| | |
|---|---|
| C11—C1—C2—C3 | −48.9 (4) |
| C21—C1—C2—C3 | −176.8 (3) |
| C1—C2—C3—C4 | −172.9 (3) |
| C2—C1—C11—C12 | −41.8 (5) |
| C2—C1—C21—C22 | 81.1 (4) |
| C2—C3—C31—C32 | −49.7 (5) |
| C14—C13—C18—C181 | −62.1 (5) |
| C14—C13—C18—C182 | 178.7 (4) |
| C14—C13—C18—C183 | 59.3 (5) |
| C24—C23—C28—C281 | −178.9 (4) |
| C24—C23—C28—C282 | 61.7 (5) |
| C24—C23—C28—C283 | −58.7 (5) |
| C34—C33—C38—C381 | 58.9 (5) |
| C34—C33—C38—C382 | 178.1 (4) |
| C34—C33—C38—C383 | −62.8 (5) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···N1 | 0.82 | 1.95 | 2.759 (4) | 170 |
| O2—H2···N2$^i$ | 0.82 | 2.03 | 2.828 (4) | 165 |
| O3—H3···O1$^{ii}$ | 0.82 | 2.05 | 2.828 (4) | 158 |

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was indicated by the systematic absences. H atoms were treated as riding atoms (C—H 0.93–0.98 and O—H 0.82 Å), except for those treated as part of rigid methyl groups (allowed to rotate but not tip). Starting coordinates for methyl and OH groups were taken from difference syntheses.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*96. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1228). Services for accessing these data are described at the back of the journal.

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# Perylo[1,12-*b*,*c*,*d*]thiophene†

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## Abstract

The title compound, $C_{20}H_{10}S$, contains discrete molecules which are essentially planar and are regularly stacked along the *b* axis [interplanar separation 3.474 (4) Å]; columns are bridged by short S···S interstack contacts of 3.506 (2) Å about inversion centres.

## Comment

Perylene ($C_{20}H_{12}$) is a well known donor molecule used in the preparation of conducting and semiconducting radical cation salts (Akamutu, Inokuchi & Matsunaga, 1954; Alcácer & Maki, 1974, 1976; Endres, Keller, Müller & Schweitzer, 1985; Almeida & Henriques, 1997). In our research group, special attention has been given to the (quasi) one-dimensional family of conductors (perylene)$_2$*M*(mnt)$_2$, where *M* is a transition metal and mnt is maleonitriledithiolate or *cis*-2,3-disulfanylbut-2-enedinitrile (Gama *et al.*, 1991, 1993). In the search for perylene derivatives, perylo[1,12-*b*,*c*,*d*]thiophene, hereafter designated by pet, was chosen, aiming at the introduction of both an increase of intermolecular interaction, due to the presence of the outer S atom, and possible effects on lowering molecular symmetry. So far, instead of the common 2:1 stoichiometry, only (pet)$_3$[Ni(mnt)$_2$]$_2$ compounds were obtained (Alcácer, Morgado, Henriques & Almeida, 1995). In order to gain

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† Alternative name: 1,12-epithioperylene.

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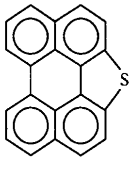
some additional information in relation to the different crystallization behaviour of pet and perylene, the crystal structure of pet has been determined.



pet

The asymmetric unit contains one pet molecule. The atom-labelling scheme is shown in Fig. 1. The pet molecule shows a sizeable distortion in relation to the neutral perylene, due to the presence of the five-membered S-containing ring. Thus, the two central bonds of the perylene-like backbone become asymmetrical: the C2—C19 bond, with a length of 1.407 (3) Å, is much shorter than C10—C11 [1.481 (3) Å]. Furthermore, the angles of the thiophene-like ring centred at C2 and C19 [114.1 (2) and 113.9 (2)°, respectively] are much smaller than those centred at C10 and C11 [124.6 (2) and 124.7 (2)°, respectively].

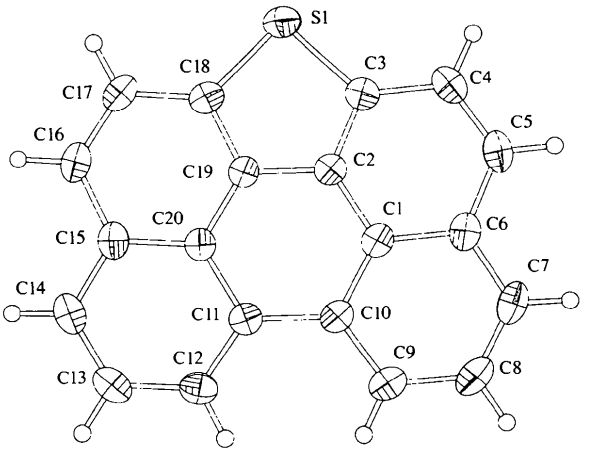


Fig. 1. The molecular structure of pet showing the atom-labelling scheme and displacement ellipsoids drawn at the 40% probability level. H atoms are shown as spheres of arbitrary radii.

