An Unusual Example of Packing Among Molecular Layers: The Structures of Two Crystalline Forms of 2,2-Aziridinedicarboxamide, $C_4H_7N_3O_2$

By Sergio Brückner

Instituto di Chimica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

Abstract

The structures of two crystalline forms of 2,2-aziridine-dicarboxamide have been determined by X-ray diffraction. Form A, obtained from a solution in methanol, is tetragonal, space group $P4_12_12$, with $a = 12\cdot382$ (2), $c = 30\cdot211$ (3) Å, $V = 4632$ (1) Å^3, $Z = 32$; form B, obtained from a solution in N,N-dimethylformamide, is triclinic, space group $P1$, with $a = 15\cdot829$ (2), $b = 12\cdot381$ (2), $c = 12\cdot391$ (2) Å, $\alpha = 90\cdot0$ (1), $\beta = 74\cdot3$ (1), $\gamma = 83\cdot1$ (1)°, $V = 2312$ (1) Å^3, $Z = 16$. The former has been refined to a final R of $0\cdot051$ for 1074 significant reflections while the latter has been refined to a final R of $0\cdot070$ for 2534 significant reflections. The pyramidal geometry of the ring nitrogen is discussed. In both cases crystal packing may be described in terms of layers, all having the same internal structure. The two crystalline forms are characterized by a different stacking of layers. The symmetry present within each layer is not extended to the whole packing, thus giving rise in both cases to an unusually high number of independent molecules, while a high non-crystallographic symmetry strongly affects the intensity statistics.

Introduction

The structure of the title compound has been determined as the first step of an investigation of the correlation between the pyramidal geometry of nitrogen within the aziridine ring and the barrier height of the nitrogen inversion process. 2,2-Aziridinedicarbox-amide was recrystallized by slow evaporation of two solutions, one in methanol and the other in N,N-dimethylformamide. Two different crystalline forms were obtained, the first, indicated A, being tetragonal, the second, indicated B, triclinic. The tetragonal form was analysed first. Intensity data were collected on a Philips PW1100 automatic four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, the $\theta/2\theta$ step-scan method being used. 2158 independent reflections with $2\theta \leq 48°$ were collected, of which 1074 had $I > 2\cdot5$ $\sigma(I)$. In the case of form B it was rather

difficult to find a fragment of crystal free from twinning. Intensities of 5683 independent reflections were collected on an Enraf–Nonius CAD-4 four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation, by a $\theta/2\theta$ scan to $\theta_{max} = 22°$. After data reduction, 2534 reflections with $I > 2\cdot5\sigma(I)$ were taken as observed. Intensity data for both structures were corrected for Lorentz and polarization effects; no absorption correction was applied.

Structure solution and refinement

The structure of form A was solved by *MULTAN* 78 (Main, Woolfson, Hull, Lessinger, Germain & Declercq, 1978) which showed all the non-hydrogen atoms belonging to the four molecules of the asymmetric unit. The intensity statistics of the program showed some interesting features. A hypercentrosymmetric structure was clearly indicated by the intensity distribution while the mean values $\langle E_{hkl}^2 \rangle$ according to parity groups were $\sim 1\cdot8$ for *eee* and *eeo* reflections, $\sim 1\cdot0$ for *oee*, *eoe*, *oeo* and *eoo* reflections, $\sim 0\cdot25$ for *ooe* and *ooo* reflections. These features depend, as will be shown in the description of the structure, on a high non-crystallographic symmetry. Non-hydrogen atoms were refined with anisotropic temperature factors optimizing atomic parameters of one molecule at a time, while contributions of the others were kept constant, with a blocked full-matrix least-squares procedure (Immirzi, 1967, 1973). The final $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was $0\cdot051$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final parameters are listed in Table 1.*

The structure of form B was solved by taking into account the results already obtained for form A. Intensity statistics were in fact very similar to those of the structure already solved. One whole layer was

