Journal of Molecular Structure, 131 (1985) 55—60
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ELECTRONIC STRUCTURE AND CONFORMATIONAL PROPERTIES OF THE AMIDE LINKAGE

Part 3[1]. Conformational properties and molecular structure of 1,1'-carbonylbisaziridine determined by MNDO calculations and X-ray diffraction

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(Received 31 January 1985)

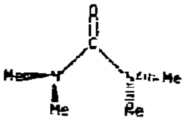
ABSTRACT

The conformational properties of 1,1'-carbonylbisaziridine (2) have been studied by MNDO calculations. A structure with C_2-symmetry has been found as the most stable conformer. C_{2v}-structures correspond to conformers of higher energy. The X-ray structure analysis confirmed the theoretical results. The following structural parameters have been found: C=O 1.211(2), C—N 1.389(1), N—C(ring) 1.455(2) and 1.460(2), C—C 1.485(2) Å, O—C—N 123.5(1), C—N—C(ring) 120.2(1) and 121.6(1)°, torsional angle φ = 83.8(1)°. Substituent effects on the structure of the aziridine ring are discussed

INTRODUCTION

The bonding system of urea and its simple derivatives, $O{=}C(NR_2)_2$, may be described as an acceptor (C=O) bound to two donor groups (NR_2). While the parent compound, urea, $O{=}C(NH_2)_2$, is planar in the crystalline state [2], the molecule probably has a nonplanar structure in the gas phase [3]. Although NR_2-groups show an enhanced donor capacity, a nonplanar structure can be expected for tetraalkyl derivatives due to steric repulsion of the substituents. Accordingly, an electron diffraction analysis of tetramethylurea (1) revealed a structure of C_2-symmetry with pyramidal amino groups [4].

Vibrational spectroscopy combined with a normal coordinate analysis led



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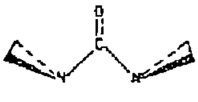

2a

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0022-2860/85/$03.30

Spell and Laane to suggest C_{2v}-structure 2a for 1,1′-carbonyl-bisaziridine (2) [5]. Although the relative low donor capacity of the aziridine ring is well known [6], a structure such as 2a with completely removed n/π-conjugation is unlikely. Therefore, we studied the conformational properties of 2 by MNDO [7] calculations and determined the molecular structure by X-ray diffraction.

EXPERIMENTAL

General

The ^{1}H-NMR spectrum was run on a Hitachi/Perkin-Elmer R24 spectrometer with tetramethylsilane as internal standard. For the mass spectrum a Finnigan MAT312 was used. The elemental analysis was carried out on a Heraeus EA301 C,H,N-analyzer. The melting point is uncorrected.

Synthesis of 2

17.0 g (172 mmol) phosgene in 150 ml abs. toluene are added dropwise to a stirred solution of 16.0 g (372 mmol) aziridine and 80.8 g (800 mmol) triethylamine in 150 ml abs. toluene. The temperature of the solution is maintained below —5°C. After stirring for an additional 3 h at room temperature, the solution is filtered and distilled under reduced pressure. Yield 13.1 g (68%) M p. (from n-pentane) 39—40°C (lit. [8] 39—41°C). Found: C 53.48, H 7.09, N 25.10%, calc for $C_5H_8N_2O$: C 53.56, H 7.19, N 24.98% ^{1}H-NMR ($CDCl_3$): $\delta = 2.3$ ppm s. MS: $m/z = 112, 70, 56, 42$.

*X-ray structure analysis**

Due to the low melting point of 2, the X-ray analysis was executed at a temperature of —105°C. The crystals have monoclinic symmetry and belong to space group $C2/c$. A crystal of 2, with the dimensions 0.51 × 0.44 × 0.40 mm, sealed in a glass capillary, was measured on a Syntex four-circle diffractometer using graphite monochromized MO-K_α radiation. Twenty reflections have been indexed by an autoindexing method using the Nicolet-P3-program. Unit cell dimensions: $a = 8.285(3)$ Å, $b = 11.148(4)$ Å, $c = 6.866(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 114.54(3)°$. Volume of the unit cell: 576.9(4) Å^3, $D_x = 1.13$ g cm^{-3}, $Z = 4$.

