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# The Structure of 1-Methyl-2,2-aziridinedicarboxamide, $C_5H_9N_3O_2$

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**Abstract.** $M_r = 143\cdot2$, monoclinic, $C2/c$, $a = 23\cdot150$ (6), $b = 7\cdot008$ (5), $c = 8\cdot137$ (5) Å, $\beta = 91\cdot86$ (5)°, $V = 1319$ (1) Å$^3$, $Z = 8$, $D_x = 1\cdot44$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot06$ cm$^{-1}$, $F(000) = 608$, room temperature, final $R = 0\cdot055$ for 844 observed reflections. The N ring atom is pyramidal lying 0·656 (3) Å out of the plane of its three substituents and the plane defined by the substituted ring C atom and the C atoms of the carboxamide groups is almost perpendicular to the aziridine ring. Molecules are associated in the crystal in layers parallel to the *bc* plane by an extended hydrogen-bonding network.

**Introduction.** The structure of the title compound was determined as part of a continuing study into the aziridine system in order to investigate the pyramidal nature of the ring nitrogen atom and the change of molecular geometry in several different N-substituted compounds. The structure of 2,2-aziridinedicarboxamide has already been published (Brückner, 1982) and the crystal structure of other analogous compounds will be discussed in the following two papers (Brückner, Malpezzi, Prosyanik & Bondarenko, 1985).

**Experimental.** Colourless crystals, 0·20 × 0·20 × 0·30 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, least-squares fit of 15 reflections with $18 \leq 2\theta \leq 40°$ to obtain cell parameters; 1591 independent $\pm hkl$ ($-30 \leq h \leq 30$, $0 \leq k \leq 9$, $0 \leq l \leq 10$) with $\theta \leq 30°$, 844 with $I \geq 2\cdot5\sigma(I)$; $\theta/2\theta$ scan technique, scan speed 0·05° s$^{-1}$, scan width 1·2°, three periodically monitored standard reflections with no significant intensity variation; Lp corrections, absorption ignored; direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), 360 normalized structure factors with $E \geq 1\cdot5$; anisotropic full-matrix refinement, isotropic for H (located from difference Fourier map), 136 parameters refined; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1\cdot9114\,[\sigma^2(F_o) + 0\cdot0006\,(F_o)^2]^{-1}$; final $R = 0\cdot055$ and $R_w = 0\cdot054$; $(\Delta/\sigma)_{\text{mean}}$ for non-H atoms = 0·04, $(\Delta/\sigma)_{\text{max}} = 0\cdot18$, $\Delta\rho_{\text{max}} = 0\cdot24$ e Å$^{-3}$ at 1·08 Å from O(1), $S = 0\cdot37$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computer program: *SHELX*76 (Sheldrick, 1976).†

**Discussion.** Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1 and a view of the molecule with atom labelling is presented in Fig. 1. Table 2 details bond angles and some torsion angles.

The geometry of the ring and of the associated exocyclic bonds shows the characteristic behaviour of analogous compounds where the presence of a heteroatom is coupled with the high strain of the three-membered ring and the effect of the substituents may cause bond-length asymmetry in the ring. With respect to cyclopropane, introduction of a heteroatom into the small ring decreases the distal C—C ring bond length (Bak & Skaarup, 1971; Ito & Sakurai, 1973; Delker, Wang, Stucky, Lambert, Haas & Seyferth, 1976; Allen, 1982), while the $\pi$-acceptor substituents shorten the distal bond and lengthen the vicinal (Lauher & Ibers, 1975; Deakyne, Allen & Laurie, 1977; Allen, 1980, 1982): the result may be approximated as a summation of asymmetries induced by each individual effect. In the title compound the C(3)—C(4) bond is shorter than the normal $C_{sp^3}$—$C_{sp^3}$ bond but is longer than the corresponding bond in pure unsubstituted aziridine [mean value 1·484 (3) Å in Allen, 1982]; the N(3)—C(4) bond is longer than the N(3)—C(3) bond in accord with the substituent effect. The valence angles within the three-membered ring are thus different, with the smallest angle at C(4). The ring N atom is pyramidal, lying 0·656 (3) Å out of the plane defined by its three substituents; the C(5)—N(3) bond makes an angle of 122·3 (3)° with the aziridine plane and has a mean valence angle at N of 117·4 (4)°. The plane

