organic papers

Arunchalam Kannan,[a] Ina Dix,[a] Henning Hopf[a] and Peter G. Jones[b]*

[a]Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and [b]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Correspondence e-mail: p.jones@tu-bs.de

Key indicators

Single-crystal X-ray study
$T = 143$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.107
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

[2.2]Dihydroisobenzothiophenophane

In the unit cell of the title compound, $1^1,1^3,4^1,4^3$-tetrahydro-1,4(4,7)-di(benzo[c]thiophena)cyclohexaphane, $C_{20}H_{20}S_2$, there are four independent but closely similar molecules, each with crystallographic inversion symmetry. The packing is interpreted in terms of layers formed *via* C—H···π interactions.

Comment

2,5-Dihydroisobenzothiophene and its derivatives are useful substrates for the generation of *o*-xylylene intermediates, which can subsequently be trapped by various double- and triple-bond dienophiles to yield six-membered ring systems (Gajewski, 2004). In order to produce such intermediates in the cyclophane series, we required the title [2.2]cyclophane, (2), as a precursor. This is easily obtained from the tetra-bromide, (1) (El-Tamany & Hopf, 1980; see *Experimental* section). Here, we report the structure determination of (2) by single-crystal X-ray crystallography.
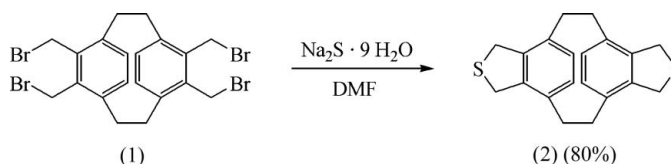
Compound (2) crystallizes with four independent molecules in the unit cell, each with inversion symmetry (Fig. 1). Molecule 1 is centred at $(\frac{1}{2}, 0, 0)$, molecule 2 (primed atom names) at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, molecule 3 (doubly primed atom names) at $(0, \frac{1}{2}, 0)$,
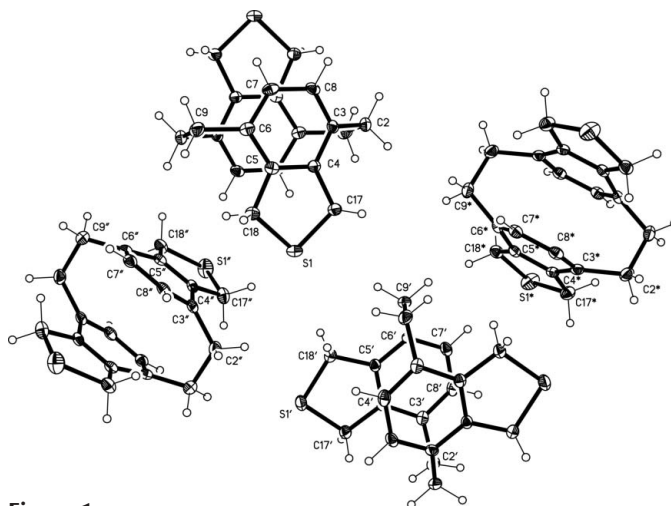

Figure 1
The four independent molecules of the title compound in the crystal structure. Ellipsoids are drawn at the 30% probability level. Only the asymmetric unit is numbered.
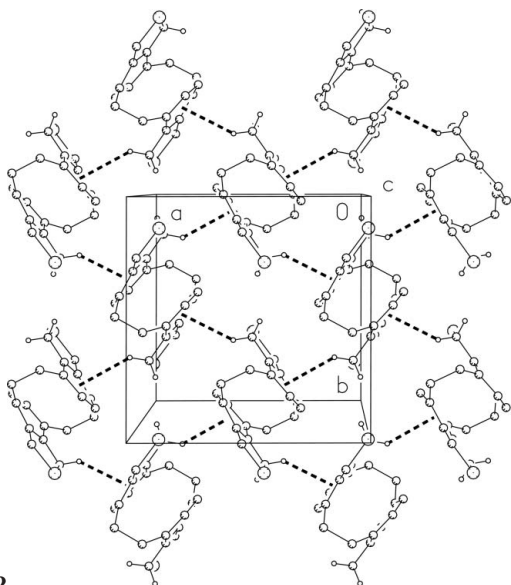
Figure 2
A packing diagram of the title compound, showing a view of one layer at $z \simeq 0$. C—H$\cdots\pi$ contacts (see text) are indicated by dashed lines; H atoms not involved in these interactions have been omitted.

