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1,3,5-Tris(4-formylphenoxymethyl)-2,4,6-trimethylbenzene ethyl acetate solvate

David J. Bray, Leonard F. Lindoy and John C. McMurtrie*

Centre for Heavy Metals Research, School of Chemistry, University of Sydney, New South Wales 2006, Australia

Correspondence e-mail:
j.mcmurtrie@chem.usyd.edu.au

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In the crystal structure of the title compound, $C_{33}H_{30}O_6 \cdot C_4H_8O_2$, two 4-formylphenoxy pendant arms protrude on one side of the mean plane of the central benzene ring and the other protrudes on the opposite side. The molecules are arranged in chains parallel to the *a* axis that propagate *via* edge-to-face aryl–aryl intractions. Each chain is connected to four adjacent chains, also by edge-to-face interactions, to produce a three-dimensional network.

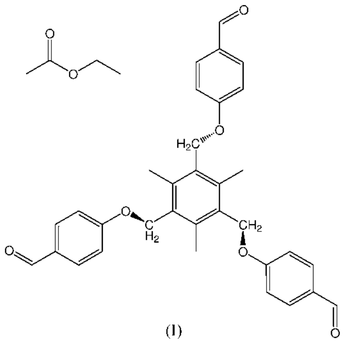
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.147
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

We are investigating the structural and metallo-supramolecular chemistry of metal complexes with tripodal ligands. The title compound, (I), is a synthetic intermediate that was obtained during the preparation of these ligands.



(I)

The asymmetric unit of (I), illustrated in Fig. 1, comprises one 1,3,5-tris(4-formylphenoxymethyl)-2,4,6-trimethylbenzene molecule and one ethyl acetate molecule. Two 4-formylphenoxy pendant arms project on one side of the central benzene ring while the other projects on the opposite side, in a similar arrangement to that observed in the structure of the related compound 2,4,6-trimethyl-1,3,5-tris(phenoxymethyl)benzene (Bray *et al.*, 2003). The acute torsion angles that define the rotation of the $H_2C—O$ bonds from the plane of the central benzene ring are listed in Table 1.

The 4-formylphenoxy pendant arms are arranged in a T-shaped configuration with the benzene ring at the junction. In the crystal structure, illustrated in Fig. 2, the molecules are arranged in chains that run parallel to the *a* axis. These chains propagate by edge-to-face aryl–aryl interactions between two pairs of pendant arms of adjacent molecules and also by edge-to-face interactions incorporating the remaining pendant arms and the central benzene rings of adjacent molecules. The T-shaped configuration of the molecule appears to be a function of the crystal packing, driven largely by the formation of the edge-to-face interactions that propagate the chains.

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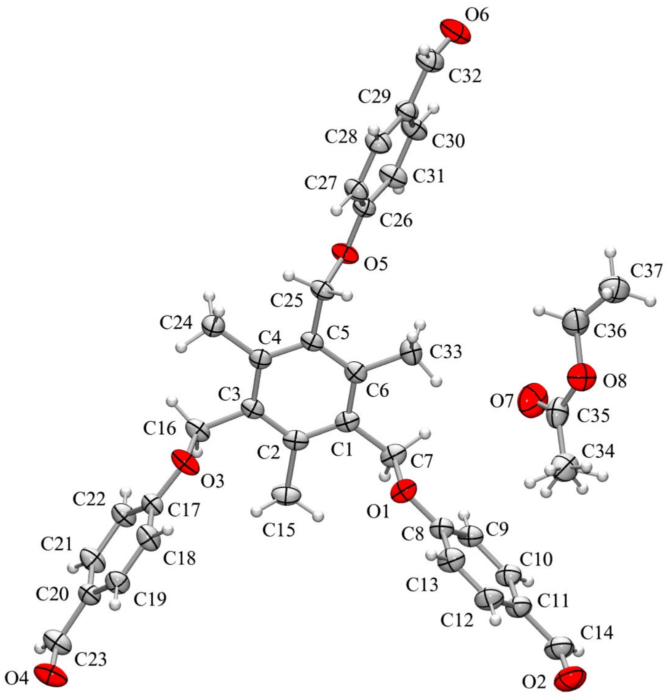

Figure 1
A view of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

The individual chains are surrounded by six coaligned chains, with each connected to four others by edge-to-face aryl–aryl interactions between pendant arms to produce a three-dimensional network. The ethyl acetate molecules occupy space between pairs of chains, precluding formation of aryl interactions between them.

