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A spiro-linked pyrene–naphthoquinone

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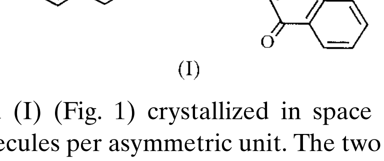
The title molecule, 2′-pyrenylspiro[2,3-dihydro-1*H*-cyclopenta[*b*]naphthalene-2,5′-1′,3′-dioxane]-4,9-dione, $C_{32}H_{22}O_4$, contains an electron-donating pyrene group spiro-linked to an electron-accepting naphthoquinone. The molecules are V-shaped in profile and stack to form columns along **b** with alternating, approximately coplanar, pyrene and naphthoquinone fragments. Intermolecular contacts within a column are consistent with some degree of π contact and possible long-range delocalization. Individual columns form a herringbone pattern when the crystal is viewed along **b**.

Comment

As part of a project designed to study the distance dependence of electron transfer, a series of porphyrin–quinone compounds containing oligospirocyclobutane linkers were prepared and studied (Knapp *et al.*, 1991). Theory suggests that the rate of through-bond electron transfer depends on the edge-to-edge porphyrin-to-quinone distance R_e according to $k_{\rm ET} = \exp(-bR_e)$, where b is a constant determined experimentally (Wasielewski, 1992; Closs & Miller, 1988). Difficulty in crystallizing several porphyrin–quinone compounds in order to determine R_e values prompted us to prepare the title complex, (I), in which a bulky tetraarylporphyrin group is replaced by pyrene. We report here the crystal structure of the model compound (I) which, in conjunction with an oligospirocyclobutane model, permitted reasonable estimates of R_e for the porphyrin–quinone compounds to be obtained (Knapp *et al.*, 1991).



(I)

Compound (I) (Fig. 1) crystallized in space group $Pna2_1$ with two molecules per asymmetric unit. The two independent molecules exhibit similar metric parameters (Table 1) and are related by a pseudo-2_1 screw axis parallel to **b** at $x = 0.633$ (4) and $z = 0.464$ (1). The crystal is pseudo-centrosymmetric with inversion centers located at [0.883 (4), −0.006 (5), 0.464 (1)] and related locations (the z coordinates of the pseudo-symmetry elements are consonant with the structural parameters as refined). These observations suggest that the crystal is possibly inversion twinned. Based on $\Delta f''$ values of 0.009 and 0.032 for C and O, respectively, anomalous scattering is calculated to be approximately 0.16% of the total, a value too small to produce a significant Flack (1983) parameter evaluation. Indeed, refinement of the original structure, the structure inverted through the origin, and the structure inverted through the pseudo-center of symmetry gave identical $R(F^2)$, $wR(F^2)$ and S values, and Flack parameters of 0.3 (3), 0.7 (3) and 0.3 (3), respectively.

Molecules of (I) may be viewed as containing an electron-donating group (pyrene) separated from an electron-accepting group (naphthoquinone) by a fused cyclopentene ring and a spiro-linked 1,3-dioxane ring. The pyrene fragments (C2–C17) exhibit a maximum atomic deviation from planarity of 0.04 Å while the naphthoquinone fragments (C23–C32, O3, O4) are less planar and show a maximum deviation of 0.08 Å. Deviations of these magnitudes are consistent with those reported for other pyrene- (Kai *et al.*, 1978) and naphthoquinone-containing (Michael *et al.*, 1990) structures. Dihedral angles between the pyrene and naphthoquinone fragments are 71.17 (5) and 70.72 (5)° for the unlettered and *A* molecules, respectively. The five-membered cyclopentene and six-membered dioxane rings are in the expected envelope and chair conformations, respectively. These geometric features, coupled with the torsion angles about C1—C2 and the spiro linkage at C19 (Table 1), combine to give the molecules a V-shaped appearance when viewed approximately in profile (Fig. 1). The largest correlation coefficients, ranging from ±0.71 to ±0.82, are between the z, U_{22} or U_{33} parameters for C3, C9, O2, C20, C17 and C31, and their pseudo-inversion mates. These values are consistent with the slightly unusual appearance of the displacement ellipsoids of these atoms (Fig. 1).

The crystal contains columns of equally spaced molecules related by the pseudo-2_1 screw axis parallel to **b**. Within a column, pyrene and naphthoquinone fragments alternate and

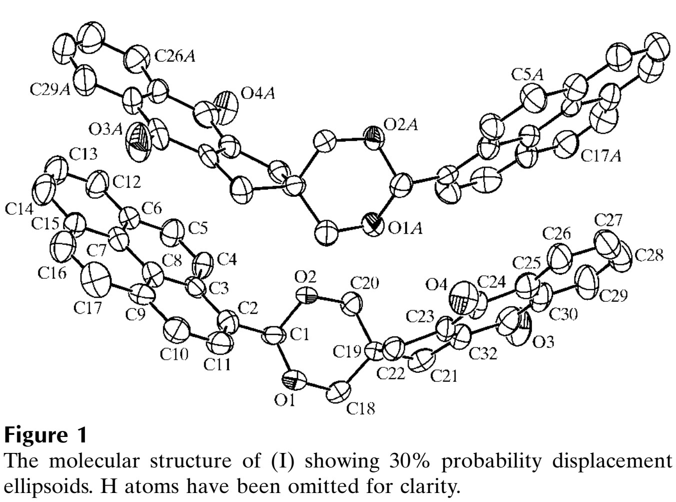


Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

are approximately coplanar; the intermolecular $P\cdots Q_A$ and $P_A\cdots Q$ dihedral angles are 3.2 (1) and 4.2 (1)°, respectively, where P and Q refer to the pyrene and naphthoquinone fragments, and A is used to designate the second molecule in the asymmetric unit. Several short intermolecular $P\cdots Q$ contacts within a column [the shortest is C8$\cdots$C26A, 3.468 (9) Å] are consistent with some degree of π contact between adjacent pyrene and quinone units, while the regular spacing of $P—Q$ units along **b** suggests the possibility of long-range delocalization in that direction. When the crystal is viewed along **b**, the columns are seen to pack together in a herring-bone arrangement generated by the n and a glide planes.