and molecule 4 (starred atom names) at $(1, 0, \frac{1}{2})$. IUPAC-consistent numbering has been chosen as far as possible consistent with the crystallographic symmetry.

All four molecules are closely similar. Bond lengths and angles, *e.g.* those at the S atoms (Table 1), may be considered normal. The six-membered rings show the flattened boat conformation typical of [2.2]cyclophanes, with the bridgehead atoms lying 0.15–0.16 Å out of the plane of the other four atoms. The C—C bonds in the bridges are lengthened (Table 1), also typical of cyclophanes. The thiophenyl rings are planar (r.m.s. deviations < 0.01 Å) and subtend angles of 0–2° with the above planes. Full numerical details are given in the deposited CIF.

The molecular packing involves layers parallel to (001). Molecules 1 and 3 form a layer at $z \simeq 0$ (Fig. 2), and molecules 2 and 4 a layer at $z \simeq \frac{1}{2}$ (Fig. 3). Both within and between the layers there are a number of C—H$\cdots$S contacts (Table 2), but these are long (> 2.9 Å) and have no clear upper length limit. For this reason, we prefer to analyse the packing in terms of C—H$\cdots\pi$ interactions, as we have done previously for other cyclophane systems (*e.g.* El Shaieb *et al.*, 2003). There are four such interactions, listed in Table 2 for normalized C—H bond lengths of 1.08 Å (Steiner, 1998) and for centroids $Cg1$–$Cg4$ calculated from the four non-bridgehead atoms C4, C5, C7 and C8 of the six-membered rings. However, we note that all four contacts display either narrow angles or long distances.

Experimental

A solution of the tetrabromide, (1), (1.74 g, 3.0 mmol) in dimethylformamide (DMF; 100 ml) was added to a well stirred suspension of sodium sulfide enneahydrate (1.44 g, 6.0 mmol) in DMF (350 ml) at room temperature over 8 h. After the addition was complete, the mixture was stirred for another 12 h. Extraction with dichloromethane, drying of the organic phase over sodium sulfate and solvent
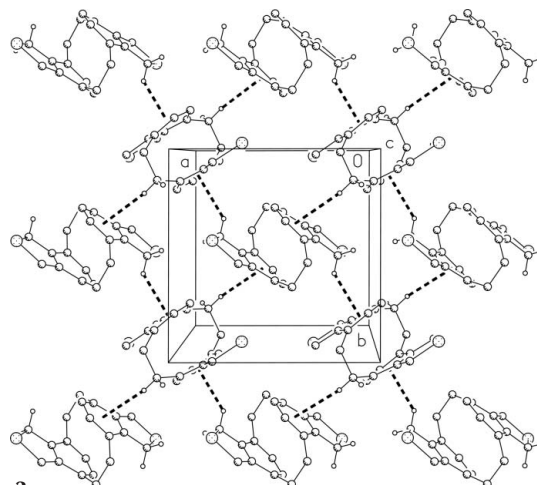

Figure 3
A packing diagram of the title compound, showing a view of one layer at $z \simeq \frac{1}{2}$. C—H$\cdots\pi$ contacts (see text) are indicated by dashed lines; H atoms not involved in these interactions have been omitted.

removal provided (2) (0.7 g, 80%) after silica-gel chromatography. The structure of (2) is also supported by all other spectroscopic and analytical data (Kannan & Hopf, unpublished results).

