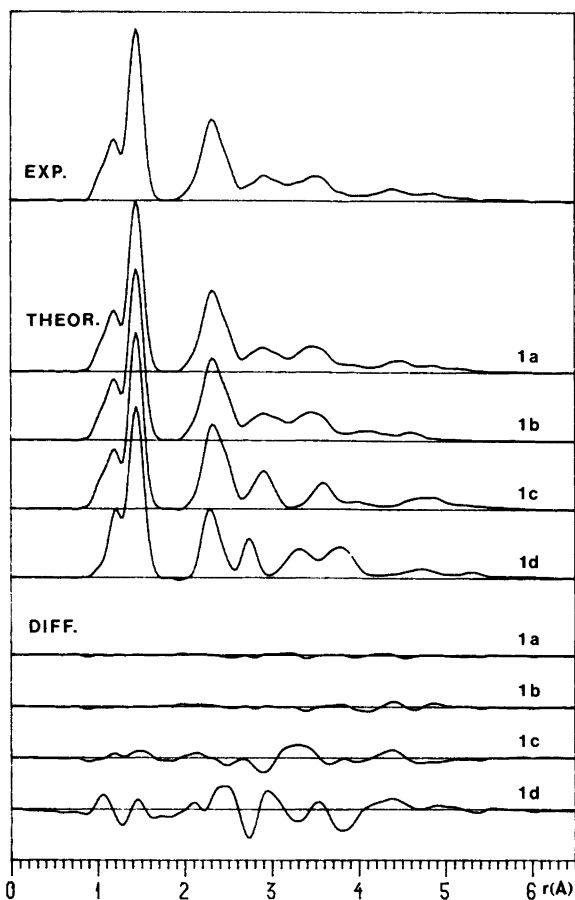
Fig. 3. The experimental radial distribution curve for **1** and theoretical RD curves for models **1a–d** together with the difference curves.

Table 2. Structural parameters determined for **1** by least-squares intensity refinements. Distances in Å, angles in degrees.

	$R_a/\angle_\alpha$	st. dev.	st. err.	R_g	R_α
$r(C=O)$	1.215	.001	.005	1.216	1.207
$r(C^2-N)$	1.412	.001	.005	1.415	1.411
$r(N-C)_{ring}$	1.450	.001	.004	1.451	1.438
$r(C-C)_{ring}$	1.519	.002	.007	1.521	1.504
$r(C-H)$	1.097	.002	.009	1.102	1.076
$\angle C^2-N-M=\angle\beta$	126.6	.2	.6		
$\angle O=C-N$	124.4	.6	1.7		
$\angle H-C-H$	113.6	1.0	3.0		
tilt$(-N-M)=\angle\delta$	5.6	.3	.9		
$\Phi(O=C-N-M)$	71.0	2.0	6.0		
% cont. (Mod. **1a**)	96	5	15		
% cont. (Mod. **1b**)	4	5	15		
$\angle C^2-N^3-C^4$	123.3	.3	.8		
$\angle C^2-N^3-C^5$	117.9	.2	.6		
R_1	.048				
R_2	.078				

Table 3. Correlation matrix (100 ϱ) and standard deviations (σ_o) from the least-squares refinements of 1.

	$\sigma_o{}^a$	2	3	4	5	6	7	8	9	10	11
1. r(C=O)	.001	−33	11	16	24	26	−2	19	5	−4	−1
2. r(C²−N)	.001		−47	3	−4	8	9	−22	15	−5	1
3. r(N−C)ᵣ	.001			−29	−1	−35	−4	8	−12	5	1
4. r(C−C)ᵣ	.002				−7	27	−4	30	9	1	−7
5. r(C−H)	.002					3	0	37	1	−2	0
6. ∠C²−N−M	.21						22	−27	25	−28	3
7. ∠O=C−N	.56							−18	−1	−97	51
8. ∠HCH	1.01								4	18	−12
9. ∠tilt	.31									−2	−10
10. Φ(−C²−N−)	2.00										−56
11. α(Mod. **1a**)	.051										

ᵃDistances in Å, angles in degrees.

valence angle inaccuracy has no observable influence on the results.

The final results are presented in Table 2. The theoretical molecular intensity function for the final model is shown in Fig. 1, together with the experimental intensities and the difference curves. The corresponding radial distribution curves are presented in Fig. 4 while the correlation matrix is given in Table 3.

