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Bis(2,2-dimethylaziridinyl)phosphinic amide

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Abstract

The asymmetric unit of the title compound, $C_8H_{18}N_3OP$, contains one bis(2,2-dimethylaziridinyl)phosphinic amide molecule. The crystal structure is characterized by hydrogen bonds from the amide-N atom, which involve both H atoms of the amino group, to the phosphinic-O atom in two different molecules, thus forming infinite double-stranded chains along the base vector [100], and by hydrophobic contacts between these chains.

Comment

Bis(2,2-dimethylaziridinyl)phosphinic amide, (I), was synthesized as a member of a series of antitumour agents incorporating a bis(2,2-dimethylaziridinyl) phosphinoyl moiety (MacDiarmid *et al.*, 1985). These compounds are significantly different from conventional aziridine-type chemical alkylating agents, and have demonstrated tumour regression activity in a variety of neoplasms (Belgrad & Wampler, 1982). An amino-substituted derivative of the title compound is currently being developed as a treatment for œsophageal cancer and multiple myeloma, and the title compound itself is scheduled to be tested in the 60-panel human tumour screen of the National Cancer Institute of USA in the near future (Dunn, 1998).

(I)
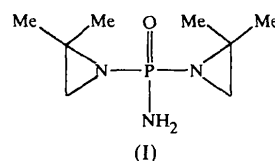
The molecular structure of (I) is presented in Fig. 1. Normals to the two planes through the aziridinyl rings intersect at an angle of 68.1 (2)°. The bond lengths and angles of the aziridinyl rings are similar to those in 5-(1-aziridinyl)-2,4-dinitrobenzamide (Iball *et al.*, 1975), and 1-(1-aziridinyl)-2,4,6-trinitrobenzene (Barnes *et al.*, 1977). The aziridinyl moieties are, within experimental error, equilateral triangles. Significant shortening of the C—C single bond of the aziridinyl rings displayed in this structure [1.484 (3) and 1.475 (4) Å] is also found in other compounds which contain strained three-membered rings, such as the two cited above, *meso*-1,4-diaziridinyl-2,3-butanediol (Gould & Pasternak, 1961) and aziridine borane (Ringertz, 1969). Even shorter distances were observed in 5-(1-aziridinyl)-3-nitro-1-(3-oxo-1-butyl)-1,2,4-triazole [1.445 (4) Å; McKenna *et al.*, 1988] and in 2,5-diaziridinyl-3-phenyl-*p*-benzoquinone [1.462 (6) and 1.467 (6) Å; Hargreaves *et al.*, 1997]. Distances from atom P1 to atoms O2, N3, N4 and N9 are 1.481 (2), 1.623 (2), 1.654 (2) and 1.662 (2) Å,
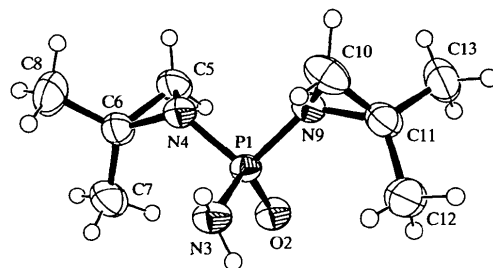

Fig. 1. *ORTEP-3* (Farrugia, 1997) view of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small circles of an arbitrary radius.

respectively, and these are well within the accepted values. The sum of the bond angles at the N3 amino group, involving bonds with atoms H31, H32 and P1, is 345°, indicating the sp^3 hybridization on N3. The geometry of bonding at atoms N3, N4 and N9 is trigonal pyramidal.

