

$0.006655|F_o|^2$], max. shift to e.s.d. = 0.09. A final difference Fourier map was featureless with $\Delta\rho$ within $\pm 0.25 \text{ e } \text{Å}^{-3}$. The atomic scattering factors used in the calculations for all non-H atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), while those for the H atoms were taken from Stewart, Davidson & Simpson (1965). Computer programs: *PARST* (Nardelli, 1983) for geometrical calculation; *MOLDRW* (Ugliengo, Borzani & Viterbo, 1988) for molecular illustrations. All calculations were performed on a VAX 11/780 computer.

Discussion. The final positional parameters and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Fig. 1 shows the molecular diagram and atomic numbering scheme. Bond lengths and angles for non-H atoms are listed in Table 2. Bond lengths and angles in the benzene and pyrone rings are close to the mean values observed for the same distances and angles in other coumarin derivatives. Calculation of the least-squares plane shows that the benzene and pyrone rings are planar with maximum deviations of 0.016 Å at C(3) and -0.015 Å at C(10). The NH_2 group is coplanar with the benzene and pyrone rings. The deviation of atom N(7) is -0.02 Å. The C—N distance of 1.356 Å is normal. A similar result has been observed for 7-diethylamino-4-methylcoumarin

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, least-squares-planes calculations and H-atom parameters, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54440 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Messagar & Delugeard, 1974). The carbonyl O atom O(2) lies in the plane of the benzene and pyrone rings [the deviation of O(2) is -0.04 Å].

Coumarins are well known photosensitizing agents in photodynamic action. Song & Gordon (1970) concluded from both spectroscopic results and theoretical calculations that this property might be assigned either to carbonyl stretching or to C=C stretching in the pyrone moiety. Because of steric effects, the O(2)—C(2)—O(1) angle is generally smaller than the O(2)—C(2)—C(3) angle in coumarin and its derivatives. It is also found that the angles C(8)—C(9)—O(1) and C(4)—C(10)—C(5) at the junctions of the two rings are smaller and greater respectively than 120° . This causes the approach of O(1) to C(8) and the separation of C(4) from C(5). All of these common features found in coumarin derivatives are also present in the title compound. There are no short contacts. The structure is stabilized by van der Waals interactions.

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Structure of 2,2-Dimethyl-3-(2-methyl-1,3-dithian-2-yl)-3-phenylaziridine

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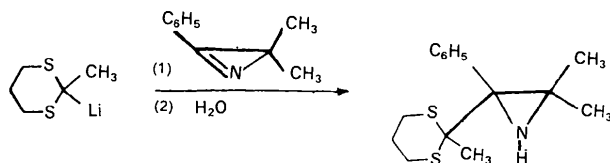
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Abstract. $\text{C}_{15}\text{H}_{21}\text{NS}_2$, $M_r = 279.45$, triclinic, $P\bar{1}$, $a = 741.7$ (6) Å³, $Z = 2$, $D_m = 1.25$ (2), $D_x = 7.472$ (3), $b = 10.535$ (2), $c = 10.857$ (5) Å, $\alpha = 1.254$ (1) Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 99.99$ (3), $\beta = 90.97$ (4), $\gamma = 117.53$ (2)°, $V = 3.01$ mm⁻¹, $F(000) = 300$, room temperature, $R =$

0.049 for 2265 observed reflexions and 248 parameters. The structure contains a three-membered aziridine ring linked to a phenyl ring and a chair-shaped six-membered 1,3-dithiane ring. There are two methyl radicals on the aziridine ring and one methyl radical on the dithiane ring.

Introduction. Applications of aziridine chemistry to synthesis, mechanistic studies and biological investigations have become increasingly numerous. Some aziridines have antitumoral effects and others anti-AIDS properties (Dagani, 1986; Hassner, 1983; Dermer & Ham, 1969). The synthesis of the title aziridine has been carried out to prove the general mechanism of the reaction of 2*H*-azirines with carbanions. This compound was prepared by Ben Cheikh, Bouzouita, Ghabi & Chaabouni, (1990), using the reaction of the 2-methyl-1,3-dithiane anion with 2,2-dimethyl-3-phenylazirine.



