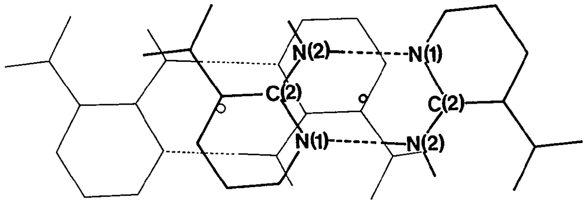

Fig. 3. A drawing of the dimer stacking, viewed perpendicular to the planes of the pyridine rings.

from the plane by > 10σ. From torsion angles involving O(1), O(2), N(3), C(3), C(2) and C(4) a slight rotation (< 3°) of the nitro group can be inferred. C(3), N(3), O(1) and O(2) are coplanar within 0·002 Å; this plane makes an angle of 3·7° with the plane of the pyridine ring.

Table 2. *Deviations from the least-squares plane of the pyridine ring*

The direction cosines of the least-squares plane of N(1)–C(6), weighted equally, are 0·7630, −0·6460 and −0·1961 relative to the crystal axes *a*, *b* and *c*; the origin-to-plane distance is 0·281 Å.

N(1)	−0·004 Å	N(2)	0·003 Å	H(1)	0·07 Å
C(2)	0·004	N(3)	0·028	H(2)	0·07
C(3)	−0·001	O(1)	0·109	H(4)	−0·02
C(4)	−0·004	O(2)	−0·022	H(5)	0·02
C(5)	0·004			H(6)	0·01
C(6)	0·002				

A drawing of the structure is shown in Fig. 2. Centres of symmetry are utilized in forming dimers linked by N(2)–H(1)···N(1) hydrogen bonds [N(2)···N(1) = 3·009; H(1)···N(1) = 2·04 Å]. The second H atom of the amino group is involved in an intramolecular hydrogen bond [H(2)···O(1) = 2·03 Å].

Molecules related to one another by translation along **b** form a column of relatively close, off-set stacked dimers; the stacking distance is 3·16 Å. The shortest heavy-atom contacts within the stacked dimers are: O(2)···N(2), 3·231; N(3)···N(2), 3·244; C(4)···N(1), 3·311; C(2)···N(1), 3·333; C(6)···N(2), 3·338; N(1)···N(2), 3·383; and C(2)···C(2), 3·385 Å. A drawing of one of these columns, viewed perpendicular to the planes of the dimers, is shown in Fig. 3.

The shortest contacts between atoms in different stacks involve atoms of the nitro group. They include: N(2)···O(1) (at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$), 3·046; C(4)···O(2) (at $-x, -1-y, 1-z$), 3·345; and C(5)···O(2) (at $-x, -y, 1-z$), 3·388 Å.

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3-Cyano-2-phenylglyoxyl-*N*-methoxyaziridine (*E*)

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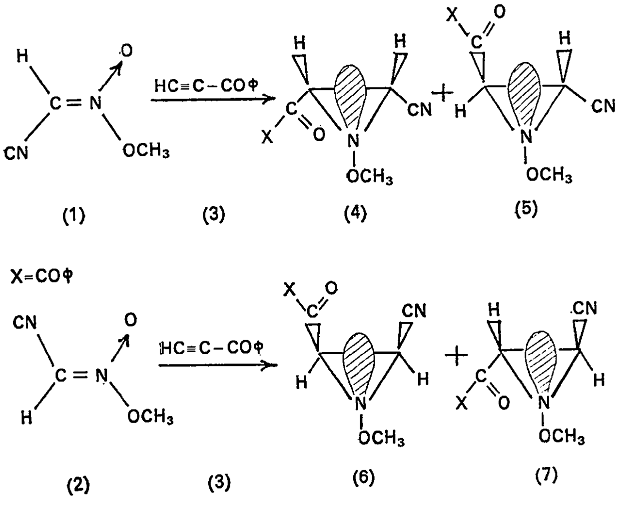
Abstract. $C_{12}H_{10}N_2O_3$, orthorhombic, *Pbca*, $a = 15{\cdot}70$ (2), $b = 6{\cdot}45$ (1), $c = 23{\cdot}19$ (2), $Z = 8$, $D_c = 1{\cdot}30$ g cm^{-3}. This determination has been carried out to establish unambiguously the stereochemistry at the nitrogen atom N(1). The methoxy group bonded to N(1) is *cis* with respect to the cyano group and *trans* to the phenylglyoxyl group.

