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4,6-Bis(methylsulfanyl)-1-(4-phenoxybutyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine[1]

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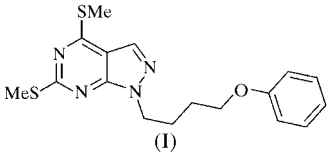
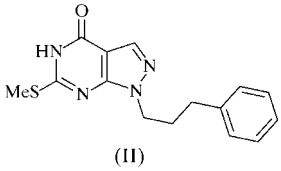
The molecular structure of the title compound, $C_{17}H_{20}N_4OS_2$, does not show any intramolecular aromatic π–π interactions, but the crystal packing reveals the presence of intermolecular C—H···O and C—H···π interactions. The C—H···O interactions generate chains of molecules that are linked into sheets by C—H···π interactions about inversion centres.

Comment

Arene interactions are known to play an important role in chemistry (Hunter & Sanders, 1990; Hunter *et al.*, 2001; Tsuzuki *et al.*, 2002) and biology, particularly in molecular recognition, stabilization of DNA/RNA structures (Hobza & Sponer, 1999), crystal engineering (Desiraju, 1995) and drug development (Meyer *et al.*, 2003). Use of a polymethylene, especially a trimethylene (propylene), linker for studying intramolecular π–π interactions was pioneered by Browne *et al.* (1968), and early work has been reviewed by Leonard



(I)



(II)

(1979). In 1995, we reported the synthesis (Avasthi *et al.*, 1995) and X-ray structure (Biswas *et al.*, 1995) of a 'trimethylene linker' molecule, based on a pyrazolo[3,4-*d*]pyrimidine core, which exhibits intramolecular stacking and which is isomeric with the biologically important purine system. The robustness of the unusual U-motif formed as a result of the intramol-

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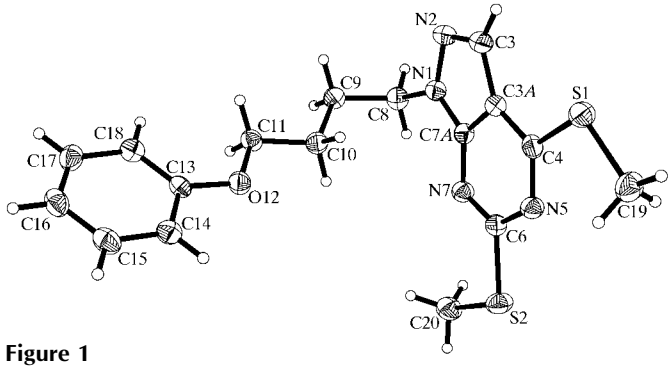

Figure 1
A displacement ellipsoid plot (30% probability level), showing the molecular structure of (I) and the atomic labelling scheme.