Elemental analysis, mass spectroscopy, IR, and ¹H and ¹³C NMR established its chemical nature. X-ray diffraction was carried out in order to define the structural details of the molecule and to determine the conformation of the six-membered dithiane ring and its position relative to the aziridine ring.

Experimental. Transparent plate-like crystals were obtained from a solution of the material in petroleum spirit. Density was determined by flotation. A sample $\sim 0.05 \times 0.27 \times 0.35$ mm was chosen for X-ray diffraction. Unit-cell parameters obtained initially from oscillation and Weissenberg photographs were refined by a least-squares procedure from the setting of 25 strong reflexions measured on a CAD-4 diffractometer with $9.23 < \theta < 65.87^\circ$. Intensity data were then collected using graphite-monochromated Cu *K* α radiation in the range $0 < \theta < 70^\circ$ corresponding to $(\sin \theta / \lambda)_{\max} = 0.61 \text{ \AA}^{-1}$. $\omega/2\theta$ scan mode was used with a max. speed of $0.11^\circ \text{ s}^{-1}$ and a scan range of $(2.5 + 0.15 \tan \theta)^\circ$. Range of *hkl* (*h*: $-9 \rightarrow 9$; *k*: $-12 \rightarrow 12$; *l*: $0 \rightarrow 13$). Three standard reflections (251, 0 $\bar{1}$ 1, 021) measured every 2 h gave small decreases of intensity leading to an average correction of 1.013. The total number of reflexions measured was 2813. Only 2350 reflexions with $I > 3\sigma(I)$ were used for structure refinement. Intensities were corrected for Lorentz-polarization. An empirical absorption correction was performed: the transmission coefficients were in the range 79–99%. No

Table 1. Atomic coordinates and displacement parameters for non-H atoms

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
S(1)	0.1737 (1)	0.6778 (1)	0.3617 (1)	0.0533 (3)
S(2)	0.0255 (1)	0.7245 (1)	0.1197 (1)	0.0513 (3)
N	0.5110 (3)	0.9490 (2)	0.3602 (2)	0.0482 (8)
C(1)	0.5184 (3)	0.9331 (2)	0.2239 (2)	0.0392 (8)
C(2)	0.3413 (3)	0.9406 (2)	0.2809 (2)	0.0429 (8)
C(3)	0.1331 (3)	0.8056 (2)	0.2839 (2)	0.0547 (14)
C(4)	0.0806 (5)	0.5216 (3)	0.3334 (3)	0.0429 (8)
C(5)	0.1653 (5)	0.4578 (3)	0.1964 (3)	0.0645 (17)
C(6)	0.2035 (4)	0.5613 (3)	0.1317 (3)	0.0639 (18)
C(7)	0.0062 (5)	0.8520 (3)	0.3583 (3)	0.0569 (14)
C(8)	0.3265 (3)	1.0791 (2)	0.2815 (2)	0.0454 (9)
C(9)	0.2618 (4)	1.1033 (3)	0.1713 (3)	0.0510 (14)
C(10)	0.2442 (4)	1.2299 (3)	0.1718 (3)	0.0655 (17)
C(11)	0.2916 (5)	1.3318 (3)	0.2811 (4)	0.0635 (17)
C(12)	0.3549 (5)	1.3085 (3)	0.3906 (4)	0.0589 (16)
C(13)	0.3737 (4)	1.1833 (3)	0.3916 (3)	0.0683 (18)
C(14)	0.6742 (4)	1.0662 (3)	0.1798 (3)	0.0599 (16)
C(15)	0.5114 (5)	0.7941 (3)	0.1521 (3)	0.0726 (21)

correction was made for extinction. The structure determination was performed using *SHELXS86* (Sheldrick, 1986) and refined with *SHELXL76* (Sheldrick, 1976). All H atoms were found in the difference map and refined with the same overall isotropic displacement parameter. Weighting scheme, $w(F) = 0.83/[\sigma^2(F) + 0.01F^2]$. Final electron-density difference peaks were between -0.3 and 0.15 e \AA^{-3} . $(\Delta/\sigma)_{\max} = 0.1$ for non-H atoms. Final convergence occurred at $R(F) = 0.049$, $wR = 0.078$ and $S = 0.98$. Scattering factors and f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed on a VAX 11/780 of the Khawarezmi Computer Centre of Tunis University.