Introduction. The addition of nitronic esters (1) and (2) to benzoylacetylene (3) leads to a quantitative yield of stable nitrogen invertomers of aziridines (4) to (7).* This reaction is stereoselective (Grée & Carrié, 1975); (1) gives only (4) and (5), and (2) leads to (6) and (7):



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* It is well known that the nitrogen inversion barrier of aziridines is considerably raised when this nitrogen bears a methoxy substituent (Brois, 1970; Lehn, 1970; Rauk, Allen & Mislow, 1970).

The relative configuration of the ring C atoms of aziridines (4) to (7) was established by n.m.r. spectroscopy (Grée & Carrié, 1975), but it is not possible to establish unambiguously the N stereochemistry by spectroscopic techniques, particularly for aziridines (5) and (7) with *trans* H atoms.* In order to study the mechanism of the formation of these aziridines it is necessary to know their stereochemistry and to this end we undertook the X-ray analysis of one of them (5). To our knowledge this is the first stable invertomer of aziridine to have been subjected to an X-ray analysis.

Crystals were obtained by slow evaporation at room temperature of a saturated solution in carbon tetrachloride (90%) and chloroform (10%). The cell constants were determined from oscillation and Weissenberg photographs (Cu $K\alpha_1$, $\lambda = 1{\cdot}54051$ Å).

The intensities were collected on an Enraf–Nonius three-circle automatic diffractometer with Zr-filtered Mo $K\alpha$ radiation and a $\theta/2\theta$ scan. 2097 reflexions were recorded to a maximum θ of 35°. Reflexions which were less than twice their standard deviation were considered as unobserved; 1380 reflexions were used in the crystal analysis. The intensities were corrected for Lorentz and polarization factors but absorption corrections were not applied ($\mu_r \simeq 1{\cdot}03$ cm^{-1}).

The structure was solved by a modified version of the *MULTAN* direct phase determination procedure (Germain, Main & Woolfson, 1971). The statistical method of Wilson was used to derive an approximate scale and temperature factor. Then the structure factors were converted to the normalized values $|E_{hkl}|$. The statistical averages are listed in Table 1 and yield ad-

Table 1. *Statistical averages and distribution of* $|E|$ *values*

	Experimental	Theoretical	
		Non-centric	Centric
$\langle\lvert E\rvert\rangle$	0·7354	0·8860	0·7980
$\langle\lvert E\rvert^2\rangle$	1·00	1·00	1·00
$\langle\lvert E\rvert^2-1\rangle$	0·9864	0·7360	0·9680
$\lvert E\rvert > 0{\cdot}5$ (%)	60·7	77·9	61·7
$\lvert E\rvert > 1{\cdot}0$ (%)	33·3	36·8	31·7
$\lvert E\rvert > 1{\cdot}5$ (%)	12·7	10·5	13·4
$\lvert E\rvert > 2{\cdot}0$ (%)	4·4	1·8	4·6
$\lvert E\rvert > 2{\cdot}5$ (%)	1·7	0·2	1·2

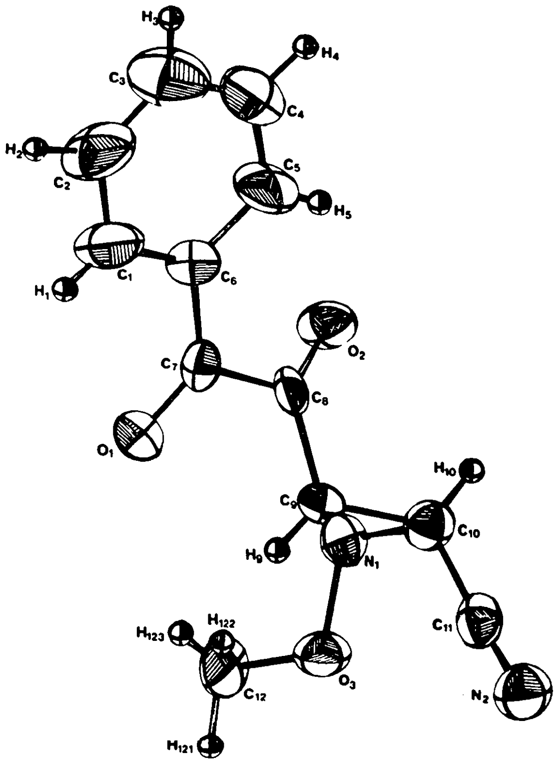

Fig. 1. Stereoscopic view of the molecule. The non-hydrogen atoms are represented by ellipsoids defined by the principal axes of thermal vibration and scaled to include 50% probability. The hydrogen atoms were represented by spheres of 0·1 Å radius.

