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An anthracene dimer with a fused 1,3-dithiole ring at 193 K

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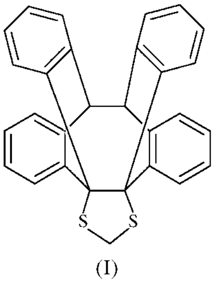
The first butterfly-shaped anthracene dimer including S atoms, 8,9-dihydro-3a,8[1′,2′]:9,13b[1″,2″]dibenzenodibenzo[3,4:7,8]-cycloocta[1,2-*d*]-1,3-dithiole, $C_{29}H_{20}S_2$, contains an exceptionally long Csp^3—Csp^3 bond of 1.672 (2) Å in the fused 1,3-dithiole ring. The length of the other bond bridging the anthracene moieties is 1.604 (3) Å.

Comment

The title compound, (I), is the only anthracene dimer reported so far where the S atoms are bonded to the anthryl groups and additionally form a fused heterocyclic ring. According to CA Index nomenclature, (I) is called 8,9-dihydro-3a,8[1′,2′]:-9,13b[1″,2″]dibenzenodibenzo[3,4:7,8]cycloocta[1,2-*d*]-1,3-dithiole. The synthesis and photochemical studies of an analogous anthracene dimer with a fused 1,3-dioxole ring have been published, but unfortunately without X-ray data (Desvergne *et al.*, 1992, 1995).



(I)

A typical feature of the highly strained butterfly shaped anthracene dimers is the remarkable elongation of the central C—C bonds connecting the anthracene moieties compared with the standard C—C single-bond length of 1.54 Å (Battersby *et al.*, 1995). Even in unsubstituted 9,9:10,10-bianthracene, the central bond is reported to reach a value of 1.620 Å at 120 K (Batsanov & Howard, 2000, private communication), 1.618 Å at 198 K (Abboud *et al.*, 1990), and 1.612 (Ehrenberg, 1966) and 1.623 Å (Choi & Marinkas, 1980) at 295 K [DPANTH in the Cambridge Structural Database (CSD), Version 5.21; Allen & Kennard, 1993]. The longest reported central C—C bonds of 1.669 and 1.670 Å for 9,9:10,10-bianthracene derivatives are in the asymmetric photodimer of (*Z*)-1-(9-anthryloxy)-1,2-bis(9-anthryl)-2-methoxyethene, (II) (HAVTAZ; Langer & Becker, 1993*a*), and in symmetric 9,10-(10-methoxy-9-methylanthraceno)-9-methoxy-10-methylanthracene (HAVVEF; Langer & Becker, 1993*b*), respectively. The even longer C3a—C13b bond length of 1.672 (3) Å in (I) (Fig. 1 and Table 1) is apparently due to the greater steric demand of the fused heterocyclic 1,3-dithiole ring. The length of the other central bond (C8—C9) is only 1.604 (3) Å in (I) and 1.619 Å in (II). Similar large differences in the central bond lengths appear also in the anthracene dimer with a fused cyclobutadione ring, 1.655 (5) and

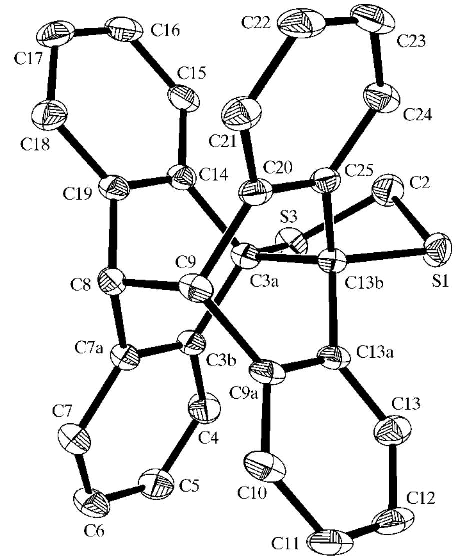


Figure 1
View of (I) showing the atom labels. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