Discussion. The atomic coordinates and U_{eq} values for non-H atoms are listed in Table 1.* Bond lengths and angles are given in Table 2. Some torsional and dihedral angles are reported in Table 3. A projection of the molecule with thermal vibration ellipsoids is shown in Fig. 1 and the packing of the molecules in the unit cell is presented in Fig. 2.

In the aziridine ring, the C—C single-bond length of $1.499(3) \text{ \AA}$ agrees well with that reported by Ko, Olansky & Moncrief (1975) and with the C—C bonds observed in three-membered ring compounds such as cyclopropane (1.493), ethylene oxide (1.472) and ethylene sulfide (1.492 \AA). The two C—N bonds [$1.465(3)$ and $1.480(3) \text{ \AA}$] are in good agreement

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54531 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

C(3)—S(1)	1.838 (2)	C(12)—C(13)	1.391 (4)
C(4)—S(1)	1.824 (3)	C(9)—C(8)	1.389 (3)
C(3)—S(2)	1.829 (2)	C(5)—C(6)	1.520 (4)
C(6)—S(2)	1.808 (3)	C(4)—C(5)	1.515 (4)
C(2)—N	1.480 (3)	C(9)—C(10)	1.398 (4)
C(1)—N	1.465 (3)	C(10)—C(11)	1.371 (5)
C(2)—C(3)	1.555 (3)	C(1)—C(15)	1.512 (3)
C(2)—C(8)	1.512 (3)	C(1)—C(14)	1.515 (3)
C(2)—C(1)	1.499 (3)	C(3)—C(7)	1.528 (3)
C(7)—C(3)	1.528 (3)	C(11)—C(12)	1.373 (5)
C(8)—C(13)	1.389 (4)		
C(4)—S(1)—C(3)	100.8 (1)	C(13)—C(8)—C(2)	121.2 (2)
C(6)—S(2)—C(3)	102.8 (1)	C(9)—C(8)—C(2)	120.2 (2)
C(1)—N—C(2)	61.2 (1)	C(9)—C(8)—C(13)	118.7 (2)
C(3)—C(2)—N	114.0 (2)	C(4)—C(5)—C(6)	113.2 (2)
C(8)—C(2)—N	18.6 (2)	C(11)—C(10)—C(9)	120.2 (3)
C(8)—C(2)—C(3)	113.8 (2)	C(2)—C(1)—N	59.9 (1)
C(1)—C(2)—N	58.9 (1)	C(15)—C(1)—N	117.7 (2)
C(1)—C(2)—C(3)	124.6 (2)	C(15)—C(1)—C(2)	124.1 (2)
C(1)—C(2)—C(8)	116.4 (2)	C(14)—C(1)—N	115.8 (2)
S(2)—C(3)—S(1)	111.8 (1)	C(14)—C(1)—C(2)	118.3 (2)
C(2)—C(3)—S(1)	109.2 (1)	C(14)—C(1)—C(15)	111.4 (2)
C(2)—C(3)—S(2)	105.9 (1)	C(10)—C(9)—C(8)	120.5 (3)
C(7)—C(3)—S(1)	108.3 (2)	C(5)—C(6)—S(2)	113.5 (2)
C(7)—C(3)—S(2)	110.9 (2)	C(5)—C(4)—S(1)	115.3 (2)
C(7)—C(3)—C(2)	110.6 (2)	C(11)—C(12)—C(13)	120.7 (3)
C(12)—C(13)—C(8)	120.2 (3)	C(12)—C(11)—C(10)	119.8 (3)

Table 3. Selected torsional and dihedral angles (°)