---

* Lists of structure factors and anisotropic thermal parameters for forms A and B and atomic coordinates for form B have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36838 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$ *for non-hydrogen atoms and* $\times 10^3$ *for hydrogens*) *and equivalent values* B_{eq} (Å^2) *of the anisotropic temperature factors* B_{ij} *for the A crystal form of the title compound*

$$B_{eq} = \tfrac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \, \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}/B		x	y	z	B_{eq}/B
Molecule (I)					Molecule (III)				
O(1)	3164 (4)	4859 (4)	4212 (2)	3·4	O(1)	1360 (4)	5319 (4)	6688 (2)	3·5
O(2)	1537 (4)	7812 (5)	4404 (2)	4·4	O(2)	4349 (4)	6878 (5)	6868 (2)	4·3
N(1)	1544 (5)	5664 (5)	4259 (3)	3·8	N(1)	2176 (5)	6926 (5)	6742 (2)	3·8
N(2)	3107 (6)	8677 (6)	4264 (3)	4·5	N(2)	5158 (5)	5295 (5)	6769 (3)	4·6
N(3)	4274 (5)	6784 (5)	4198 (2)	2·7	N(3)	3285 (5)	4184 (5)	6706 (2)	3·2
C(1)	2573 (7)	5688 (7)	4248 (3)	3·4	C(1)	2162 (7)	5838 (6)	6749 (3)	2·9
C(2)	2511 (7)	7760 (6)	4322 (3)	2·9	C(2)	4298 (7)	5884 (7)	6814 (3)	3·2
C(3)	4071 (7)	6665 (7)	4674 (3)	4·0	C(3)	3130 (7)	4405 (7)	7167 (3)	3·9
C(4)	3162 (6)	6739 (6)	4356 (2)	2·5	C(4)	3210 (6)	5325 (6)	6849 (3)	3·2
H(1N1)	106 (5)	615 (5)	431 (2)	1 (2)	H(1N1)	277 (6)	726 (7)	681 (2)	5 (2)
H(2N1)	106 (7)	478 (8)	414 (3)	7 (3)	H(2N1)	152 (5)	729 (5)	672 (2)	2 (2)
H(1N2)	282 (6)	938 (5)	433 (2)	2 (2)	H(1N2)	578 (4)	565 (5)	675 (2)	1 (2)
H(2N2)	381 (8)	854 (8)	418 (3)	6 (3)	H(2N2)	516 (7)	463 (6)	672 (3)	4 (2)
H(N3)	435 (8)	609 (8)	413 (3)	8 (3)	H(N3)	271 (6)	398 (6)	658 (2)	1 (2)
H(1C3)	416 (6)	716 (6)	486 (2)	3 (2)	H(1C3)	247 (6)	431 (6)	732 (2)	3 (2)
H(2C3)	421 (7)	588 (7)	483 (3)	5 (2)	H(2C3)	369 (8)	423 (7)	739 (3)	6 (3)
Molecule (II)					Molecule (IV)				
O(1)	5288 (4)	−157 (4)	4262 (2)	3·8	O(1)	8592 (4)	8144 (4)	5773 (2)	3·7
O(2)	6899 (4)	2779 (4)	4423 (2)	3·8	O(2)	5628 (4)	6550 (4)	5630 (2)	4·5
N(1)	6924 (5)	622 (5)	4290 (3)	4·0	N(1)	7782 (5)	6548 (5)	5754 (2)	3·9
N(2)	5322 (5)	3608 (5)	4264 (2)	3·5	N(2)	4773 (5)	8127 (6)	5746 (2)	3·7
N(3)	4137 (5)	1736 (5)	4265 (2)	3·5	N(3)	6641 (6)	9271 (5)	5752 (2)	3·8
C(1)	5890 (7)	644 (6)	4303 (3)	2·7	C(1)	7772 (5)	7608 (6)	5709 (2)	2·2
C(2)	5930 (6)	2769 (7)	4364 (3)	2·8	C(2)	5655 (5)	7551 (7)	5662 (3)	2·8
C(3)	4422 (6)	1651 (7)	4741 (3)	3·7	C(3)	6761 (7)	9014 (7)	5294 (3)	4·2
C(4)	5299 (6)	1698 (6)	4385 (2)	2·9	C(4)	6705 (6)	8132 (5)	5632 (2)	2·4
H(1N1)	724 (9)	114 (9)	431 (3)	9 (3)	H(1N1)	713 (7)	628 (7)	571 (3)	6 (2)
H(2N1)	730 (5)	2 (5)	431 (2)	1 (2)	H(2N1)	837 (7)	623 (6)	587 (2)	4 (2)
H(1N2)	549 (8)	426 (7)	423 (3)	6 (2)	H(1N2)	413 (6)	787 (7)	572 (2)	3 (2)
H(2N2)	461 (7)	357 (7)	432 (3)	6 (2)	H(2N2)	493 (7)	856 (7)	591 (2)	4 (2)
H(N3)	394 (6)	101 (6)	417 (2)	3 (2)	H(N3)	741 (7)	942 (6)	587 (2)	4 (2)
H(1C3)	434 (9)	87 (9)	484 (3)	10 (3)	H(1C3)	732 (8)	905 (7)	511 (3)	6 (3)
H(2C3)	412 (6)	244 (8)	491 (3)	5 (2)	H(2C3)	596 (7)	921 (6)	512 (3)	4 (2)