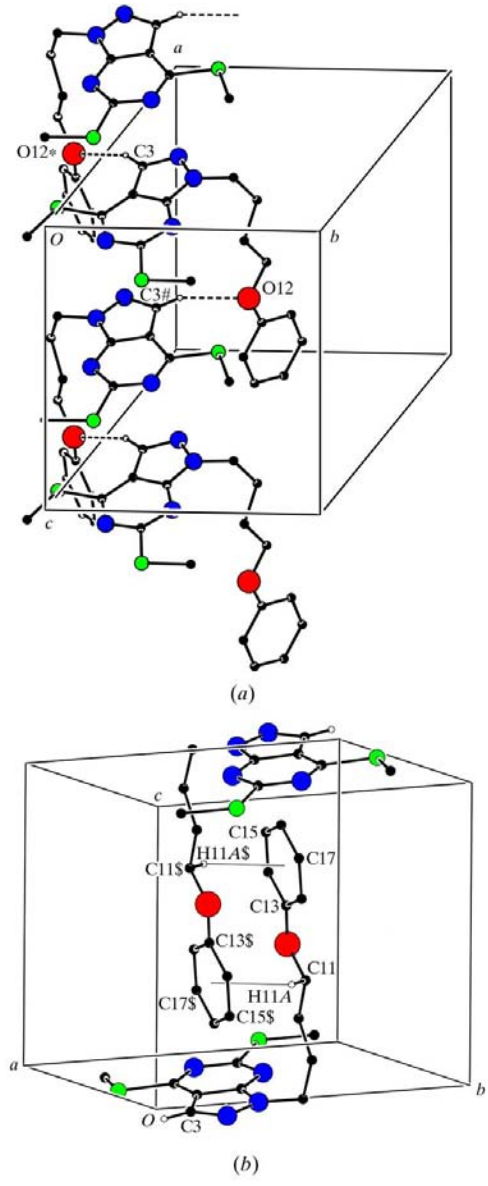

Figure 2
(*a*) Part of a crystal-packing diagram of (I), showing chains of molecules extending in the *c* direction *via* C—H···O hydrogen bonding and the *c*-glide translation. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, \frac{1}{2}-y, z-\frac{1}{2})$ and $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively. (*b*) A view of pairs of C—H···π interactions linking molecules about the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Atoms marked with a dollar symbol ($) are at the symmetry position $(1-x, 1-y, 1-z)$.

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ecular stacking has been further demonstrated by X-ray diffraction analysis of other closely related 'propylene linker' compounds (Maulik *et al.*, 1998; Avasthi, Aswal & Maulik, 2001; Avasthi, Rawat *et al.*, 2001). Interestingly, no intramolecular stacking is observed by X-ray diffraction when the 'trimethylene linker' is replaced by an 'ethylene linker' (Avasthi, Rawat *et al.*, 2001), a 'tetramethylene linker' (Maulik *et al.*, 2000) or a 'pentamethylene linker' (Avasthi *et al.*, 2003). All of these compounds have pyrazolo[3,4-*d*]pyrimidine-derived moieties at both ends of the polymethylene linker.

We report here the structure of the disymmetric title compound, (I) (Fig. 1), which has normal dimensions and which has the same pyrazolo[3,4-*d*]pyrimidine core as the previously reported disymmetric 'propylene linker' compound (II) (Avasthi *et al.*, 2002). Compound (I) has a 'tetramethylene linker' flanked by pyrazolo[3,4-*d*]pyrimidine and electron-rich phenoxy moieties. It was anticipated that this configuration might have facilitated intramolecular stacking between the electron-rich phenoxy moiety and the electron-deficient pyrimidine group, but Fig. 1 and various geometric calculations do not show any intramolecular stacking between the pyrazolo[3,4-*d*]pyrimidine and phenoxy moieties.

In the crystal structure, the molecules are linked by C—H···O hydrogen bonds (Table 1 and Fig. 2*a*), and chains of molecules are developed in the *c* direction by the operation of a *c*-glide plane. There are also C—H···π interactions (Desiraju & Steiner, 1999) between inversion-related molecules (Fig. 2*b*), involving atom C11 and the centroid (*Cg*) of the C13–C18 phenyl ring at $(1-x,\ 1-y,\ 1-z)$ (H11···*Cg* = 2.87 Å and C11—H11*A*···*Cg* = 146°). These interactions link the chains of molecules into sheets.

Experimental

Compound (I) was prepared by stirring an equimolar mixture of 4,6-bis(methylsulfanyl)-1*H*-pyrazolo[3,4-*d*]pyrimidine and 4-phenoxybutyl bromide in a dimethylformanmide/K_2CO_3 solution. A diffraction-quality crystal was obtained from a solution of (I) in ethyl acetate and methanol by slow evaporation at room temperature.

Compound (I)

Crystal data

$C_{17}H_{20}N_4OS_2$
M_r = 360.49
Monoclinic, $P2_1/c$
a = 17.966 (1) Å
b = 10.089 (1) Å
c = 10.055 (1) Å
β = 104.97 (1)°
V = 1760.7 (3) Å^3
Z = 4
D_x = 1.360 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 5.0–12.5°
μ = 0.31 mm^{-1}
T = 293 (2) K
Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
θ–2θ scans
4550 measured reflections
3468 independent reflections
2333 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 26.0°
$h = -22 \rightarrow 21$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 12$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.105
S = 1.05
3468 reflections
220 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.9524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0064 (6)

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O12^{i}	0.93	2.49	3.368 (3)	157

Symmetry code: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

All H atoms were placed in idealized positions and allowed to ride on their parent atoms for the final cycles of refinement, with C—H distances in the range 0.93–0.97 Å

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1701). Services for accessing these data are described at the back of the journal.

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