C(13)—C(8)—C(2)—C(1)	-97.5 (5)	C(3)—S(1)—C(4)—C(5)	69.7 (5)
C(8)—C(13)—C(12)—C(11)	-0.8 (5)	C(3)—S(2)—C(6)—C(5)	-66.6 (5)
C(8)—C(9)—C(10)—C(11)	-0.1 (5)	C(7)—C(3)—S(1)—C(4)	81.0 (5)
C(14)—C(1)—C(2)—C(8)	0.8 (5)	H(1)—N—C(2)—C(8)	-1.9 (5)
C(7)—C(3)—C(2)—C(1)	174.3 (5)	H(1)—N—C(1)—C(14)	5.7 (5)
C(7)—C(3)—C(2)—C(8)	-28.8 (5)	H(41)—C(4)—C(5)—H(51)	-177.8 (5)
S(1)—C(3)—C(2)—N	-14.3 (5)	H(62)—C(6)—C(5)—H(52)	88.3 (5)
C(1)—C(15)—C(14)		S(1)—S(2)—C(6)	-54.9 (5)
C(2)—C(1)—N	76.2 (5)	C(6)—C(5)—C(4)	
C(9)—C(8)—C(13)		C(7)—C(3)—C(2)	97.4 (5)
C(10)—C(11)—C(12)	179.5 (5)	C(2)—C(3)—S(1)	
C(9)—C(8)—C(13)		C(15)—C(1)—C(14)	105.7 (5)
C(2)—C(1)—N	-54.3 (5)	C(13)—C(8)—C(9)	
C(3)—S(2)—S(1)	1.6 (5)	C(15)—C(1)—C(14)	106.4 (5)
C(6)—C(5)—C(4)		S(2)—C(3)—C(1)	
C(3)—S(2)—S(1)	-60.4 (5)	C(13)—C(8)—C(9)	6.6 (5)
C(2)—C(1)—N		S(2)—C(3)—S(1)	
C(6)—S(2)—S(1)	-179.7 (5)		
C(6)—C(4)—S(1)			

with the values of 1.462 (5) and 1.478 (5) Å (Gopalakrishna, 1972) found for similar bonds with a three-covalent nitrogen. The distances and angles observed in the title compound are similar to those found in other aziridine compounds (Delugeard, Vaultier & Meinnel, 1975).

The C—C bond distances in the benzene ring linked to C(2) vary from 1.371 (5) to 1.398 (4) Å, as compared to the normal C—C resonance bond distance of 1.395 (3) Å (Gopalakrishna, 1972). This ring is planar within experimental errors and makes a dihedral angle of -54.3° with the aziridine heterocycle.

The dithiane six-membered ring is, as expected, non-planar and adopts a chair conformation. The dihedral angles between C(6)—S(2)—S(1) and S(2)—C(3)—S(1), and S(1)—S(2)—C(6) and C(6)—C(5)—C(4) are -53.3 and -54.9° respectively. The torsional angles C(3)—S(1)—C(4)—C(5) and C(3)—S(2)—C(6)—C(5) are 69.7 and -66.6° . The distances of C(3) and C(5) from the least-squares plane fitted to the atoms S(1), S(2), C(6) and C(4) are 0.919 and -0.765 Å respectively. The dithiane heterocycle is linked to the aziridine ring through an equatorial C(2)—C(3) bond, and the methyl group linked to it

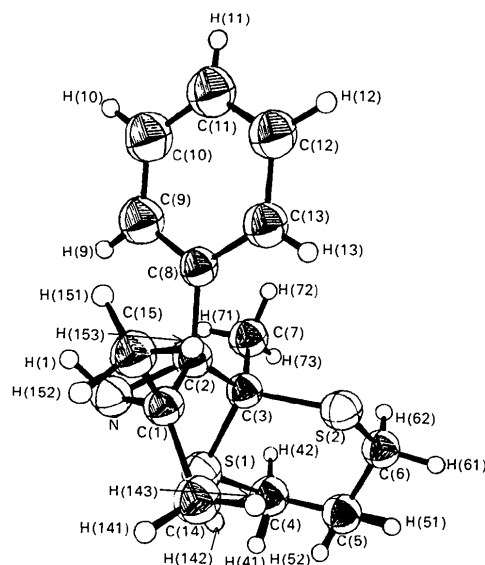


Fig. 1. Molecular structure and atom numbering.