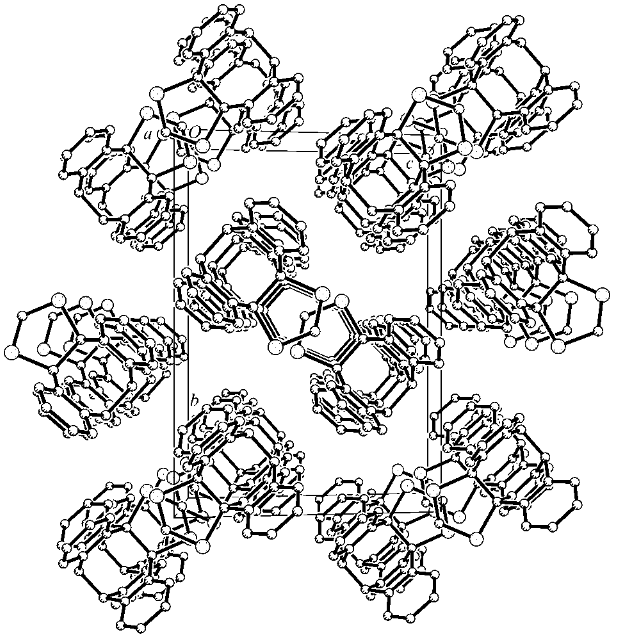


Figure 2
The packing of (I) viewed along the *a*-axis direction.

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1.607 (6) Å (SIWDOR; Becker *et al.*, 1991), and in the dimer with a fused cyclohexene ring, 1.663 and 1.614 Å (REFVED; Kammermeier *et al.*, 1996). Several discussions based on experimental results and their comparison with theoretical calculations have been presented on the lengthening of the bridging C—C bond in anthracene dimers and related molecules (Dougherty *et al.*, 1986; Battersby *et al.*, 1995; Baldridge *et al.*, 1997).

The bond angles in the 1,3-dithiole ring of (I) are rather close to those in the non-fused 4,5-tetrasubstituted 1,3-dithiole derivatives found in the CSD. The main difference is the shape of the ring. They all possess a more or less twisted envelope conformation, but (I) is the only compound where the S atoms are in the same plane as the two C atoms between them. This is clearly seen in the torsion angle S—C—C—S, which is only 0.69 (15)° in (I), but 38.4° in SOSHIR (Mloston *et al.*, 1991), 49.0° in ZAMLOO (Leino *et al.*, 1995), 44.5° in LEVFAT (Mloston *et al.*, 1999), 52.4° in HASBIM and 53.6° in HASBEI (Kagi *et al.*, 1993). The C—S—C—C torsion angles in (I) are 27.15 (14) and −28.03 (14)°, thus proving the ring to be almost symmetric with a pseudo-mirror plane.

The C—C distances of the 1,3-dithiole fragment in the abovementioned structures are mostly only slightly longer than normal, the longest being 1.617 Å in LEVFAT (Mloston *et al.*, 1999), probably due to bulky adamantyl and two phenyl groups. In compound (I), the S—C2 bonds are clearly shorter than the S—C bonds to the anthryl groups and both pairs of S—C bonds are shorter than the corresponding S—C bonds in the 1,3-dithiole structures of comparison.

In butterfly-shaped dimers, the anthracene moieties are typically bent at the central C atoms where the molecules are joined. The bent halves within each anthryl group in (I) form interplanar angles of 136.32 (8) and 130.72 (8)°, which agree well with the values of 136.2 (2) and 129.7 (2)° found in SIWDOR (Becker *et al.*, 1991). Due to the small value (0.69°) of the S—C—C—S torsion angle in (I), the S atoms and C2 deviate by 0.029 (3), 0.056 (3) and −0.761 (4) Å, respectively, from the plane defined by atoms C8, C9, C3a and C13b. According to the present data, the 1,3-dithiole ring in (I) is strained.

The molecular packing of (I) shows tubular channels and separate molecular columns in the *a*-axis direction. Molecules are oriented in such a way that the inversion-related S atoms seem to form rows of four S atoms, one row passing through the origin and the other through the centre of the unit cell (Fig. 2).