introduced into the input data as a rigid fragment with known orientation. *MULTAN* gave the correct solution only when the non-centrosymmetric space group $P1$ was tested. A refinement procedure was adopted so that the four independent layers were adjusted one at a time while contributions of the others were kept constant. To keep the number of variables as low as possible non-hydrogen atoms which did not appear to be strongly affected by anisotropic vibrations were refined isotropically during the last optimization cycles. A difference Fourier map clearly showed all H atoms of two layers while in the remaining two, small diffuse peaks appeared both around atoms refined as nitrogens and atoms refined as oxygens. This, together with some inconsistencies in C=O and C—NH$_2$ bond lengths present in these two layers also, makes it impossible to distinguish between N and O atoms and the designation in the table of coordinates is only tentative. The final R was 0·070 (0·16 with unobserved reflections

included). The final parameters have been deposited for the sake of brevity.*

Discussion

The structures of both crystalline forms may be conveniently described in terms of layers characterized by the same two-dimensional structure.

(1) *Form A. Tetragonal*

Fig. 1 shows the layer at $z \sim 0.43$ for form A. It may be seen that this plane is built of rows of hydrogen-bonded molecules which extend along the **b** direction according to an approximate t_2 chain-repetition group (Corradini, 1968). The t_i symmetry is

---

* See previous footnote.

excluded by the lack of inversion of the NH and CH_2 groups belonging to the three-membered ring but, as will be shown later, the presence of an approximate centre of inversion within each row is important in explaining the intensity statistics evaluated by *MULTAN*. Rows are so related as to give rise to an approximate *pgg* two-dimensional space group with glide planes parallel to (100) and (010) (for the layer shown in Fig. 1 they are at $x \sim 0.42$ and $y \sim 0.17$). The presence of non-crystallographic glide planes together with crystallographic binary screw axes orthogonal to them gives rise to non-crystallographic centres of inversion which relate layers to one another. One of such centres may be seen in Fig. 2, where we
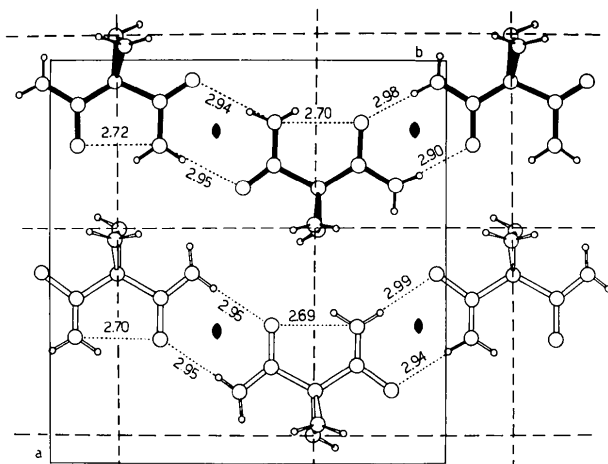

Fig. 1. The layer at $z \sim 0.43$ in crystal form A. Filled and open bonds are used to distinguish between different chains of hydrogen-bonded molecules. The non-crystallographic symmetry *pgg* is also indicated.
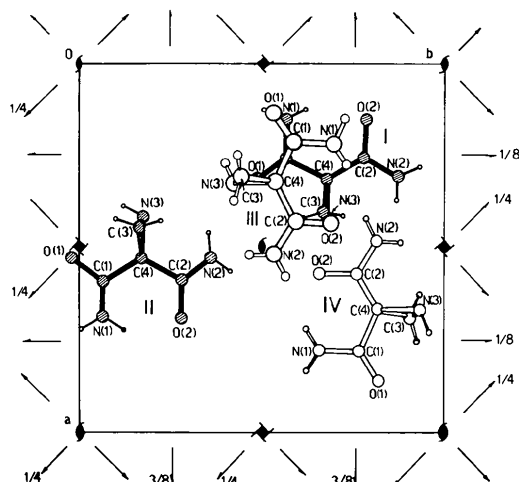

Fig. 2. The four independent molecules in form A whose parameters have been refined. Molecules (III) and (IV) are related by a non-crystallographic centre of inversion at $0.5, 0.67, 0.625$.

report the four molecules whose parameters have been refined; molecules (III) and (IV) are related by an inversion centre at 0.5, 0.67, 0.625. The hyper-centrosymmetric structure predicted by the intensity statistics of *MULTAN* may now be justified even if there is no crystallographic centre of symmetry.

