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### 1,3-Bis[4,6-bis(methylthio)-1H-pyrazolo[3,4-d]pyrimidin-1-yl]propane†

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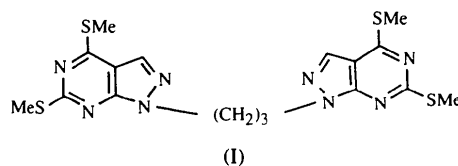
#### Abstract

In the crystal structure of 1,3-bis[4,6-bis(methylthio)-1H-pyrazolo[3,4-d]pyrimidin-1-yl]propane,  $C_{17}H_{20}N_8S_4$ , the molecules exhibit a skewed mode of stacking of the two pyrazolo[3,4-d]pyrimidine rings due to an intramolecular  $\pi$ - $\pi$  interaction between the heterocyclic rings.

† CDRI communication No. 5392.

#### Comment

Interactions are observed between nucleic acid bases connected by polymethylene chains, particularly the trimethylene chain:  $B-(CH_2)_3-B'$ , where  $B$  and  $B'$  are 9-substituted adenine or guanine, 1-substituted cytosine, thymine or uracil residues (Browne, Fisinger & Leonard, 1968). X-ray studies of the trimethylene-bridged compounds 8,8'-trimethylenebistheophylline (Rosen & Hybl, 1971) and 1,1'-trimethylenebisthymine (Frank & Paul, 1973) have revealed unusual intramolecular interactions. The importance of the trimethylene bridge as a synthetic spacer for the detection of intramolecular interactions has been reviewed previously (Leonard, 1979). Pyrazolo[3,4-d]pyrimidine compounds which are isomeric with purine compounds are important as they exhibit a variety of biological properties (Elion, 1978; Hupe, 1986; Avasthi *et al.*, 1993). These considerations have led us to develop a general synthesis of 1,*n*-bis[4,6-bis(methylthio)-1H-pyrazolo[3,4-d]pyrimidin-1-yl]-alkanes of general structure  $P-(CH_2)_n-P'$ , where  $P$  and  $P'$  are pyrazolo[3,4-d]pyrimidinyl moieties and  $n = 2-5$  (Avasthi, Chandra & Bhakuni, 1995). The unusual features, exhibited by some of these compounds in their high-resolution NMR spectra (Avasthi, Chandra & Bhakuni, 1995) as compared to those of simpler 1-alkylated 4,6-bis(methylthio)-1H-pyrazolo[3,4-d]pyrimidines (Garg, Avasthi & Bhakuni, 1989), have prompted us to undertake X-ray crystallographic studies of a few of these compounds. The structure determination of the title compound, (I), reported here, is to our knowledge the first X-ray study of a bis(pyrazolo[3,4-d]pyrimidinyl)-alkane compound.



The conformation of the title molecule, along with the atom-numbering scheme, is shown in Fig. 1. The molecule contains two symmetrical pyrazolo[3,4-d]pyrimidine rings (with SMe groups substituted at the 4 and 6 positions) connected by a trimethylene bridge. Similar to the corresponding bistheophylline and bsthymine structures (Rosen & Hybl, 1971; Frank & Paul, 1973), this molecule is folded at the centre of the bridge [C(8)—C(9)—C(10) 114.1 (2)°]. The skewed mode of stacking of the two pyrazolo[3,4-d]pyrimidine rings occurs in such a way that only part of the six-membered rings overlap (Fig. 2). The overlapping regions are separated by an average distance of 3.4 Å, as observed in the case of stacked purinophanes (Seyama *et al.*, 1988). However, the most striking feature is the fact that the title molecule is connected by only one bridge, while purinophanes (Seyama *et al.*, 1988) are connected

by two polymethylene chains and, thus, are forced to assume a stacked conformation by design. Both the nine-membered pyrazolo[3,4-*d*]pyrimidine rings are nearly planar [maximum deviation 0.023 (2) Å] and the angle between their least-squares planes is 13.2 (1)°. The molecules are packed in columns in the *c*-axis direction of the unit cell (Fig. 3) and the interplane spacing between the heterocyclic rings is 3.55 Å, indicative of intermolecular stacking through  $\pi$ - $\pi$  interaction. Furthermore, these planes are almost parallel with an angle between them of 0.7°. The crystal structure is, therefore, stabilized mainly by  $\pi$ - $\pi$  interactions and van der Waals forces.

