

1:1 Complexes of 2,3,5,6-tetrachlorobenzene-1,4-dicarbonitrile with pyrene and phenanthrene: pseudo-isomorphs

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2,3,5,6-Tetrachlorobenzene-1,4-dicarbonitrile forms alternate π -stacked 1:1 complexes with pyrene, $C_8Cl_4N_2 \cdot C_{16}H_{10}$, and phenanthrene, $C_8Cl_4N_2 \cdot C_{14}H_{10}$. These complexes are pseudo-isomorphs. Phenanthrene, disordered about a centre of symmetry, takes the position of the pyrene, which sits exactly on this centre of inversion. The tetrachlorobenzenedicarbonitrile molecules in each complex also sit on centres of inversion and are in similar positions within the unit cells in the two structures, except that the orientation of the nitrile groups differs between the two.

Comment

In an earlier paper (Britton, 2002), the formation of two-dimensional arrays of the isomers of tetrachlorodicyanobenzene, TCDB, by formation of complexes with hexamethylbenzene was described. At the same time, the possibility of forming similar arrangements, with other π bases replacing the hexamethylbenzene, was explored. While a number of complexes were formed, none had the desired layers of TCDB. The structures of two of these complexes, *p*-TCDB–pyrene (1/1), (I), and *p*-TCDB–phenanthrene (1/1), (II), are described here.

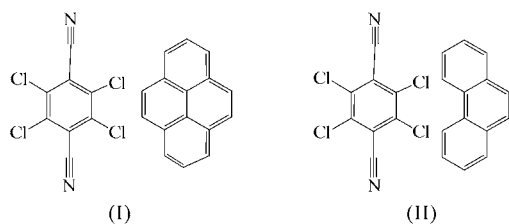


Fig. 1 shows the labelling and anisotropic displacement ellipsoids for the molecules in (I). Both molecules lie on centres of symmetry. Fig. 2 shows the labelling and anisotropic displacement ellipsoids for the molecules in (II). The TCDB molecules lie on one centre of symmetry and the phenanthrene molecules are disordered about another. Fig. 2 shows

the relative positions of the disordered phenanthrene molecules with respect to each other. In both Figs. 1 and 2, the view is along *a* with *b* vertical. Although the structures are otherwise similar, the orientation of the nitrile groups is different in the two structures; the molecules are rotated approximately 60° in the plane of the molecule with respect to each other. To the extent that bond lengths and angles were measured, they are normal in both structures.

The primary intermolecular interactions in both of these complexes are π stacks of alternating molecules parallel to the *a* axis. The molecules are tilted 3.2° away from parallel with each other in (I), and 2.8° in (II). The molecules are 3.43 (12) Å apart in (I) and 3.44 (10) Å apart in (II); the large uncertainties are a consequence of the deviations from parallel.

In both structures, the molecules also lie in puckered layers parallel to (100). In Fig. 3, one such layer is shown for (I). The TCDB molecules are tilted by 18.3 (1) $^\circ$ and the pyrene molecules by 19.0 (1) $^\circ$ with respect to (100); the two molecules are tilted by 24.6 (1) $^\circ$ with respect to each other. The corresponding tilts in (II) are 26.8 (1), 25.3 (1) and 35.3 (1) $^\circ$, respectively. The layers appear to be held together by weak $C-H \cdots Cl/N$ hydrogen bonds; these are shown in Fig. 3. The

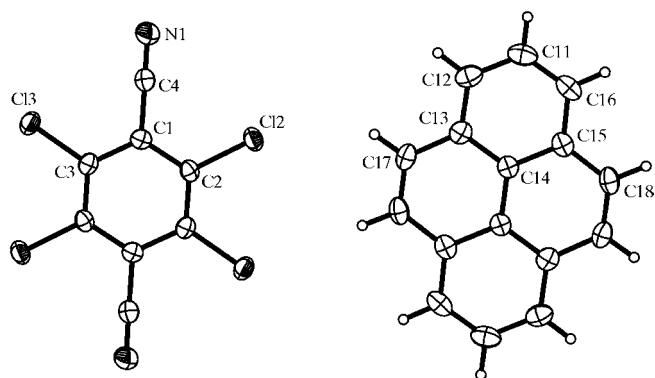


Figure 1
Both molecules in TCDB–pyrene, (I). Displacement ellipsoids are shown at the 50% probability level. Only the symmetry-independent atoms are labelled. The view is down *a* with *b* vertical.

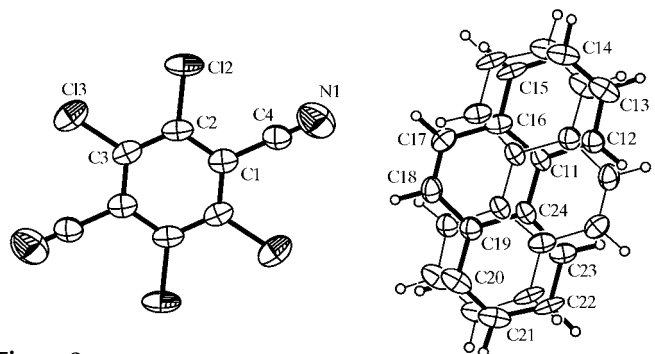


Figure 2
Both molecules in TCDB–phenanthrene, (II), including the disordered components (thinner bonds). The two overlapping orientations of the disordered components are related by a center of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Displacement ellipsoids are shown at the 50% probability level. Only the symmetry-independent atoms are labelled. The view is from the same direction and orientation as in Fig. 1.