A set of 660 independent reflections has been collected by the $2\theta:\omega$ scan method, $2\theta_{max} = 55°$, with variable scan speeds of which 595 were treated as observed ($F_o \geqslant 3.5 \times \sigma(F_o)$). The coordinates of all non-hydrogen atoms were determined by direct methods and refined using the SHELXTL program system [9] on a NOVA 3/12 (Data General) computer. The positions

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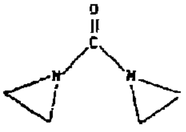
of the hydrogen atoms were obtained from a difference Fourier synthesis and refined with isotropic temperature factors.

The refinement converged to $R = 0.038$, $R_\omega = 0.044$, $\omega^{-1} = \sigma^2(F) + 2.6 \times 10^{-4} \times F^2$. The final electron density difference map showed no peaks higher than 0.33 e Å^{-3}.

MNDO CALCULATIONS

Besides **2a** a second conformation of C_{2v}-symmetry is possible, all atoms except hydrogen atoms being coplanar (**2b**) In addition two conformations with pyramidal N-atoms must be considered: **2c** has C_2- and **2d** has C_s-symmetry. The conformations can be characterized by the angle φ giving the torsion of the aziridine rings versus the C=O-bond (Fig. 1). **2a** has $\varphi = 0°$, in **2c** φ should be close to +90° and in **2d** close to ±90°.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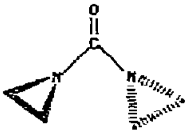
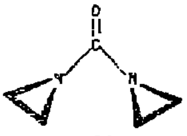

2c


2d

The calculated heats of formation for **2a** to **2d** are summarized in Table 1. The values refer to structures with completely optimized geometric parameters.

Structural parameters calculated for **2c** are given in Table 2. The data indicate **2a** being the less stable one of the conformations studied. Its energy exceeds **2b**, the second conformer of C_{2v}-symmetry, by 15 kcal mol^{-1}. The conformers of lower symmetry, **2c** and **2d**, have a pronounced higher stability than **2a** and **2b**. This is why **2** should have lower symmetry than C_{2v} in contradiction to the previously assumed one [5]. **2c** is more stable than **2d** by 3.5 kcal mol^{-1}, in conjunction with the higher dipole moment and stronger steric interactions in the C_s-form Indicated by the MNDO results,

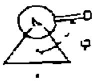


Fig. 1 Definition of the torsional angle φ of 2

TABLE 1

Heats of formation ΔH_f (kcal mol^{-1}) and dipole moments μ (D) of several conformations of 2 calculated by the MNDO method

Conformer	ΔH_f	μ
2a	49.22	3.24
2b	33.97	4.24
2c	20.80	2.73
2d	24.31	4.01

2 should prefer a structure with high n/π-conjugation which does not differ substantially from 1. The photoelectron spectra of 1 and 2 [10] are in agreement with these assumptions.

X-RAY STRUCTURE ANALYSIS

The bond lengths and angles are given in Table 2, the atomic coordinates are listed in Table 3. The numbering of the atoms is as shown in Fig. 2.

With regard to conformation the MNDO results are confirmed by the X-ray analysis: the molecules possess conformation 2c also in the crystalline state. The conformational angle φ is 83.8°. The experimental bond lengths of the heavy atoms are in agreement with the calculated ones within 0.03 Å. However, it should be noted that the summarized MNDO bond lengths are longer than those derived from the X-ray study. Concerning bond angles, the differences are 0.6° for O—C—N and about 6° for the C—N—C(ring)-angles. The torsional angles O—C—N—C(ring) differ by approximately 1 and 6°.

TABLE 2

Bond lengths (Å) and angles (°) of 2 determined by MNDO calculations and by X-ray analysis

Parameter	X-ray[a]	MNDO
Bond lengths		
O(1)—C(1)	1.211(2)	1.225
C(1)—N(1)	1.389(1)	1.422
N(1)—C(2)	1.460(2)	1.477
N(1)—C(3)	1.455(2)	1.477
C(2)—C(3)	1.485(2)	1.519
C(2)—H(2a)	0.967(16)	1.101
C(2)—H(2b)	0.975(15)	1.101
C(3)—H(3a)	0.937(17)	1.100
C(3)—H(3b)	0.984(18)	1.101
Angles		
O(1)—C(1)—N(1)	123.5(1)	122.9
C(1)—N(1)—C(2)	121.6(1)	127.2
C(1)—N(1)—C(3)	120.2(1)	126.4
C(2)—N(1)—C(3)	61.2(1)	61.9
N(1)—C(1)—N(1')	114.0(1)	114.2
N(1)—C(2)—H(2a)	115.5(11)	120.1
N(1)—C(2)—H(2b)	113.8(11)	115.1
N(1)—C(3)—H(3a)	112.4(15)	120.8
N(1)—C(3)—H(3b)	115.4(11)	115.0
H(2a)—C(2)—H(2b)	118.9(12)	111.2
H(3a)—C(3)—H(3b)	118.6(15)	111.0
O(1)—C(1)—N(1)—C(2)	120.3(1)	121.1
O(1)—C(1)—N(1)—C(3)	47.4(1)	41.2
φ	83.8(1)	81.2

[a] Standard deviations are given in parentheses.