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† Lists of structure factors, anisotropic thermal parameters and least-squares planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39770 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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defined by C(1)—C(4)—C(2) is almost perpendicular to the ring plane, the twist being 88·3 (2)° and these two planes almost exactly bisect the angles C(3)—C(4)—N(3) and C(1)—C(4)—C(2). The bent-back angle $\beta$ defined, according to Stalick & Ibers (1970), as the angle between the normal to the C(1)—C(4)—C(2) plane and the vector C(3)—C(4) is 60·6 (4)°, nearly equal to the value of 60·0° in cyclopropane. The two carboxamide groups are as far apart as possible as required by steric hindrance and make an angle of 64·7 (3)° with each other. The planes of the two carboxamide groups N(1)—C(1)—O(1) and N(2)—C(2)—O(2) are nearly parallel to the C(4)—C(3) and C(4)—N(3) bonds respectively as shown in the Newman projection of Fig. 2. The asymmetry in the angles centred on C(1) and C(2), owing in part to the different type of substituents, is perhaps also increased by some short non-bonded contacts involving N and O atoms of carboxamide groups.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and equivalent isotropic thermal parameters* (Å$^2$)

| | $x$ | $y$ | $z$ | $B_{eq}$†/$B_{iso}$ |
|---|---|---|---|---|
| O(1) | 3574 (1) | 5859 (4) | 1934 (4) | 3·0 (2) |
| O(2) | 4715 (1) | 2204 (4) | 408 (3) | 2·5 (2) |
| N(1) | 4349 (1) | 4606 (5) | 3245 (4) | 3·0 (3) |
| N(2) | 4266 (2) | −450 (5) | 1218 (5) | 3·2 (3) |
| N(3) | 3276 (1) | 1448 (5) | 2002 (4) | 2·3 (2) |
| C(1) | 3891 (2) | 4507 (5) | 2217 (5) | 1·9 (3) |
| C(2) | 4298 (2) | 1386 (5) | 1008 (5) | 1·9 (3) |
| C(3) | 3247 (2) | 2349 (6) | 383 (5) | 2·7 (3) |
| C(4) | 3780 (2) | 2555 (5) | 1458 (4) | 1·8 (2) |
| C(5) | 2917 (2) | 2289 (6) | 3271 (5) | 2·9 (3) |
| H(1N1) | 447 (2) | 366 (6) | 348 (6) | 5 (1) |
| H(2N1) | 442 (1) | 567 (5) | 382 (5) | 3 (1) |
| H(1N2) | 401 (2) | −107 (6) | 162 (5) | 5 (1) |
| H(2N2) | 453 (2) | −103 (5) | 92 (4) | 4 (1) |
| H(1C3) | 328 (2) | 147 (6) | −63 (5) | 3 (1) |
| H(2C3) | 300 (2) | 352 (6) | 22 (5) | 6 (1) |
| H(1C5) | 254 (2) | 159 (7) | 332 (6) | 6 (1) |
| H(2C5) | 309 (2) | 208 (7) | 442 (6) | 4 (1) |
| H(3C5) | 281 (2) | 373 (6) | 313 (5) | 5 (1) |

† $B_{eq} = \frac{1}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

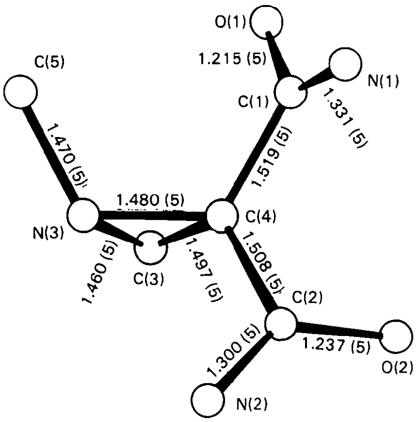

Fig. 1. Perspective view of the molecule with atomic labelling and bond distances (Å).