Experimental

Pyrene-1-carboxaldehyde dimethylacetal was prepared from commercial pyrene-1-carboxaldehyde by treatment with trimethylorthoformate (Buchler *et al.*, 1988). The pyrene acetal, (I), was prepared by acetal exchange (toluene, acetonitrile, pyridinium *p*-toluenesulfonate, reflux 30 min, 97% yield) of pyrene-1-carboxaldehyde dimethylacetal with a naphthoquinonediol (Albaneze, 1993) as described previously (Knapp *et al.*, 1991; Gentemann *et al.*, 1994). Crystals suitable for X-ray analysis were grown by slow diffusion of pentane vapor into a chloroform/toluene solution of (I) at room temperature. The crystal chosen for study showed sharp extinctions and exhibited orange–yellow dichroism when examined under polarized light.

Crystal data

$C_{32}H_{22}O_4$
$M_r = 470.50$
Orthorhombic, $Pna2_1$
$a = 16.591$ (2) Å
$b = 8.8487$ (7) Å
$c = 30.996$ (9) Å
$V = 4550.5$ (15) Å^3
$Z = 8$
$D_x = 1.374$ Mg m^{-3}
$D_m = 1.36$ (1) Mg m^{-3}
D_m measured by flotation
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 19.6$–$25.9°$
$\mu = 0.722$ mm^{-1}
$T = 295$ (2) K
Flat rod, gold
0.50 × 0.18 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-θ scans
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.867$, $T_{max} = 0.964$
10756 measured reflections
5587 independent reflections
3023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 70.03°$
$h = -18 \rightarrow 20$
$k = -10 \rightarrow 10$
$l = -34 \rightarrow 37$
3 standard reflections
frequency: 180 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.085$
$S = 0.99$
5587 reflections
650 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00027 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.417 (5)	C19A—C20A	1.535 (7)
O1A—C1A	1.415 (6)	C19—C21	1.546 (6)
O2—C1	1.434 (6)	C19A—C21A	1.564 (6)
O2A—C1A	1.424 (6)	C19—C22	1.541 (6)
C1—C2	1.508 (6)	C19A—C22A	1.553 (6)
C1A—C2A	1.519 (7)	C2—C3	1.400 (8)
C18—C19	1.525 (6)	C2A—C3A	1.396 (7)
C18A—C19A	1.498 (6)	C2—C11	1.370 (7)
C19—C20	1.518 (6)	C2A—C11A	1.382 (6)
O1—C1—O2	109.7 (4)	C20—C19—C21	110.0 (5)
O1A—C1A—O2A	111.0 (4)	C20A—C19A—C21A	108.5 (5)
O1—C1—C2	109.9 (5)	C18—C19—C21	112.0 (4)
O1A—C1A—C2A	109.3 (5)	C18A—C19A—C21A	114.5 (4)
O2—C1—C2	105.8 (5)	C21—C19—C22	103.9 (4)
O2A—C1A—C2A	104.5 (5)	C21A—C19A—C22A	104.2 (4)
C18—C19—C20	106.5 (4)	C3—C2—C11	120.4 (6)
C18A—C19A—C20A	107.1 (4)	C3A—C2A—C11A	119.5 (5)
C20—C19—C22	112.0 (4)	C1—C2—C11	119.3 (5)
C20A—C19A—C22A	109.2 (4)	C1A—C2A—C11A	120.4 (5)
C18—C19—C22	112.6 (4)	C1—C2—C3	120.1 (5)
C18A—C19A—C22A	113.1 (4)	C1A—C2A—C3A	120.1 (5)
O1—C1—C2—C11	19.3 (8)	O1—C1—C2—C3	−164.8 (5)
O1A—C1A—C2A—C11A	19.4 (7)	O1A—C1A—C2A—C3A	−163.9 (5)
O2—C1—C2—C11	−99.0 (6)	O2—C1—C2—C3	76.9 (6)
O2A—C1A—C2A—C11A	−99.5 (6)	O2A—C1A—C2A—C3A	77.2 (6)

Axial photographs revealed *mmm* reciprocal lattice point symmetry with the cell edges given in the table above. Systematic absences were consistent with space groups *Pnma* and $Pna2_1$; attempts to solve the structure in *Pnma* using either direct or Patterson methods were unsuccessful. A packing diagram viewed along **b** revealed that the mirror planes perpendicular to **c** that are required in space group *Pnam*, an alternate setting of *Pnma*, are impossible. H atoms were placed at sp^2 or sp^3 calculated positions with C—H distances equal to 0.98, 0.97 or 0.93 Å for tertiary, secondary or aromatic C—H linkages, respectively. H atom displacement parameters were set as $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection and cell refinement: *Structure Determination Package* (Enraf–Nonius, 1985); data reduction: local programs; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1564). Services for accessing these data are described at the back of the journal.

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