Experimental

Compound (I) was obtained as a minor side product in the synthesis of 2-[(9-anthracenyl)thiomethylthio]tetrahydropyran (Sipilä *et al.*, 2002) from 2-(acetylthio)tetrahydropyran and 9-chloromethylthioanthracene. The thioester was hydrolysed with 2.2 equivalents of KOH in a dimethyl sulfoxide–water solution at 273 K, 9-chloromethylthioanthracene was added at the same temperature in a one-pot reaction and the mixture was allowed to reach room temperature by stirring overnight. Water was added and the mixture was extracted with diethyl ether. The organic phase was washed with water and brine, dried with Na_2SO_4, evaporated to dryness and purified with flash chromatography (silica gel, dichloromethane). The fractions containing compound (I) were evaporated and recrystallized from dichloromethane–ethanol (m.p. 454–455 K). ^{1}H, ^{13}C, DEPT and HETCOR NMR spectra were taken for samples in $CDCl_3$ with a Varian GEMINI 200 and a Varian Inova 300 spectrometer with $SiMe_4$ as an internal reference. The assignments were based on DEPT and HETCOR measurements. ^{1}H NMR: δ 4.50 (*s*, SCH_2), 4.56 (*s*, H8, H9), 6.8–6.9 (*m*, 12H, aromatic), 7.7–7.8 (*m*, 4H, aromatic); ^{13}C NMR: δ 36.0 (SCH_2S), 53.7 (C8, C9), 125.53, 126.55, 126.70, 127.32, 142.27, 142.34.

Crystal data

$C_{29}H_{20}S_2$
$M_r = 432.57$
Monoclinic, $P2_1/c$
$a = 10.619$ (2) Å
$b = 16.605$ (3) Å
$c = 11.966$ (2) Å
$\beta = 104.67$ (3)°
$V = 2041.2$ (7) Å^3
$Z = 4$
$D_x = 1.408$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5$–10°
$\mu = 2.46$ mm^{-1}
$T = 193$ (2) K
Prismatic, light brown
0.24 × 0.22 × 0.21 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3681 measured reflections
3460 independent reflections
3057 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 65°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 19$
$l = -13 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.113$
$S = 1.04$
3460 reflections
280 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 1.5819P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.779 (2)	C3b—C7a	1.397 (3)
S1—C13b	1.833 (2)	C8—C9	1.604 (3)
S3—C2	1.789 (2)	C9a—C13a	1.403 (3)
S3—C3a	1.831 (2)	C13a—C13b	1.537 (3)
C3a—C3b	1.536 (3)	C13b—C25	1.541 (3)
C3a—C14	1.539 (3)	C14—C19	1.398 (3)
C3a—C13b	1.672 (3)	C20—C25	1.403 (3)
C2—S1—C13b	96.47 (10)	C13—C13a—C13b	124.32 (19)
C2—S3—C3a	96.24 (10)	C3a—C13b—S1	108.78 (13)
S1—C2—S3	106.00 (12)	C15—C14—C3a	124.07 (19)
C3b—C3a—S3	108.35 (14)	C24—C25—C13b	124.22 (19)
C4—C3b—C3a	124.01 (19)		
C13b—S1—C2—S3	−46.59 (13)	S3—C3a—C3b—C4	20.4 (3)
C3a—S3—C2—S1	46.98 (13)	C13—C13a—C13b—S1	−18.2 (2)
C2—S3—C3a—C3b	−147.83 (14)	C2—S1—C13b—C13a	147.28 (15)
C2—S3—C3a—C14	93.57 (15)	C2—S1—C13b—C25	−94.87 (15)
C2—S3—C3a—C13b	−28.03 (14)	C2—S1—C13b—C3a	27.15 (14)

All H atoms in (I) were placed at calculated positions and refined using a riding model with fixed distances and angles.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *WINGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: SK1514). Services for accessing these data are described at the back of the journal.

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