Crystal packing is governed by an extended hydrogen-bonding network of the type N—H···O and by some weak intra- and intermolecular interactions as reported in Table 3. The shortest non-bonded distance is the intramolecular contact N(3)···N(2), which appears to occur repeatedly in aziridine compounds whenever possible. This contact, however, is associated with an unfavourable N(3)···H—N(2) angle, thus indicating a rather weak interaction. The same pronounced deviation from linearity affects the N(1)—H(1)···O(2) contact and the bond appears to be disqualified as a hydrogen bond. This unfavourable geometry is probably due to the presence of the bifurcated bonds involving both N(2)—H(1) and N(1)—H(1) as indicated in Table 3.

Table 2. *Bond angles and selected torsion angles* (°)

| | | | |
|---|---|---|---|
| C(4)—N(3)—C(5) | 118·0 (3) | O(2)—C(2)—C(4) | 118·7 (3) |
| C(3)—N(3)—C(5) | 116·7 (3) | N(3)—C(3)—C(4) | 60·1 (2) |
| C(3)—N(3)—C(4) | 61·2 (2) | C(2)—C(4)—C(3) | 116·9 (3) |
| O(1)—C(1)—N(1) | 122·9 (4) | C(1)—C(4)—C(3) | 116·8 (3) |
| N(1)—C(1)—C(4) | 115·0 (3) | C(1)—C(4)—C(2) | 117·5 (3) |
| O(1)—C(1)—C(4) | 122·1 (3) | N(3)—C(4)—C(3) | 58·7 (2) |
| O(2)—C(2)—N(2) | 124·0 (4) | N(3)—C(4)—C(2) | 115·4 (3) |
| N(2)—C(2)—C(4) | 117·2 (3) | N(3)—C(4)—C(1) | 118·4 (3) |

| | |
|---|---|
| C(5)—N(3)—C(4)—C(1) | −1·1 (5) |
| C(3)—N(3)—C(4)—C(1) | 105·7 (4) |
| C(5)—N(3)—C(4)—C(2) | 145·8 (3) |
| C(3)—N(3)—C(4)—C(2) | −107·4 (4) |
| O(1)—C(1)—C(4)—N(3) | −69·3 (5) |
| N(1)—C(1)—C(4)—C(3) | 176·0 (3) |
| O(2)—C(2)—C(4)—N(3) | 173·7 (3) |
| N(2)—C(2)—C(4)—C(3) | −69·7 (5) |

Table 3. *Some non-bonded parameters*

| $A$—H···$B$ | $A$···$B$(Å) | H···$B$(Å) | ∠$A$—H···$B$(°) | Symmetry operation for $B$ |
|---|---|---|---|---|
| Hydrogen bonding | | | | |
| N(1)—H(1)···O(2) | 3·001 (5) | 2·77 (5) | 101 (4) | $x, y, z$ |
| N(2)—H(1)···N(3) | 2·743 (5) | 2·47 (5) | 101 (3) | $x, y, z$ |
| N(1)—H(1)···O(2) | 2·927 (4) | 2·30 (4) | 143 (4) | $1-x, y, \frac{1}{2}-z$ |
| N(1)—H(2)···O(2) | 2·952 (5) | 2·07 (4) | 168 (3) | $x, 1-y, \frac{1}{2}+z$ |
| N(2)—H(2)···O(2) | 3·004 (4) | 2·25 (4) | 166 (3) | $1-x, -y, -z$ |
| N(2)—H(1)···O(1) | 3·108 (5) | 2·39 (4) | 147 (4) | $x, y-1, z$ |
| Some intra- and intermolecular contacts | | | | |
| C(3)—H(2)···O(1) | 2·856 (5) | 2·50 (4) | | $x, y, z$ |
| C(5)—H(3)···O(1) | 3·141 (5) | 2·53 (4) | | $x, y, z$ |
| C(3)—H(1)···O(1) | 3·188 (5) | 2·83 (4) | | $x, 1-y, z-\frac{1}{2}$ |
| C(5)—H(1)···O(1) | 3·593 (5) | 2·64 (4) | | $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ |
| C(5)—H(2)···O(1) | 3·548 (5) | 2·72 (4) | | $x, 1-y, \frac{1}{2}+z$ |