Discussion

The results of the present study of gaseous 1 confirm those obtained for the solid by X-ray diffraction[18] and by photoelectron spectroscopy.[19] MNDO calculations[18] on the four conformers of 1 considered in the present study showed **1a** to be 3.5 kcal mol⁻¹ more stable than **1b**. The energies of the other two conformers were found to be 9.7
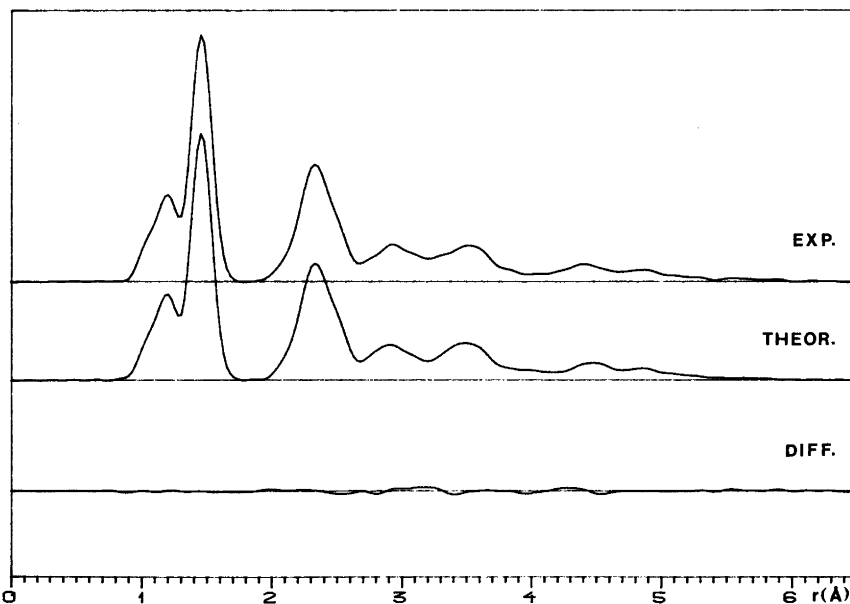

Fig. 4. The experimental RD curve together with the theoretical RD curve calculated from the parameters given in Table 2, and the difference between the two.

(1c) and 15 kcal mol⁻¹ (1d) higher than that of 1a. These results taken together therefore provide strong evidence for the superiority of conjugation between carbonyl π-electrons and the nitrogen lone-pair electrons to conjugation involving a Walsh-type *p* orbital on the nitrogen atom. The latter type of conjugation, which would favour a bisected conformation for 1 (1c), is observed for cyclopropylcarboxaldehyde[30] (55±10 % *s-cis*, 45 % *s-trans*) and also for bis(cyclopropyl) ketone.[31] The latter compound is presently being studied in our laboratory and appears to be conformationally homogeneous, having a *cis,cis* doubly bisected conformation.

Trefonas and Majeste[5] state that a unique feature of the aziridine structural unit is the insensitivity of the three-membered ring to the presence of a variety of simple substituents. They find that the "composite substituted aziridine molecule" based on available data has a geometry essentially identical to that of the parent aziridine molecule, where the bond lengths in the ring are approximately equal [r(N−C) = 1.475 Å; r(C−C) = 1.481 Å]. The present results are not consistent with this view, as the C−C bond is found to be ca. 0.07 Å longer than the N−C bonds. This observed difference is approximately six times larger than the combined error limits of the two bond lengths. In the X-ray study of 1,[18] a bond length difference of 0.03 Å was observed. Ethyleneimine quinone, containing two aziridine groups substituted through their N atoms in the 2 and 5 positions of *p*-quinone, has been studied by X-ray diffraction.[28] The bond lengths in the aziridine rings were found to be 1.469 Å, 1.457 Å (N−C) and 1.498 (C−C).

In the aziridine molecule the N−H bond forms an angle of 112° with the plane of the three-membered ring.[5] The corresponding angle made by the N−CO bond in 1 is found to be ca. 14° larger (126.6°). This indicates that the lone-pair orbitals in 1 have a higher percentage of *p* character than that of aziridine and might therefore contribute more effectively to the conjugative interaction with the π-electrons of the carbonyl group. The angle between the N−CO bond and the plane of the (NCC) ring in *N*-acetylethyleneimine[29] has been found to be ca. 120°, while it is 125.5° in *N*-phenylaziridine.[12]

The correlation matrix in Table 3 shows that there is only minor internal correlation between the various geometrical parameters of 1. The on-

ly exceptions are ∠O=C−N (124.4°) and the tilt angle of the aziridine groups (5.6°), which have high negative correlation coefficients. The O=C−N angle in 1 is found to be slightly larger than that in tetramethylurea (122.3°) and also than the O=C−C angle in cyclopropylcarboxaldehyde (122.0°). A decrease in the tilt angle would further increase the difference between the O=C−N angle in 1 and those referred to above.

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