Table 2. *Fractional atomic coordinates and thermal parameters* (× 10^5) *with standard deviations*

Anisotropic temperature factors are in the form exp $(-b_{11}h^2-b_{22}k^2-b_{33}l^2-2b_{12}hk-2b_{13}hl-2b_{23}kl)$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	0·58228 (27)	0·69731 (70)	0·16911 (17)	543 (29)	4227 (192)	185 (12)	300 (62)	−124 (14)	−236 (39)
C(2)	0·58273 (30)	0·72017 (78)	0·22937 (21)	809 (34)	4588 (207)	257 (13)	633 (74)	−105 (18)	−611 (45)
C(3)	0·62023 (31)	0·57980 (82)	0·26300 (21)	745 (32)	5831 (252)	171 (13)	216 (79)	26 (16)	40 (44)
C(4)	0·65594 (28)	0·41006 (68)	0·23823 (21)	794 (37)	3566 (194)	241 (14)	339 (64)	−98 (17)	174 (40)
C(5)	0·65808 (31)	0·38022 (68)	0·17786 (17)	817 (36)	3651 (164)	102 (11)	237 (70)	−13 (13)	146 (35)
C(6)	0·62042 (22)	0·52731 (55)	0·14374 (16)	274 (22)	2493 (143)	127 (10)	22 (51)	2 (13)	−25 (32)
C(7)	0·61474 (21)	0·50910 (49)	0·07991 (15)	267 (23)	1259 (129)	177 (11)	−57 (43)	10(12)	−37 (29)
C(8)	0·65887 (21)	0·32619 (48)	0·04714 (13)	343 (22)	1018 (112)	165 (11)	−47 (43)	−28 (11)	146 (29)
C(9)	0·61729 (23)	0·26352 (60)	−0·00787 (15)	379 (21)	1853 (128)	95 (8)	25 (48)	−23 (11)	49 (29)
C(10)	0·63380 (24)	0·04472 (57)	−0·02712 (15)	330 (23)	2173 (135)	154 (10)	−110 (51)	−11 (12)	23 (30)
C(11)	0·56709 (24)	−0·05770 (49)	−0·05971 (14)	436 (27)	1749 (135)	153 (10)	−8 (46)	43 (13)	11 (31)
C(12)	0·66698 (39)	0·45754 (67)	−0·13013 (20)	1163 (38)	1991 (136)	166 (12)	−736 (62)	−38 (15)	263 (29)
N(1)	0·68044 (17)	0·21718 (39)	−0·05525 (11)	345 (16)	1850 (103)	169 (8)	114 (33)	−9 (9)	−19 (26)
N(2)	0·51573 (20)	−0·14790 (46)	−0·08468 (12)	544 (22)	2892 (112)	194 (9)	−218 (45)	−18 (12)	29 (27)
O(1)	0·57851 (14)	0·63473 (37)	0·04877 (9)	443 (16)	2058 (78)	189 (7)	149 (33)	−63 (8)	47 (21)
O(2)	0·72555 (14)	0·25399 (32)	0·06362 (9)	324 (13)	3067 (98)	199 (7)	321 (31)	−73 (8)	−174 (21)
O(3)	0·63952 (14)	0·25919 (35)	−0·11015 (9)	499 (16)	2798 (88)	125 (6)	−248 (36)	−50 (8)	78 (22)

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* The study of the thermodynamic stabilities of (4) and (6) reveals the stereochemistry (Grée & Carrié, 1975).

Table 2 (*cont.*)

Fractional atomic coordinates and isotropic thermal parameters for hydrogen atoms.

	x	y	z	B(Å^2)
H(1)	0·5559 (22)	0·7881 (51)	0·1506 (14)	5·0
H(2)	0·5640 (22)	0·8485 (60)	0·2374 (14)	5·0
H(3)	0·6156 (23)	0·5766 (51)	0·3035 (16)	5·0
H(4)	0·6904 (19)	0·3033 (56)	0·2570 (15)	5·0
H(5)	0·6740 (22)	0·2713 (50)	0·1627 (16)	5·0
H(9)	0·5793 (19)	0·3521 (58)	−0·0226 (15)	5·0
H(10)	0·6705 (20)	−0·0414 (45)	−0·0067 (17)	5·0
H(121)	0·6455 (27)	0·4840 (52)	−0·1726 (18)	6·0
H(122)	0·7290 (27)	0·4615 (55)	−0·1386 (15)	6·0
H(123)	0·6596 (29)	0·5456 (52)	−0·1059 (19)	6·0