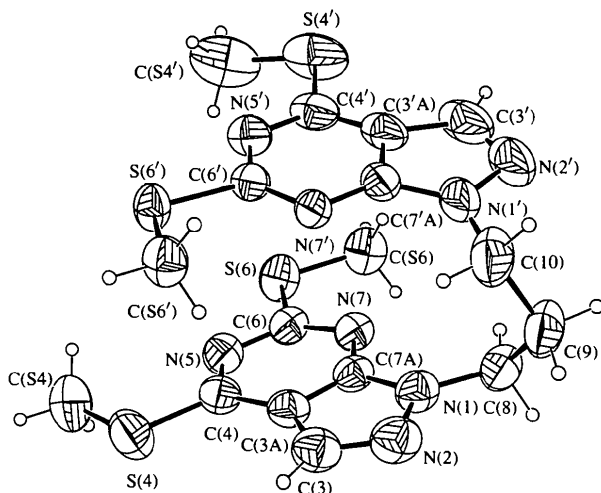


Fig. 1. ORTEP (Johnson, 1965) diagram showing displacement ellipsoids at 50% probability for the non-H atoms. H-atom labels have been omitted for clarity.

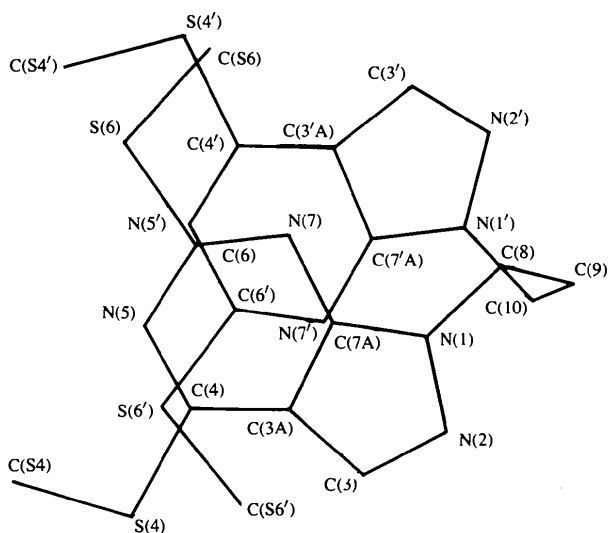


Fig. 2. View of the title molecule [perpendicular to the plane through atoms C(4), N(5) and C(6)] of one six-membered ring showing the overlapping portion of the rings owing to skewed stacking.

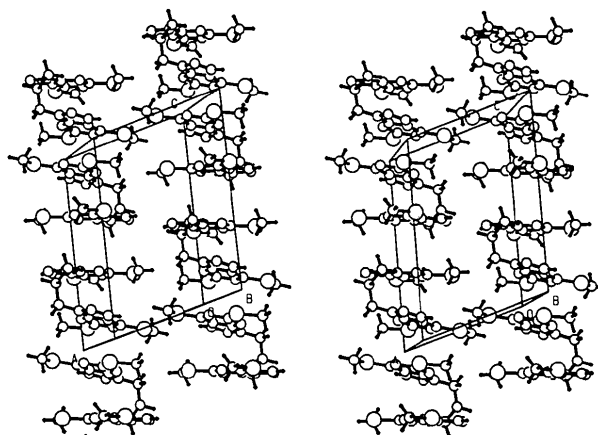


Fig. 3. Stereoview (PLUTO; Motherwell & Clegg, 1978) of the crystal packing.

### Experimental

The synthesis of 1,3-bis[4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl]propane was carried out by reaction of 4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidine with dibromopropane in anhydrous dimethylformamide in the presence of anhydrous potassium carbonate (Avasthi, Chandra & Bhakuni, 1995). Diffraction-quality crystals were obtained by slow evaporation of an ethyl acetate/*n*-hexane mixture at room temperature.

#### Crystal data

C<sub>17</sub>H<sub>20</sub>N<sub>8</sub>S<sub>4</sub>  
*M<sub>r</sub>* = 464.65  
 Triclinic  
*P* $\bar{1}$   
*a* = 9.397 (6) Å  
*b* = 9.627 (8) Å  
*c* = 13.805 (8) Å  
 $\alpha$  = 96.20 (6)°  
 $\beta$  = 102.31 (5)°  
 $\gamma$  = 115.17 (6)°  
*V* = 1076.1 (13) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.434 Mg m<sup>-3</sup>

#### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 4029 measured reflections  
 3776 independent reflections  
 3364 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

#### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.037  
*wR*(*F*<sup>2</sup>) = 0.079  
*S* = 0.782

#### Mo K $\alpha$ radiation

$\lambda$  = 0.71073 Å  
 Cell parameters from 25  
 reflections  
 $\theta$  = 10–15°  
 $\mu$  = 0.463 mm<sup>-1</sup>  
*T* = 293 K  
 Rectangular  
 0.4 × 0.3 × 0.2 mm  
 Colourless

*R*<sub>int</sub> = 0.015

$\theta_{\max}$  = 24.98°

*h* = -11 → 9

*k* = 0 → 11

*l* = -16 → 16

3 standard reflections

frequency: 60 min  
 intensity decay: <0.5%

$w = 1/[\sigma^2(F_o^2) + 10.0 + 0.45P + (0.047P)^2]$   
 where  $P = (0.33F_o^2 + 0.667F_c^2)$