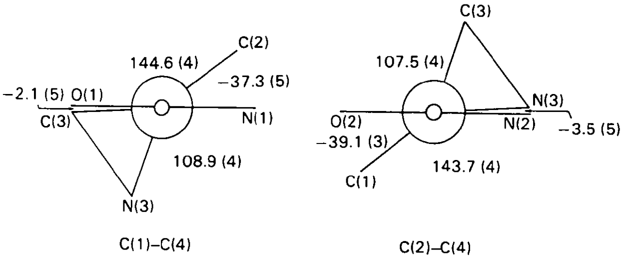

Fig. 2. Newman projection along the C(1)—C(4) and C(2)—C(4) bonds. (Angles in deg.)

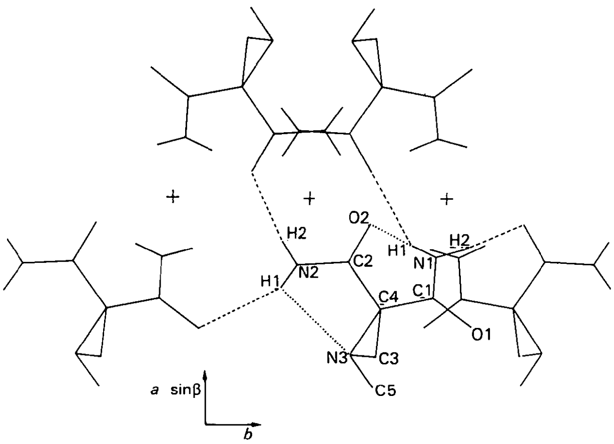

Fig. 3. Schematic representation of the molecular network formed by intra- (dotted line) and intermolecular (dashed line) hydrogen bonds.

Two intermolecular contacts involve H(2)—N, acting as a single hydrogen donor, and O(2) and their geometry implies two weak hydrogen bonds. There are also some short distances of the type C—H···O, all involving the O(1) atom; the relative parameters are reported in Table 3. The packing arrangement in the crystal is shown in Fig. 3, together with the hydrogen-bonding scheme.

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# The Structures of Two Crystalline Forms of 1-Phenyl-2,2-aziridinedicarboxamide, $C_{10}H_{11}N_3O_2$

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**Abstract.** $M_r = 205\cdot2$. (*A*): monoclinic, $P2_1/n$, $a = 6\cdot180\,(5)$, $b = 28\cdot147\,(12)$, $c = 5\cdot919\,(2)$ Å, $\beta = 105\cdot90\,(4)°$, $V = 990\,(1)$ Å$^3$, $Z = 4$, $D_x = 1\cdot376$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot928$ cm$^{-1}$, $F(000) = 432$, room temperature, final $R = 0\cdot054$ for 813 observed reflections. (*B*): orthorhombic, $P2_12_12_1$, $a = 7\cdot236\,(4)$, $b = 8\cdot761\,(1)$, $c = 15\cdot700\,(4)$ Å, $V = 995\cdot3\,(6)$ Å$^3$, $Z = 4$, $D_x = 1\cdot370$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot923$ cm$^{-1}$, room temperature, final $R = 0\cdot050$ for 1576 observed reflections. Two crystalline forms of the title compound have been obtained from ethanol in dilute solution by fast evaporation (form *A*) and in concentrated solution by slow evaporation (form *B*). The pyramidal geometry of the N ring atom is discussed and compared with previous data. The molecular dimensions of the two structures are similar, the orientation of the phenyl plane with respect to the aziridine ring is perpendicular in *A* and quasi perpendicular in *B*.

**Introduction.** The crystal structures of the title compound were determined as part of a continuing study into aziridine systems in order to investigate the pyramidal nature of the ring nitrogen atom and the

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