The crystal packing in (I) is very interesting. The molecules are held together by hydrogen bonds from N3 to O2 atoms in two different molecules, forming infinite double-stranded chains parallel to the a axis, with hydrophobic dimethylaziridinyl groups occupying the spaces on all sides of the chains (Fig. 2).
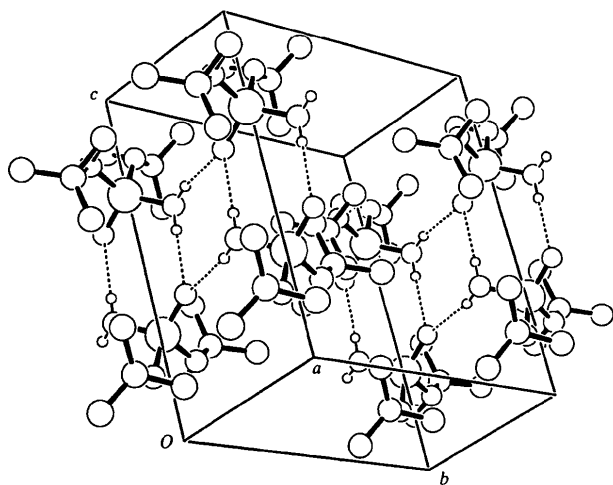

Fig. 2. *ORTEP*-3 (Farrugia, 1997) view of the crystal packing. Only H atoms participating in hydrogen bonds are shown.

Experimental

The compound was synthesized in the Department of Medicinal Chemistry at SUNY, Buffalo, USA (MacDiarmid *et al.*, 1985). The crystals were obtained by crystallization from an absolute ethanol–diethyl ether mixture at 278 K.

Crystal data

$C_8H_{18}N_3OP$	Cu $K\alpha$ radiation
$M_r = 203.22$	$\lambda = 1.54178$ Å
Triclinic	Cell parameters from 16
$P\bar{1}$	reflections
$a = 5.275\,(3)$ Å	$\theta = 22$–$50°$
$b = 9.747\,(4)$ Å	$\mu = 1.909$ mm^{-1}
$c = 11.451\,(5)$ Å	$T = 293\,(2)$ K
$\alpha = 96.44\,(3)°$	Block
$\beta = 84.11\,(3)°$	$0.35 \times 0.25 \times 0.22$ mm
$\gamma = 78.88\,(4)°$	Colourless
$V = 569.4\,(5)$ Å^3	
$Z = 2$	
$D_x = 1.185$ Mg m^{-3}	
D_m not measured	

Data collection

Picker FACS-1 four-circle	$R_{int} = 0.015$
diffractometer	$\theta_{max} = 65°$
$\theta/2\theta$ scan	$h = -6 \rightarrow 6$
Absorption correction:	$k = 0 \rightarrow 11$
empirical *via* φ scan	$l = -13 \rightarrow 13$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.57$, $T_{max} = 0.66$	every 100 reflections
2124 measured reflections	intensity decay: $< 1\%$
1935 independent reflections	
1812 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
$wR(F^2) = 0.116$	$\Delta\rho_{min} = -0.38$ e Å^{-3}
$S = 1.08$	Extinction correction:
1935 reflections	*SHELX*97 (Sheldrick,
191 parameters	1997)
All H-atom parameters	Extinction coefficient:
refined	0.094 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2$	Scattering factors from
$+ 0.1850P]$	*International Tables for*
where $P = (F_o^2 + 2F_c^2)/3$	*Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N4—C5	1.475 (3)	N9—C10	1.467 (3)
N4—C6	1.477 (3)	N9—C11	1.475 (3)
C5—C6	1.484 (3)	C10—C11	1.475 (4)
C5—N4—C6	60.36 (14)	C10—N9—C11	60.19 (16)
N4—C5—C6	59.88 (14)	N9—C10—C11	60.16 (15)
N4—C6—C5	59.76 (14)	N9—C11—C10	59.65 (15)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O2^i	0.86 (3)	2.18 (3)	3.044 (3)	178 (3)
N3—H32···O2^{ii}	0.79 (3)	2.10 (3)	2.872 (3)	164 (2)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x - 1, y, z$.