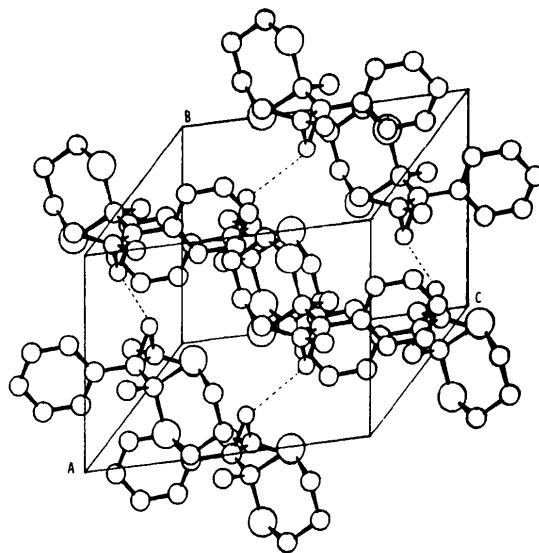


Fig. 2. Packing of the molecules in the unit cell.

at C(3) is in an axial position. The sulfur—carbon single-bond lengths [1.808 (3)–1.838 (2) Å] are similar to those reported by Grand, Robert & Filhol (1977) and Noordik, Smits, Sicherer-Roetman, Jansen & de Groot (1985).

The crystalline cohesion is ensured by a pair of symmetry-related intermolecular N⋯N' bonds spanning a centre of symmetry at ($\frac{1}{2}, 1, \frac{1}{2}$), leading to bonded dimers. The intermolecular distances and angles are N⋯N' 3.073, H(1)⋯N' 2.720, H(1)⋯H(1') 2.669 Å, N—H(1)⋯N' 103 and H(1)—N⋯H(1') 77°. All these distances are far too large for conventional hydrogen bonding and it seems that the usual van der Waals interactions hold the molecules together.

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Structure of (*R*)-3-Amino-3-phosphonopropionic Acid

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Abstract. C₃H₈NO₃P, *M_r* = 169.1, orthorhombic, *P*2₁2₁2₁, *a* = 5.103 (2), *b* = 15.209 (6), *c* = 8.114 (3) Å, *V* = 629.7 (4) Å³, *Z* = 4, *D_m* = 1.78 (1), *D_x* = 1.783 (1) Mg m⁻³, λ(Cu Kα) = 1.5418 Å, μ = 3.68 mm⁻¹, *F*(000) = 352, *T* = 293 K, final *R* = 0.037 for 704 observed reflexions. The molecule exists as a zwitterion; the amino group is protonated, the carboxyl group un-ionized, and the phosphonic acid group ionized. The conformation about the C^α—C^β bond is *trans-gauche*, the angles P—C—C—C and N—C—C—C are 176.5 (3) and -60.0 (4)°, respectively. There is extensive intermolecular hydrogen bonding, two of the three N—H⋯O hydrogen bonds are bifurcated. The crystal contains short intermolecular hydrogen bonds of 2.617 (2) (O—H⋯O=P) and 2.629 (4) Å (P—OH⋯O=P).

Introduction. A large number of phosphorus analogs of amino acids, containing a phosphonic instead of

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carboxylic moiety are now known. Almost all counterparts of naturally occurring protein amino acids have been synthesized in various laboratories. The range of applications of α-aminophosphonic acids, e.g. as antibiotics, herbicides, insecticides and enzyme inhibitors (Kafarski & Mastalerz, 1984), shows that they are particularly interesting from a biological viewpoint.

In order to study interactions between aminophosphonates and biological material it is obviously important to have significant amounts of the optically active aminophosphonic acids with known absolute configurations. Recently, we have described the synthesis, molecular structure and absolute configuration of optically active (1-amino-2-phenylethyl)phosphonic acid (PheP), an analog of phenylalanine (Kowalik, Sawka-Dobrowolska & Głowiak, 1984). Here we describe the preparation of the phosphonic analog of aspartic acid, AspP (laevorotary), from the *N*-acetyl derivative of optically pure (–)-PheP, (1). Since all reactions took place outside the asymmetric center, the absolute configurations of