ditional evidence for a centrosymmetric space group. From 920 $\sum_2$ relations, the program *MULTAN* produced 16 sets of signs for the phases of 150 reflexions ($E > 1{\cdot}55$). The set of best consistency was determined unambiguously (ABS FOM = 1·0906, PSI ZERO = 171, RESID = 33·23 and COMBINED FOM = 3·00: these four figures of merit are the best values of ABS FOM and COMBINED FOM maximum, PSI ZERO and RESID minimum). The corresponding E map revealed most of the atoms of the molecule. After a Fourier synthesis the remaining non-hydrogen atoms were located. Refinement of atomic positions and anisotropic temperature factors was carried out with the least-squares program of Busing, Martin & Levy (1962). The following weighting scheme was introduced at this stage and used throughout refinement.

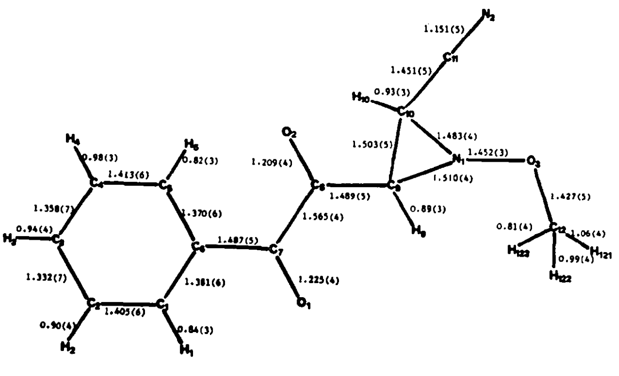

Fig. 2. Interatomic distances in the molecule. Standard deviations are in parentheses.

$$W^{-1} = \sigma^2(|F_o|) = \frac{1}{N}\frac{F_o^2}{4I^2}\left(\mathrm{CN} + B + \frac{I^2}{400}\right)$$

where CN is the total number of counts collected during the scan. B is the total background counts, I is the net intensity and N is the number of cycles of measurement for the reflexion. H atoms were located by a difference Fourier map and were included in the subsequent refinement cycles. The isotropic temperature factors for H atoms were arbitrarily fixed at mean values and were not refined. Further least-squares calculations lowered the final agreement indices R_1 and R_2 to respectively 0·063 and 0·054 [$R_1 = \sum w||F_o| - |F_c||/\sum w|F_o|$ and $R_2 = \sum w^2(|F_o| - |F_c|)^2/\sum w^2|F_o^2|^{1/2}$].

The final positional and thermal parameters are given in Table 2.*

Table 3. *Bond angles* (°)

C(2)—C(2)—C(3)	120·9 (5)	C(6)—C(1)—H(1)	123 (2)
C(2)—C(3)—C(4)	118·9 (5)	C(2)—C(1)—H(1)	116 (2)
C(3)—C(4)—C(5)	122·6 (4)	C(1)—C(2)—H(2)	108 (2)
C(4)—C(5)—C(6)	117·9 (4)	C(3)—C(2)—H(2)	130 (2)
C(5)—C(6)—C(1)	119·4 (4)	C(2)—C(3)—H(3)	124 (2)
C(6)—C(1)—C(2)	120·3 (4)	C(4)—C(3)—H(3)	116 (2)
C(1)—C(6)—C(7)	117·4 (3)	C(3)—C(4)—H(4)	127 (2)
C(5)—C(6)—C(7)	123·1 (3)	C(5)—C(4)—H(4)	109 (2)
C(6)—C(7)—O(1)	124·2 (3)	C(4)—C(5)—H(5)	123 (2)
C(8)—C(7)—O(1)	114·7 (3)	C(6)—C(5)—H(5)	118 (2)
C(6)—C(7)—C(8)	121·1 (3)	C(8)—C(9)—H(9)	116 (2)
C(7)—C(8)—C(9)	115·3 (3)	C(10)—C(9)—H(9)	127 (2)
C(7)—C(8)—O(2)	121·4 (3)	N(1)—C(9)—H(9)	107 (2)
C(9)—C(8)—O(2)	123·1 (3)	N(1)—C(10)-H(10)	111 (2)
C(8)—C(9)—C(10)	115·7 (3)	C(9)—C(10)-H(10)	121 (2)
C(8)—C(9)—N(1)	112·9 (3)	C(11)—C(10)-H(10)	116 (2)
C(10)-C(9)—N(1)	59·0 (2)	O(3)—C(12)-H(121)	111 (2)
C(9)—C(10)-N(1)	60·7 (2)	O(3)—C(12)-H(122)	113 (2)
C(9)—N(1)—C(10)	60·3 (2)	O(3)—C(12)-H(123)	111 (3)
C(9)—C(10)-C(11)	117·3 (3)	H(121)-C(12)-H(122)	97 (3)
N(1)—C(10)-C(11)	118·0 (3)	H(121)-C(12)-H(123)	119 (4)
C(10)-C(11)-N(2)	176·7 (4)	H(122)-C(12)-H(123)	105 (4)
C(9)—N(1)—O(3)	108·1 (3)		
C(10)-N(1)—O(3)	107·9 (2)		
N(1)—O(3)—C(12)	108·5 (3)		