All H atoms were located from a difference map and refined isotropically. The C—H bonds range from 0.92 (4) to 1.04 (3) Å and the N—H bonds are 0.79 (3) and 0.86 (3) Å.

Data collection: Picker software. Cell refinement: Picker software. Data reduction: Picker software. Program(s) used to solve structure: *SHELX*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELX*97. Molecular graphics: *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *SHELX*97.

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2,2′-Ethylenedioxydibenzaldehyde bis(thiosemicarbazone) bis(dimethyl sulfoxide)

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Abstract

The two thiosemicarbazone moieties of the title compound, $C_{18}H_{20}N_6O_2S_2 \cdot 2C_2H_6OS$, are positioned in a *trans* fashion. The molecule lies on a crystallographic twofold axis. Both O and S atoms of the dimethyl sulfoxide are disordered.

Comment

Thiosemicarbazones belong to a large group of organic derivatives, the biological activities of which are a function of the parent aldehydes and ketones (Hagenbach & Gysin, 1952; Blanz & French, 1968; French *et al.*, 1974). Antitumour activity has been attributed to 2-ethoxybutyraldehyde bis(thiosemicarbazones) (Tosi, 1982) and thiosemicarbazones derived from diketones (Jones & McCleverty, 1970), which has led to interest in their coordination chemistry. As part of our continuing study of mixed NS donor ligands (Duan *et al.*, 1996;

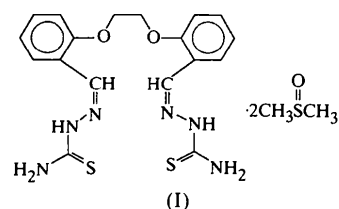Tian *et al.*, 1997), we have determined the structure of the title compound, (I).

(I)

Fig. 1 shows the *ORTEPII* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. The C1—S1 bond distance of 1.689 (2) Å (Table 1) agrees well with those in related compounds (Tian *et al.*, 1997) and with the value for a C=S double bond (1.67 Å) reported by Allen *et al.* (1987). The thiosemicarbazone moiety shows an *E* configuration about the C2—N3 and C1—N2 bonds and the resulting plane (C2/N2/N3/C1/S1, mean deviation from the best plane 0.029 Å) is twisted relative to the phenyl ring (C3–C8) by 17.9 (1)°. This twisted conformation is comparable to that observed for formaldehyde thiosemicarbazone (twist angle 14.6°; Restivo & Palenik, 1970). The title molecule lies on a crystallographic C_2 axis and the two thiosemicarbazone moieties in the centrosymmetric molecule are, of course, equivalent and are positioned in a *trans* fashion, which minimizes their intramolecular interactions. The molecular packing pattern is stabilized by the incorporation of two dimethyl sulfoxide molecules, and both O and S atoms of the solvent are disordered.
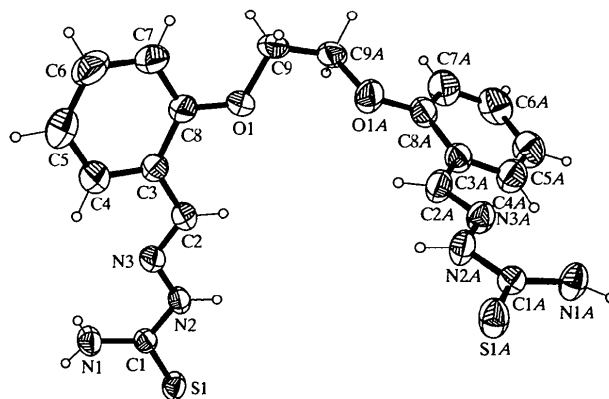

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

Experimental

The title compound was synthesized by refluxing 2,2′-ethylenedioxydibenzaldehyde with thiosemicarbazide in a 1:2 molar ratio in ethanol for 3 h. Single crystals, suitable for X-ray diffraction, were obtained from a dimethyl sulfoxide solution.