3770 reflections  
266 parameters  
H atoms riding on parent atoms

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.339 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.192 \text{ e } \text{\AA}^{-3}$   
Atomic scattering factors from *SHELXL93* (Sheldrick, 1993)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: VJ1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	x	y	z	$U_{\text{eq}}$
N(1)	0.2198 (2)	0.3973 (2)	0.5828 (1)	0.052 (1)
N(2)	-0.3518 (2)	0.4263 (2)	0.5537 (1)	0.063 (1)
C(3)	-0.2912 (3)	0.5793 (3)	0.5655 (2)	0.061 (1)
C(3A)	-0.1181 (2)	0.6553 (2)	0.6022 (1)	0.050 (1)
C(4)	0.0143 (2)	0.8077 (2)	0.6316 (1)	0.052 (1)
S(4)	-0.0266 (1)	0.9665 (1)	0.6251 (1)	0.074 (1)
C(S4)	0.1731 (4)	1.1298 (3)	0.6667 (2)	0.095 (1)
N(5)	0.1670 (2)	0.8285 (2)	0.6654 (1)	0.054 (1)
C(6)	0.1871 (2)	0.6973 (2)	0.6713 (1)	0.049 (1)
S(6)	0.3950 (1)	0.7464 (1)	0.7194 (1)	0.065 (1)
C(S6)	0.3849 (3)	0.5562 (3)	0.7172 (2)	0.069 (1)
N(7)	0.0743 (2)	0.5481 (2)	0.6465 (1)	0.048 (1)
C(7A)	-0.0780 (2)	0.5332 (2)	0.6122 (1)	0.045 (1)
C(8)	-0.2413 (3)	0.2386 (2)	0.5801 (2)	0.057 (1)
C(9)	-0.3672 (3)	0.1468 (2)	0.6317 (2)	0.070 (1)
C(10)	-0.3419 (3)	0.2333 (3)	0.7375 (2)	0.077 (1)
N(1')	-0.1751 (3)	0.2977 (2)	0.8019 (1)	0.073 (1)
N(2')	-0.1037 (4)	0.2018 (3)	0.8212 (2)	0.097 (1)
C(3')	0.0457 (5)	0.2939 (4)	0.8776 (2)	0.094 (1)
C(3'A)	0.0809 (3)	0.4546 (3)	0.8969 (2)	0.066 (1)
C(4')	0.2108 (3)	0.6056 (3)	0.9443 (2)	0.062 (1)
S(4')	0.4018 (1)	0.6248 (1)	1.0074 (1)	0.101 (1)
C(S4')	0.5287 (3)	0.8342 (5)	1.0370 (3)	0.111 (1)
N(5')	0.1881 (2)	0.7315 (2)	0.9415 (1)	0.054 (1)
C(6')	0.0357 (2)	0.7084 (2)	0.8917 (1)	0.044 (1)
S(6')	0.0253 (1)	0.8858 (1)	0.9001 (1)	0.052 (1)
C(S6')	-0.1887 (2)	0.8208 (2)	0.8450 (2)	0.056 (1)
N(7')	-0.0965 (2)	0.5743 (2)	0.8426 (1)	0.048 (1)
C(7'A)	-0.0671 (3)	0.4499 (2)	0.8464 (1)	0.056 (1)

Table 2. Selected torsion angles ( $^\circ$ )

C7A—N1—C8—C9	130.1 (2)	C8—C9—C10—N1'	-49.5 (3)
N2—N1—C8—C9	-49.7 (3)	C9—C10—N1'—N2'	-57.7 (3)
N1—C8—C9—C10	-50.0 (3)	C9—C10—N1'—C7'A	119.0 (2)

Data were processed using the *BRANDX* and *DATRD2* routines of the *NRCVAX* program package (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined anisotropically for the non-H atoms by full-matrix least-squares methods using *SHELXL93* (Sheldrick, 1993). All H atoms were placed in geometrically idealized positions. Six reflections (most disagreeable,  $\Delta F^2/\sigma > 5.0$ ) were suppressed during the last cycles of refinement. Geometrical calculations were performed using *SHELXL93* and the *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1978) plots were produced with the aid of *NRCVAX*. All calculations were performed on a PC/AT 486DX computer.

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## 5-(2,6,6-Triméthyl-2-cyclohexen-1-yl)-3-[2-(2,6,6-triméthyl-2-cyclohexen-1-yl)-éthényl]-2-cyclohexen-1-one

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## Abstract

5-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-[2-(2,6,6-trimethyl-2-cyclohexen-1-yl)vinyl]-2-cyclohexen-1-one,  $\text{C}_{26}\text{H}_{38}\text{O}$ , is a disubstituted 2-cyclohexenone. The cyclohexene ring of the 2,6,6-trimethyl-2-cyclohexen-1-ylvinyl substituent is disordered. There are two conformations with equal occupancies of the sites.