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31281 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. A stereoscopic drawing of the molecule made with *ORTEP* (Johnson, 1965) is shown in Fig. 1. The bond distances and angles are respectively given in Fig. 2 and Table 3 with their estimated standard deviations. The mean value of the benzene ring bonds is 1·377 Å and is shorter than the expected value of 1·395 Å. One bond distance, C(2)–C(3), differs considerably: the difference between the observed value and the normal value (0·06 Å) is about nine standard deviations. There is, however, no obvious explanation for this discrepancy; the most plausible is the mediocre measurement of the weak and zero reflexions. The least-squares plane of the phenyl ring and the deviations of the atoms from this plane are shown in Table 4. The values of the C–H bond lengths are in a reasonable range of 0·81–1·06 Å (mean value: 0·92 Å). The four atoms C(7), C(8), C(9) and O(2) lie approximately in a plane (maximum deviation from the least-squares plane: 0·030 Å). The torsional angle between the two carbonyl groups C(7)–O(1) and C(8)–O(2) is 36·16° while that between the planes O(1)–C(7)–C(8) and C(7)–C(8)–C(9) is 30·63°.

The X-ray structure determination of this aziridine compound gives the nitrogen stereochemistry which enables the mechanism of formation and the physical and chemical properties of these heterocycles to be studied.

Table 4. *Deviations* (Å) *from least-squares plane of the phenyl ring* $0{\cdot}8667X + 0{\cdot}4955Y - 0{\cdot}0571Z = 9{\cdot}9325$

C(1)	−0·0042	H(1)	−0·0487
C(2)	−0·0047	H(2)	0·1398
C(3)	0·0125	H(3)	−0·1142
C(4)	−0·0112	H(4)	0·0912
C(5)	0·0023	H(5)	−0·1096
C(6)	0·0052		

The authors thank Dr R. Grée and Dr R. Carrié for suggesting the problem and providing the compound.

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Stacking Patterns of Halogenated Purines: Crystal Structure of 6-Chloropurine Riboside

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Abstract. $C_{10}H_{11}N_4O_4Cl$, monoclinic, $C2$, $a=13{\cdot}615$ (6), $b=8{\cdot}067$ (2), $c=12{\cdot}474$ (3) Å, $\beta=121{\cdot}14$ (2)°, $Z=4$, M.W. 286·67, $D_c=1{\cdot}605$, $D_m=1{\cdot}61$ g cm^{-3}, $\mu=30{\cdot}6$ cm^{-1}. The base stacking pattern involves Cl–purine contacts.

Introduction. Many investigators have suggested that halogen substituents affect purine and pyrimidine stacking interactions in aqueous solutions of nucleosides, in crystal structures of purine and pyrimidine derivatives, and within polynucleotides [*e.g.* review by Bugg & Sternglanz (1975) and references therein]. We determined the crystal structure of 6-chloropurine riboside to obtain additional information about the base-stacking patterns of halogenated purines. Prismatic crystals were obtained by slowly evaporating an acetonitrile–n-butyl ether solution of the nucleoside. Oscillation and Weissenberg photographs showed that the optically active crystals are monoclinic, and the space group $C2$ was indicated by the systematic absence of reflections hkl with $h+k$ odd. A crystal approximately 0·15 × 0·18 × 0·2 mm was mounted on a Picker FACS-1 diffractometer with **b** slightly inclined to the φ axis of the goniostat. Approximate cell parameters for use in collection of intensity data were calculated by least-squares analysis of the angular settings for eight medium-angle reflections (Cu $K\bar{\alpha}$, $\lambda=1{\cdot}5418$ Å). Intensity data were collected on the diffractometer with a scintillation counter, Ni-filtered Cu radiation, and a θ–2θ scan. The scan speed was 1° min^{-1}, and the background was counted for 20 s at each terminus of the scans. Measurements were made for each of the 1162 independent reflections with $2\theta \le 128°$. Three reference reflections, which were monitored periodically,