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Di-9-anthryl disulfide at 193 K

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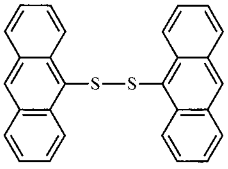
The title compound, $C_{28}H_{18}S_2$, crystallizes in the monoclinic space group $P2_1/n$ and the structure shows pseudosymmetry close to the space group $C2/c$. At 193 K the compound has a long S—S bond of 2.1089 (12) Å and the S atom to anthracene bond distances are 1.776 (3) and 1.770 (2) Å. The C—S—S—C torsion angle is 76.06 (13)°.

Comment

The crystal structure determination of 9-dianthryl disulfide, (I), is part of our investigation dealing with polyaromatic sulfides (Kansikas & Sipilä, 1997, 2000; Sipilä & Hase, 1997; Sipilä *et al.*, 1999). A simple preparation method for (I) has been reported by Majumdar *et al.* (1986), who synthesized the product in 90% yield by refluxing anthrone, P_2S_5 and anhydrous pyridine for 5 h. The compound used in this X-ray analysis was obtained as a side product when testing preparation methods for 9-anthracenethiol. The orange-coloured blocks used for the structure determination were slowly recrystallized from absolute ethanol. The melting point (490 K) was measured in an open capillary tube with an electrothermal apparatus and is uncorrected. The melting points reported earlier vary from 477 to 496 K (Friedländer & Simon, 1922; Majumdar *et al.*, 1986).



(I)

When compared with other aromatic bis-compounds joined by the disulfide group, the S—S′ distance of 2.1089 (12) Å found in (I) is relatively long. An even longer S—S bond of 2.113 (1) Å has been reported in an exceptional structure of the chloro[bis(2-pyrimidyl)dzisulfide]copper(I) complex, where the torsion angle C—S—S—C is 180° due to symmetry (Simmons *et al.*, 1979). Some other long S—S bonds reported in the Cambridge Structural Database (CSD; Allen *et al.*, 1991) are 2.073 in bis(1-methyluracil) 5,5′-disulfide (Shefter, 1970), 2.075 in bis(2-methylbenzo[*b*]thien-3-yl) disulfide (Schaumann *et al.*, 1979) and 2.080 Å in bis(2-phenylthieno[3,2-*g*]quinoxaline-3-yl) disulfide (Soricelli *et al.*, 1991). The S—$C_{aromatic}$ bond distances of 1.776 (3) and 1.770 (2) Å comparable with those found in the literature (Simmons *et al.*, 1979 and references therein).

The value of 76.06 (13)° for the C9—S—S′—C9′ torsion angle is small compared with those in most disulfide groups joining aromatic rings listed in the CSD. The relatively small angle of 37.1 (1)° between the phenanthrene planes within one molecule causes stacking in the molecular packing, where the S—S′ bonds connect the more or less parallel aromatic layers. The appearance is closely similar to the packing of bis[2-(phenyl)thieno[3,2-*g*]quinoxaline-3-yl] disulfide, where, however, a C_2 axis through the S—S bond exists (Soricelli *et al.*, 1991).