It may be seen in Fig. 1 that, while along y there is a repeat vector $\mathbf{b}$, along x there is an approximate repeat vector $\mathbf{a}/2$ (there are O atoms substituting NH_2 groups and *vice versa* but the overall shapes of the molecules are approximately the same). This situation is maintained within layers at $z \sim 0.32, 0.82$, and 0.93 while y is interchanged with x in the others. This is the reason for the strong differences in $\langle E_{hkl}^2 \rangle$ detected by *MULTAN* among reflections according to their parity groups (see *Structure solution*). If we indicate with P the layers with hydrogen-bonded molecules extending along x and with Q the layers where they extend along y, the three-dimensional structure is a stacking of layers described as ...$PPQQPP$..., the distance between two layers of the same kind being 3.3 Å while that between two different layers is 4.2 Å. This difference is due to the fact that in the first case the layers face each other with the NH groups, while in the second case the bulkier CH_2 groups are involved. The unusual presence of four molecules in the asymmetric unit may be considered as due to the very stable two-dimensional network which, however, cannot retain its *pgg* symmetry within the crystal according to the general rule pointed out by Kitaigorodsky (1973), which states that the preservation within the crystal of symmetries different from the inversion centre is usually associated with a lower density.

(2) *Form B. Triclinic*

The structure may be described in terms of layers which have the same two-dimensional structure as found in form A and which give rise to a similar ...$PPQQPP$... stacking. More specifically form B is to be considered as a derivative structure of form A, obtained from it by suppressing the symmetry axes orthogonal to the layers. In fact the vector $\mathbf{a}$ of the unit cell of B is also present in A as the translation vector which links the layer at z with that at $z + \frac{1}{2}$. But, while in form A the sequence of layers from $z + \frac{1}{2}$ to $z + 1$ gives rise to a second translation vector with the two components parallel to the layers having a sign which is opposite to that of the first vector, this compensating effect is absent in B. This situation is schematically represented in Fig. 3.

It is not easy to provide a satisfactory explanation for the apparent disorder, involving NH_2 groups and O atoms, which alternately affects the layers, since a statistical disorder in the occupancy of sites in one layer should also extend to its neighbours. The great difficulty encountered in finding a fragment of crystal

free from twinning could suggest the possibility that a small twin, still present in the fragment selected for crystal structure analysis, could affect the intensities to a small extent, sufficient, however, to perturb some details of the structure.
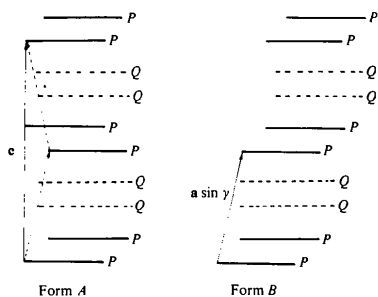

Fig. 3. A schematic representation of the different stacking of layers in the two crystalline forms of the title compound. The views are along **b** (form *A*) and along **c** × **a*** (form *B*).

Table 2. *Bond lengths* (Å), *angles* (°) *and some selected torsion angles* (°) *for the four independent molecules*