The crystal structure of the title compound contains almost planar pet molecules which are regularly stacked along the *b* axis, with interplanar distances of 3.474 (4) Å. The angle between the normal to the molecular plane and the stacking axis is 39.84 (4)°. The overlap mode of the neighbouring molecules is essentially a graphite-like mode. They are slipped along the longer axis of the perylene backbone. This overlap mode is also found in the perylene-based molecular metals such as the members of the $(\mathrm{per})_2M(\mathrm{mnt})_2$ series (Alcácer *et al.*, 1980; Domingos *et al.*, 1989; Gama *et al.*, 1991, 1992). It should be mentioned that in the structure found for neutral perylene (Donalson, Robertson & White, 1953), there are no such stacks, the perylene molecules being grouped in pairs, with an interplanar distance of 3.47 Å.

The contacts between pet molecules of different stacks are shown in Fig. 2. One S···S contact of 3.506 (2) Å is shorter than the sum of the van der Waals radii (3.6 Å; Bondi, 1964) and occurs between molecules of neighbouring stacks related by an inversion centre.

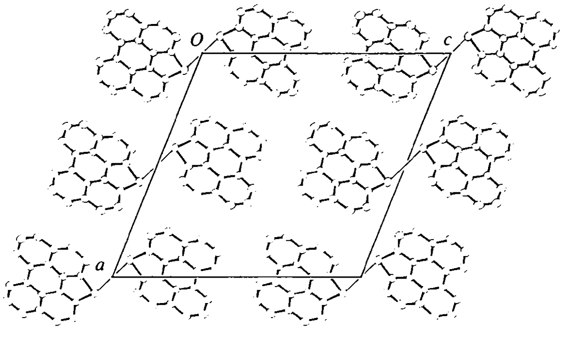


Fig. 2. Crystal structure viewed along the *b* axis. The S···S interstack contacts are indicated by thin lines.

## Experimental

Pet was prepared from 3,4,9,10-perylenetetracarboxylic dianhydride according to reported procedures (Rogovik, 1974). In order to increase the yield, an alternative procedure (Iwashima & Aoki, 1968) for the decarboxylation of perylo[1,12-*b*,*c*,*d*]-thiophene-3,4,9,10-tetracarboxylic acid was used. Crystals of pet suitable for X-ray diffraction studies were obtained by slow evaporation of acetonitrile–dichloromethane solutions.

*Crystal data*

$C_{20}H_{10}S$
$M_r = 282.34$
Monoclinic
$P2_1/a$
$a = 16.921\ (2)$ Å
$b = 4.5252\ (4)$ Å
$c = 17.898\ (2)$ Å
$\beta = 112.655\ (11)°$
$V = 1264.7\ (2)$ Å$^3$
$Z = 4$
$D_x = 1.483$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.243$ mm$^{-1}$
$T = 293\ (2)$ K
Needle
0.60 × 0.10 × 0.05 mm
Yellow

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scan
Absorption correction: empirical *via* $\psi$ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.974$, $T_{\max} = 1.000$
3106 measured reflections
3014 independent reflections

1969 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.023$
$\theta_{\max} = 27.95°$
$h = -22 \rightarrow 20$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 23$
5 standard reflections every 100 reflections frequency: 60 min

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.124$
$S = 1.129$
3011 reflections
191 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.7365P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.282$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.282$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—C18 | 1.753 (2) | C9—C10 | 1.386 (3) |
| S1—C3 | 1.760 (2) | C10—C11 | 1.481 (3) |
| C1—C2 | 1.399 (3) | C11—C12 | 1.387 (3) |
| C1—C6 | 1.414 (3) | C11—C20 | 1.430 (3) |
| C1—C10 | 1.428 (3) | C12—C13 | 1.398 (3) |
| C2—C3 | 1.378 (3) | C13—C14 | 1.372 (4) |
| C2—C19 | 1.407 (3) | C14—C15 | 1.403 (3) |
| C3—C4 | 1.415 (3) | C15—C20 | 1.410 (3) |
| C4—C5 | 1.364 (3) | C15—C16 | 1.434 (3) |
| C5—C6 | 1.435 (3) | C16—C17 | 1.367 (3) |
| C6—C7 | 1.407 (3) | C17—C18 | 1.410 (3) |
| C7—C8 | 1.369 (4) | C18—C19 | 1.382 (3) |
| C8—C9 | 1.401 (4) | C19—C20 | 1.397 (3) |
| C18—S1—C3 | 92.17 (11) | C19—C18—S1 | 110.0 (2) |
| C2—C3—S1 | 109.8 (2) | C17—C18—S1 | 131.6 (2) |
| C4—C3—S1 | 131.7 (2) | | |

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1306). Services for accessing these data are described at the back of the journal.

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# *cis*-3,5a-Dimethyl-1-oxo-5a,6,8,9-tetrahydro-1*H*,7*H*-pyrano[4,3-*b*][1]benzopyran-6-yl Formate

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## Abstract

Characterization of the title compound, $C_{15}H_{16}O_5$, by X-ray diffraction affirms its linearly fused tricyclic structure and the chair conformation of the cyclohexane ring on which the methyl and adjacent formyloxy groups are *cis*, the former being axial and the latter equatorial. The C═C bond $\gamma,\delta$ to the carbonyl is longer, while the C═C bond $\alpha,\beta$ to the carbonyl is shorter than their counterparts in a 3-substituted 4-hydroxy-6-methyl-2-pyrone.

## Comment

In studies of the synthesis of (+)-pyripyropene A (Tomoda *et al.*, 1994) and structurally related biologically active compounds (Omura *et al.*, 1995), a new condensation reaction leading to the polycyclic pyran ring system was developed. (+)-Pyripyropene A is a