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Herring-bone π–π interactions in *trans*-2,6-diphenyl-2,3,5,6-tetrahydrothiapyran-4-one

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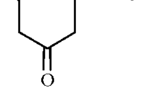
The structure of the title compound, $C_{17}H_{16}OS$, is primarily stabilized by T-shaped and parallel-displaced aromatic clusters. The distances between the centroids of the aromatic pairs are in the range 4.34–5.30 Å. In the crystal packing, the molecules dimerize by means of π–π interactions of both face-to-face and edge-to-face types, and the aromatic rings associate in a cyclic edge-to-face tetrameric arrangement of the herring-bone type. These herring-bone interactions appear to insulate hydrogen-bond interactions in the crystal structure.

Comment

Several experimental and theoretical investigations of aromatic interactions have emphasized their role in many important chemical and biological phenomena, such as shaping molecular conformations, determining intermolecular interactions (Meyer *et al.*, 2003) and supramolecular assembly (Desiraju & Steiner, 1999). Two types of clusters, namely parallel-displaced (face-to-face) and T-shaped (edge-to-face), have been shown to be energetically favourable and have been observed in a large number of crystal and molecular structures (McGaughey *et al.*, 1998). The association of these aromatic clusters into different types of arrangements, similar to what is commonly observed for hydrogen bonds, and the prediction of preferred intermolecular, *i.e.* aromatic *versus* hydrogen-bonding, interactions, for the design of supramolecular assemblies are currently important topics of investigation in crystal engineering. The present discussion of the title compound, (I), is concerned with intermolecular π–π interactions and their arrangements in crystal packing.



(I)

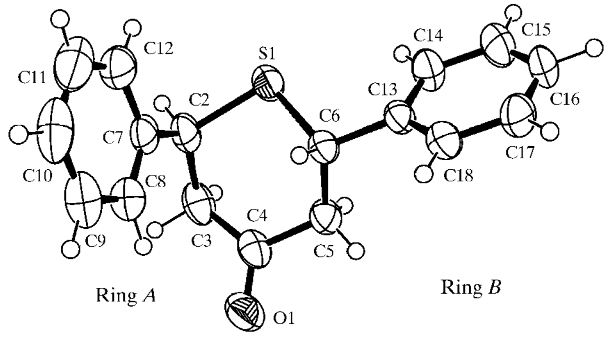


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

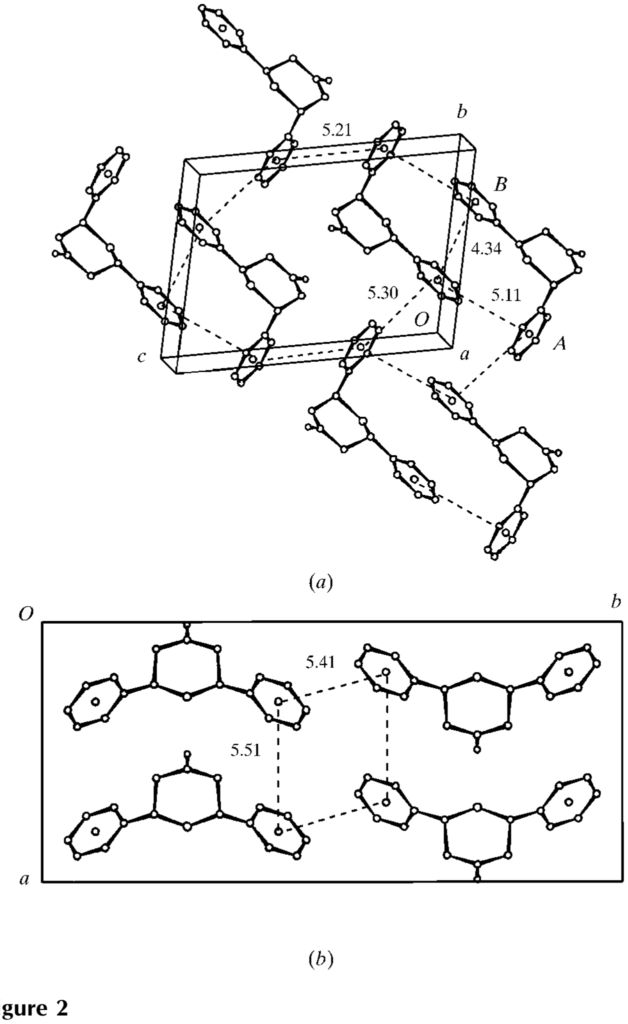


Figure 2
Herring-bone π–π interactions. The values indicate centre-to-centre distances (Å) between interacting aromatic pairs. (*a*) The association of molecules into dimers (diads) and cyclic edge-to-face tetrameric arrangements of aromatic clusters. (*b*) The similar edge-to-face tetrameric arrangement for the symmetrical stereoisomer (II), reported by Narasimhamurthy *et al.* (2000).