	(I)	(II)	(III)	(IV)
Bond lengths				
O(1)–C(1)	1·27 (1)	1·25 (1)	1·20 (1)	1·23 (1)
O(2)–C(2)	1·23 (1)	1·21 (1)	1·24 (1)	1·24 (1)
N(1)–C(1)	1·28 (1)	1·28 (1)	1·35 (1)	1·32 (1)
N(2)–C(2)	1·37 (1)	1·32 (1)	1·30 (1)	1·33 (1)
C(1)–C(4)	1·53 (1)	1·52 (1)	1·48 (1)	1·49 (1)
C(2)–C(4)	1·50 (1)	1·54 (1)	1·52 (1)	1·49 (1)
C(3)–C(4)	1·48 (1)	1·53 (1)	1·50 (1)	1·50 (1)
N(3)–C(4)	1·46 (1)	1·48 (1)	1·48 (1)	1·46 (1)
N(3)–C(3)	1·47 (1)	1·49 (1)	1·43 (1)	1·43 (1)
N(3)–H	0·9 (1)	1·0 (1)	0·8 (1)	1·0 (1)
Bond angles				
N(1)–C(1)–O(1)	124·1 (5)	125·3 (5)	122·9 (5)	121·0 (5)
N(1)–C(1)–C(4)	119·4 (6)	120·4 (5)	115·0 (6)	117·2 (5)
O(1)–C(1)–C(4)	115·7 (6)	114·3 (6)	122·0 (5)	121·5 (5)
N(2)–C(2)–O(2)	120·7 (5)	126·2 (2)	121·8 (5)	121·9 (5)
O(2)–C(2)–C(4)	123·7 (5)	120·3 (5)	119·2 (5)	120·0 (5)
N(2)–C(2)–C(4)	114·8 (6)	113·5 (5)	118·7 (6)	118·0 (5)
N(3)–C(3)–C(4)	59·3 (4)	58·9 (4)	60·7 (4)	59·7 (4)
N(3)–C(4)–C(1)	114·3 (5)	117·1 (5)	114·0 (5)	115·4 (5)
N(3)–C(4)–C(2)	116·9 (5)	117·0 (5)	111·1 (6)	113·9 (5)
N(3)–C(4)–C(3)	59·8 (4)	59·0 (4)	57·6 (4)	57·7 (3)
C(1)–C(4)–C(2)	116·5 (5)	119·3 (5)	124·8 (5)	123·7 (4)
C(1)–C(4)–C(3)	116·6 (5)	115·1 (5)	113·6 (6)	112·5 (5)
C(2)–C(4)–C(3)	120·3 (5)	115·0 (5)	116·8 (5)	115·8 (5)
C(3)–N(3)–C(4)	60·9 (4)	62·0 (4)	61·7 (4)	62·5 (4)
C(3)–N(3)–H(N3)	98 (6)	107 (4)	112 (4)	106 (4)
C(4)–N(3)–H(N3)	98 (6)	107 (4)	111 (4)	102 (4)
Some torsion angles				
N(1)–C(1)–C(4)–N(3)	−161 (1)	162 (1)	−160 (1)	157 (1)
N(2)–C(2)–C(4)–N(3)	−17 (1)	3 (1)	−15 (1)	7 (1)
O(1)–C(1)–C(4)–N(3)	28 (1)	−19 (1)	22 (1)	−16 (1)
O(2)–C(2)–C(4)–N(3)	173 (1)	−174 (1)	171 (1)	−170 (1)
N(1)–C(1)–C(4)–C(3)	132 (1)	−131 (1)	137 (1)	−139 (1)
N(2)–C(2)–C(4)–C(3)	52 (1)	−62 (1)	48 (1)	−58 (1)
O(1)–C(1)–C(4)–C(3)	−39 (1)	47 (1)	−42 (1)	48 (1)
O(2)–C(2)–C(4)–C(3)	−118 (1)	119 (1)	−126 (1)	126 (1)

(3) *The molecular structure*

As for the geometrical description of the molecule only the results from *A* will be taken into account. The aziridine ring is described in terms of bond lengths and angles in Table 2 (for the numbering scheme see Fig. 2). The mean length of the N–C bonds within the ring is 1·463 (4) Å, while the mean length of the C–C bonds is 1·502 (6) Å, which is shorter than a single C–C bond. A similar although more pronounced, effect has been observed (*e.g.* Gould & Pasternak, 1961) and discussed (Ko, Olansky & Moncrief, 1975).

The ring N atom in the four independent molecules is pyramidal, lying 0·666 (6), 0·636 (6), 0·533 (6) and 0·670 (7) Å respectively from the plane defined by its three substituents. Its pyramidal structure may also be conveniently described in terms of the angle between the N–H bond and the ring plane, this angle being 99 (5), 110 (5), 115 (5) and 106 (5)° respectively. The planes of the carboxamide substituents do not bisect the N(3)–C(4)–C(3) angle but, as revealed in the torsion angles reported in Table 2, their intersection with the three-membered-ring plane rotates significantly (mean value ~17°) toward N(3).

References

CORRADINI, P. (1968). *Chain Conformation and Crystallinity* in *The Stereochemistry of Macromolecules*, Vol. III, edited by A. KETLEY. New York: Marcel Dekker.

GOULD, E. S. & PASTERNAK, R. A. (1961). *J. Am. Chem. Soc.* **83**, 2658–2661.

IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.

IMMIRZI, A. (1973). *J. Appl. Cryst.* **6**, 246–249.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 71. Birmingham: Kynoch Press.

KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York and London: Academic Press.

KO, TIEN-MING, OLANSKY, L. & MONCRIEF, J. W. (1975). *Acta Cryst.* B31, 1875–1878.

MAIN, P., WOOLFSON, M. M., HULL, S. E., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.