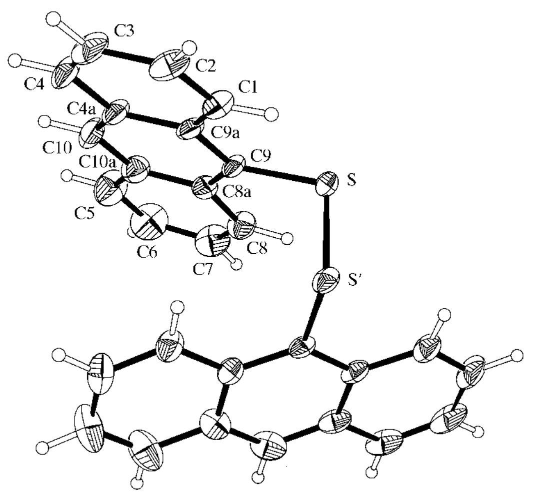


Figure 1
View of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

Experimental

Compound (I) was a side product in the preparation of anthracene-9-thiol using the method of Testaferri *et al.* (1983). Potassium propanethiolate was refluxed with 9-bromoanthracene for 2 h in dimethylformamide and the product was dealkylated with potassium *tert*-butoxide by refluxing for several hours in a one-pot reaction. A nitrogen atmosphere was not used. The reaction mixture was poured into 1 *M* HCl and extracted with diethyl ether. The organic layer was washed with water, dried with sodium sulfate and evaporated. The residue was only partly soluble in dichloromethane–ligroin (1:3) used as a solvent in the flash chromatography of the crude product. The insoluble yellow powder was crystallized from ethanol to obtain di-9-anthryl disulfide (10% yield).

Crystal data

$C_{28}H_{18}S_2$
$M_r = 418.54$
Monoclinic, $P2_1/n$
$a = 8.8330\ (18)$ Å
$b = 16.833\ (3)$ Å
$c = 14.335\ (3)$ Å
$\beta = 102.65\ (3)^\circ$
$V = 2079.7\ (7)$ Å^3
$Z = 4$
$D_x = 1.337$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 4$–10°
$\mu = 2.398$ mm^{-1}
$T = 193\ (2)$ K
Block, orange
0.29 × 0.27 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3443 measured reflections
3305 independent reflections
2639 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\rm max} = 63.69^\circ$
$h = -10 \rightarrow 9$
$k = -19 \rightarrow 0$
$l = 0 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.156$
$S = 1.027$
3305 reflections
271 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1047P)^2 + 1.0329P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.69$ e Å^{-3}

The reciprocal space exploring program *XPREP* (*SHELXTL*/*PC*; Sheldrick, 1990*a*) indicated the space group $P2_1/n$ and the structure was readily solved. However, the appearance of the molecular packing suggested a closer inspection of the reciprocal lattice planes. Those *hkl* reflections with $h + k = 2n + 1$, corresponding to the forbidden reflections in the space group $C2/c$, were considerably weaker than the other reflections but were clearly visible. When the structure was solved in this space group, the asymmetric unit consisted of half of the molecule. The final R_1 value converged to 0.079, several correlation matrix elements exceeded the value of 0.5, and isotropic displacement parameters of atoms C2, C3, C4, C6 and C7 showed disorder. For these reasons, the present solution was chosen. Both of these space groups have been reported for symmetric or pseudosymmetric disulfides, *e.g.* $P2_1/c$ (Neidlein *et al.*, 1990; Shefter, 1970) and $C2/c$ (Acheson *et al.*, 1980; Ricci & Bernal, 1969).

Table 1
Selected geometric parameters (Å, °).

S—S′	2.1089 (12)	C8a′—C9′	1.423 (4)
S—C9	1.776 (3)	C8a—C10a	1.424 (4)
S′—C9′	1.770 (2)	C8a′—C10a′	1.424 (4)
C4a—C9a	1.423 (4)	C9—C9a	1.429 (3)
C4a′—C9a′	1.433 (4)	C9′—C9a′	1.405 (4)
C4a—C10	1.389 (4)	C10—C10a	1.408 (4)
C4a′—C10′	1.406 (4)	C10′—C10a′	1.385 (4)
C8a—C9	1.401 (4)		
C9—S—S′	102.45 (9)	C8a′—C9′—S′	119.6 (2)
C9′—S′—S	102.67 (9)	C9a—C9—S	119.5 (2)
C8a—C9—S	118.76 (19)	C9a′—C9′—S′	118.62 (19)
C9—S—S′—C9′	76.06 (13)	S—S′—C9′—C9a′	−100.4 (2)
S′—S—C9—C8a	−101.0 (2)	S—S′—C9′—C8a′	79.5 (2)
S′—S—C9—C9a	79.2 (2)		

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *WinGX* (Farrugia, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*a*); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1075). Services for accessing these data are described at the back of the journal.

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