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The crystal structure of (I) is characterized by several edge-to-face and face-to-face π–π interactions. The geometrical parameters (Table 1) suggest that all of them have almost ideal T-shaped or parallel-displaced geometry. Within the molecule, the aromatic rings are asymmetrically disposed (Fig. 1) on either side of the chair conformation of the thiapyran ring, *i.e.* one is in an equatorial position (ring *A*) and the other is in an axial position (ring *B*). Each of the rings is involved in three π–π interactions. The molecules form dimers in the unit cell, and they are co-operatively connected by edge-to-face interactions between ring *A* and ring *B* and by face-to-face interactions between rings *B*.

The characteristic feature of the crystal packing in (I) is the tetrameric association of the aromatic rings, as shown in Fig. 2(*a*). The edge-to-face cyclic arrangement of the aromatic rings is similar to the herring-bone interactions observed for benzene and other aromatic clusters (Vangala *et al.*, 2002; Allen *et al.*, 1997). Previously, we have examined the structure of the *cis* isomer of (I), *viz.* (II), for its molecular symmetry, where both aromatic rings are in equatorial positions (Narsimhamurthy *et al.*, 2000). Interestingly, similar edge-to-face aromatic clusters in a herring-bone fashion are also observed in the structure of (II), although the interplanar angles between the aromatic rings (68°) are slightly distorted from the ideal T-shaped geometry (Fig. 2*b*). There are no hydrogen bonds in either of these structures. The aromatic interactions appear to insulate hydrogen bonding (Desiraju & Steiner, 1999), possibly due to the overwhelming presence of π donors and acceptors. This insulation of hydrogen bonding by herring-bone interactions, observed in the present examples of symmetric as well as in asymmetric stereoisomers, serves as a good model in the design of supramolecular assemblies and in crystal engineering.

Experimental

Crystals of (I) (Sigma Chemicals, USA) were obtained by direct evaporation of an ethanol solution.

Crystal data

$C_{17}H_{16}OS$
$M_r = 268.38$
Triclinic, $P\bar{1}$
$a = 5.909$ (2) Å
$b = 9.706$ (3) Å
$c = 13.184$ (5) Å
$\alpha = 102.02$ (3)°
$\beta = 94.39$ (3)°
$\gamma = 106.39$ (3)°
$V = 702.1$ (4) Å^3

$Z = 2$
$D_x = 1.270$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.9$–60.6°
$\mu = 1.94$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.2 × 0.1 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
2775 measured reflections
2630 independent reflections
2617 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.104$

$\theta_{\rm max} = 75.8$°
$h = -7 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 16$
2 standard reflections every 200 reflections intensity decay: 9.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.160$
$S = 1.23$
2630 reflections
237 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.44P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (3)

Table 1
Geometrical parameters of π–π interactions (Å, °).

π–π	Centre to centre distance	Closest distance of approach	Interplanar angle
Parameters for (I)			
Ring $A\cdots$Ring $A^{\rm i}$	5.210 (2)	4.034 (4)	0.0 (1)
Ring $A\cdots$Ring $B^{\rm ii}$	5.301 (2)	4.045 (6)	89.2 (1)
Ring $B\cdots$Ring $A^{\rm iii}$	5.110 (2)	3.819 (6)	89.2 (1)
Ring $B\cdots$Ring $B^{\rm iii}$	4.343 (2)	3.558 (5)	0.0 (1)
Parameters for the stereoisomeric compound (II)			
Ring$\cdots$Ring$^{\rm iv}$	5.427 (3)	3.524 (4)	0.0 (1)
Ring$\cdots$Ring$^{\rm v}$	5.405 (2)	3.815 (4)	68.3 (1)
Ring$\cdots$Ring$^{\rm vi}$	5.509 (2)	3.765 (4)	68.3 (1)

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, -z$; (iv) $x, y, z-1$; (v) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, y, \frac{3}{2}-z$.

Refined C—H distances are in the range 0.86 (4)–1.04 (5) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *INSIGHT*II (Accelrys, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1222). Services for accessing these data are described at the back of the journal.

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