TABLE 3

Fractional coordinates of 2[a]

	x/a	y/b	z/c
O(1)	0	0.5554(1)	0.25
C(1)	0	0.4468(2)	0.25
N(1)	0.8466(1)	0.3780(1)	0.1639(2)
C(2)	0.8002(2)	0.2932(1)	0.2947(2)
C(3)	0.6968(2)	0.4053(1)	0.2149(3)
H(2a)	0.7500(23)	0.2181(15)	0.2258(25)
H(2b)	0.8837(24)	0.2926(13)	0.4450(26)
H(3a)	0.5883(27)	0.4028(14)	0.0942(31)
H(3b)	0.7169(21)	0.4699(16)	0.3202(26)

[a]Standard deviations are given in parentheses.

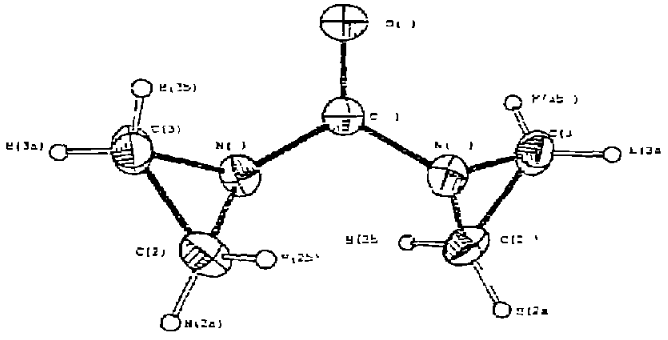
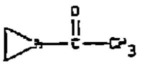


Fig 2

DISCUSSION

It is appropriate to compare the structure parameters of 2 with those of similar molecules, especially with 1. Since most data to be cited here are from electron diffraction or microwave spectroscopy, certain deviations in the structure parameters are due to different states of the compounds and methodical effects The C=O bond in 2 (1.211 Å) is shorter than in 1 [4] (1.240 Å) and in *N*-acetylaziridine [11] (3, 1.226 Å). The same holds for the C—N bonds between carbonyl and amino groups: the corresponding values for 1, 2 and 3 are 1.397, 1.389, and 1.446 Å. The C—N bond lengths in the aziridine rings of 2 (1.455 and 1.460 Å) are nearly the same as in the dimethylamino groups of 1 (1.461 Å), but should be better compared with that one in the three membered rings of 3 (1.485 Å), aziridine [12] (1.435 Å) or 1,1'-bisaziridine [13] (4, 1.457 Å)

The ring C—C bond distance of 2 (1.485 Å) is in the same range with the corresponding values of 3, 4 and aziridine: 1.484, 1.500 and 1.481 Å As a final example *meso*-1,4-diaziridinyl-2,3-butanediol [14] (5) is quoted. In an



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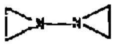

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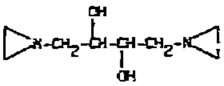

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X-ray analysis the following bond distances of the aziridine rings have been found: C—N 1.500 and 1.510 Å, C—C 1.463 Å.

There seems to be a correlation of the structural parameters of substituted aziridines with the electronic properties of the substituents similar to the cyclopropane ring [15, 16]. Due to interaction between the Walsh 3e′-orbital of the cyclopropane ring and the π^*-orbital of a substituent, the C(2)—C(3) bond is shortened and the C(1)—C(2) as well as the C(1)—C(3) bond is lengthened. The above-mentioned bond lengths seem to indicate a similar trend for *N*-substituted aziridines This becomes quite evident, when the data of 2 and 5 are compared with those of unsubstituted aziridine, although the conformation of 2 favours interaction of the double bond with the nitrogen electron lone pair instead of the Walsh orbital [17].

ACKNOWLEDGEMENT

The authors are indebted to Mr. M. Polk for assistance with the X-ray studies.

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