Crystal data

$C_{20}H_{20}S_2$	$Z = 4$
$M_r = 324.48$	$D_x = 1.379$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.088 (2)$ Å	Cell parameters from 52
$b = 10.182 (2)$ Å	reflections
$c = 15.247 (2)$ Å	$\theta = 10–11.5°$
$\alpha = 86.53 (2)°$	$\mu = 0.33$ mm^{-1}
$\beta = 88.44 (2)°$	$T = 143 (2)$ K
$\gamma = 89.81 (2)°$	Prism, colourless
$V = 1562.7 (5)$ Å^3	$0.6 \times 0.35 \times 0.3$ mm

Data collection

Stoe STADI-4 diffractometer	$\theta_{max} = 25.0°$
θ/ω scans	$h = -12 \rightarrow 6$
Absorption correction: none	$k = -12 \rightarrow 12$
9570 measured reflections	$l = -18 \rightarrow 18$
5496 independent reflections	3 standard reflections
4469 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.026$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 1.5793P]$
$wR(F^2) = 0.107$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
5496 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
397 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C18	1.814 (3)	S1″—C18″	1.807 (3)
S1—C17	1.824 (3)	S1″—C17″	1.826 (3)
C2—C9^{i}	1.589 (4)	C2″—C9″^{iii}	1.590 (4)
S1′—C17′	1.813 (2)	S1*—C18*	1.811 (3)
S1′—C18′	1.819 (3)	S1*—C17*	1.818 (3)
C2′—C9′^{ii}	1.585 (4)	C2*—C9*^{iv}	1.589 (4)
C18—S1—C17	95.62 (11)	C18″—S1″—C17″	95.74 (12)
C17′—S1′—C18′	95.44 (11)	C18*—S1*—C17*	95.87 (12)

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z$; (iv) $-x + 2, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$C2''—H2''2\cdots S1'$	0.99	2.95	3.723 (3)	136
$C9''—H9''2\cdots S1'^{iii}$	0.99	3.02	3.732 (3)	130
$C9*—H9*1\cdots S1''^{v}$	0.99	2.96	3.937 (3)	168
$C7—H7\cdots S1*^{vi}$	0.95	2.94	3.854 (3)	162
$C9'—H9'1\cdots S1$	0.99	3.07	3.907 (3)	143
$C8''—H8''\cdots S1^{vii}$	0.95	3.08	3.896 (3)	145
$C8*—H8*\cdots S1'^{v}$	0.95	3.10	3.879 (3)	140
$C17—H17B\cdots S1*^{viii}$	0.99	3.07	3.974 (3)	153
$C18''—H18F\cdots Cg1^{ix}$	1.08	2.74	3.63	140
$C18—H18A\cdots Cg3$	1.08	2.78	3.66	111
$C17'—H17C\cdots Cg4^{ii}$	1.08	2.61	3.45	135
$C2*—H2*2\cdots Cg2^{v}$	1.08	2.98	4.04	166

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z$; (v) $x + 1, y, z$; (vi) $x, y, z - 1$; (vii) $-x + 1, -y + 1, -z$; (viii) $-x + 1, -y, -z + 1$; (ix) $x - 1, y, z$.

H atoms were included in calculated positions and refined using a riding model, with fixed C—H bond lengths of 0.95 Å (sp^2 CH) or 0.99 Å (CH$_2$). U_{iso}(H) values were fixed at 1.2 times U_{eq} of the parent atom.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

References

El Shaieb, K., Narayanan, V., Hopf, H., Dix, I., Fischer, A., Jones, P. G., Ernst, L. & Ibrom, K. (2003). *Eur. J. Org. Chem.* pp. 567–577.
El-Tamany, S. H. & Hopf, H. (1980). *Tetrahedron Lett.* **21**, 4901–4904.
Gajewski, J. J. (2004). *Hydrocarbon Thermal Isomerizations*, 2nd ed., p. 225, and references therein. Amsterdam: Elsevier.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Siemens (1994). *XP. Version*, **5**, 03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Steiner, T. (1998). *Acta Cryst.* B**54**, 456–463.
Stoe & Cie (1992). *DIF4* and *REDU4*. Stoe & Cie, Darmstadt, Germany.