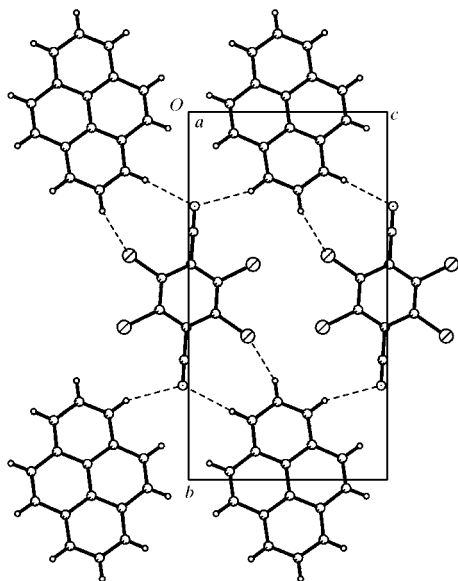


Figure 3

The packing in compound (I), viewed down *a*, showing one layer of molecules approximately parallel to (100). Weak hydrogen bonds are shown as dashed lines. The molecules alternate in π stacks parallel to *a*.

geometric data are given in Table 1. There are similar interactions in (II) but, in view of the disorder shown in Fig. 2 and the additional untreated disorder that must be present in the TCDB atomic positions, the geometric data for these interactions have not been included. The disorder of the TCDB molecules in (II) can be seen from the larger atomic displacement parameters for this moiety in Fig. 2, compared with those in Fig. 1. This disorder arises from the disorder in the adjacent phenanthrene molecules and must consist of small displacements in various directions that depend on the particular orientations of all the surrounding phenanthrene molecules; it does not seem worthwhile to attempt to model this disorder.

In the two structures, both the unit cells and the packings are similar, but, as mentioned above, the orientations of the TCDB molecules are different. The structures are probably best described as pseudo-isomorphs.

Experimental

Crystals of both complexes were obtained by dissolving equimolar quantities of the two components in acetone and allowing the solutions to evaporate.

Compound (I)

Crystal data

$C_8Cl_4N_2 \cdot C_{16}H_{10}$
 $M_r = 468.14$

Monoclinic, $P2_1/n$

$a = 7.0679$ (18) Å

$b = 15.983$ (4) Å

$c = 8.907$ (2) Å

$\beta = 104.78$ (1)°

$V = 972.9$ (4) Å³

$Z = 2$

$D_x = 1.598$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 3295 reflections

$\theta = 2.5$ – 25.0 °

$\mu = 0.62$ mm⁻¹

$T = 174$ (2) K

Needle, yellow

$0.35 \times 0.12 \times 0.05$ mm

Data collection

Siemens SMART area-detector diffractometer

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)

$T_{\min} = 0.91$, $T_{\max} = 0.97$

4778 measured reflections

1700 independent reflections

1474 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 25.0$ °

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 18$

$l = -10 \rightarrow 8$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.081$

$S = 1.06$

1700 reflections

136 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.306P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻³

Compound (II)

Crystal data

$C_8Cl_4N_2 \cdot C_{14}H_{10}$

$M_r = 444.12$

Monoclinic, $P2_1/n$

$a = 7.1731$ (18) Å

$b = 15.599$ (4) Å

$c = 9.104$ (2) Å

$\beta = 110.600$ (10)°

$V = 953.5$ (4) Å³

$Z = 2$

$D_x = 1.547$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 3496 reflections

$\theta = 2.6$ – 25.0 °

$\mu = 0.63$ mm⁻¹

$T = 174$ (2) K

Needle, yellow

$0.40 \times 0.20 \times 0.12$ mm

Data collection

Siemens SMART area-detector diffractometer

ω scans

Absorption correction: multi-scan SADABS (Sheldrick, 1996; Blessing, 1995)

$T_{\min} = 0.86$, $T_{\max} = 0.93$

4557 measured reflections

1667 independent reflections

1415 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 25.0$ °

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 18$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.115$

$S = 1.08$

1667 reflections

154 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.66P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Distances† and angles (Å, °) in the C—H...X—C contacts in (I).

C—H...X	C—H...X	H...X	H...X—C	C...X
C11—H11...Cl3 ⁱ	122	2.97	139	3.560 (2)
C12—H12...N1 ⁱⁱ	155	2.75	102	3.631 (3)
C16—H16...N1 ⁱ	153	2.63	117	3.501 (3)

† All C—H distances are 0.95 Å. Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

For (II), when the disorder of the phenanthrene molecule around the centre of symmetry at $(1, \frac{1}{2}, 1)$ was found, the molecule was restrained using DFIX (Sheldrick, 1997) to have the average bond

lengths and angles found by Petříček *et al.* (1990). When the disordered orientations were superimposed, some of the atoms of the symmetry-related orientation were close to overlapping with those of the first orientation. Atoms that resulted in such overlap were constrained to have identical anisotropic displacement parameters. Under these conditions, the refinement proceeded satisfactorily.

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1185). Services for accessing these data are described at the back of the journal.

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