Experimental

1,3,5-Tris(2-bromomethyl)-2,4,6-trimethylbenzene was prepared from 1,3,5-trimethylbenzene by the literature method of van der Made & van der Made (1993). The title compound was prepared by the following method, which is a modification of the synthesis of 2,4,6-trimethyl-1,3,5-tris(phenoxymethyl)benzene (Bray *et al.*, 2003). 4-Hydroxybenzaldehyde (4.2 g, 40 mmol) in acetonitrile (80 ml) was added over a period of 6 h to a refluxing mixture of 1,3,5-tris(2-bromomethyl)-2,4,6-trimethylbenzene (4.0 g, 10 mmol), potassium carbonate (5.52 g, 20 mmol), acetonitrile (140 ml) and tetrahydrofuran (200 ml). This mixture was refluxed for 42 h then filtered hot. The filtrate was evaporated under vacuum and the resulting solid was recrystallized from a mixture of acetone and water to give fine white crystals (4.88 g, 93%; m.p. 475–476 K). ^{1}H NMR (CDCl$_3$, 300 MHz, 300 K, δ, p.p.m.): 2.47 (9H, *s*, 3 × CH$_3$), 5.22 (6H, *s*, 3 × CH$_2$), 7.13 (6H, *d*, aromatic), 7.89 (6H, *d*, aromatic), 9.93 (3H, *s*, 3 × CHO); ^{13}C NMR (CDCl$_3$, 75.5 MHz, 300 K, δ, p.p.m.): 16.42 (CH$_3$), 65.67 (CH$_2$), 115.28, 132.48 (aromatic), 130.75, 131.68, 140.16, 164.34 (quaternary aromatic), 191.11 (CHO); MS (ESI) $m/z = 523.3$ $(M+\text{H})^+$. Elemental microanalysis, found (%): C 75.45, H 5.93; $C_{33}H_{30}O_6$ requires (%): C 75.84, H 5.79. FT–IR (KBr) $\nu_{(C=O)}$ 1691 cm^{-1}. Crystals of sufficient quality for X-ray analysis were obtained by recrystallization of the above product from ethyl acetate.

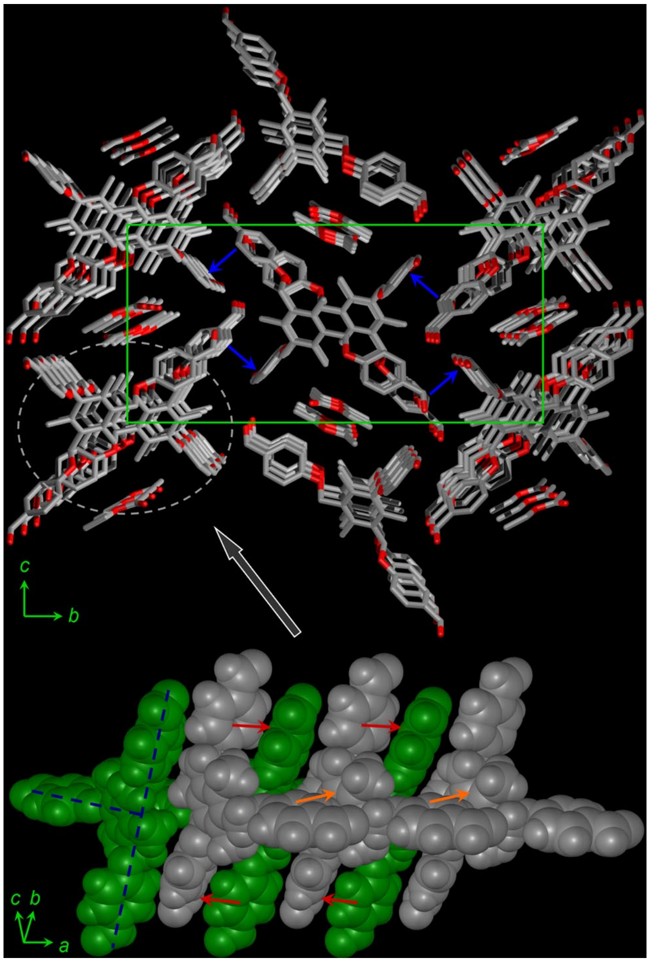

Figure 2
Crystal packing diagram of (I) (top). The molecules are arranged in chains parallel to the *a* axis. Each chain is linked to four others by edge-to-face interactions (blue arrows). Detail CPK depiction of one of the chains (bottom), viewed in the direction of the grey arrow (alternate molecules coloured green and grey). Red arrows indicate the edge-to-face interactions between pendant arms and orange arrows indicate edge-to-face interactions between pendant arms and central benzene rings of adjacent molecules. The T-shaped conformation of the molecules is highlighted by the blue dotted lines.

Crystal data

$C_{33}H_{30}O_6 \cdot C_4H_8O_2$
$M_r = 610.67$
Monoclinic, $P2_1/n$
$a = 9.242$ (2) Å
$b = 27.044$ (7) Å
$c = 12.722$ (3) Å
$\beta = 92.862$ (4)°
$V = 3176.0$ (14) Å^3
$Z = 4$
$D_x = 1.277$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 8567 reflections
$\theta = 2.3$–28.2°
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
Polyhedron, colourless
0.35 × 0.26 × 0.15 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
$T_{\min} = 0.876$, $T_{\max} = 0.990$
31 250 measured reflections
7627 independent reflections
5510 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.033$
$\theta_{\max} = 28.3$°
$h = -12 \rightarrow 12$
$k = -35 \rightarrow 34$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 1.02$
7627 reflections
409 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 1.0037P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Table 1
Selected torsion angles (°).

C2—C1—C7—O1	−84.96 (18)	C6—C5—C25—O5	70.38 (18)
C2—C3—C16—O3	84.32 (17)		

CH H atoms were included in idealized positions and refined using a riding model, with methylene, methyl, aromatic and CHO C—H bond lengths fixed at 0.99, 0.98, 0.95 and 0.95 Å, respectively. $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent C atoms for methylene, aromatic and CHO H atoms, and at $1.5U_{\rm eq}$ of the parent C atoms for methyl H atoms. The H atoms attached to the methyl atom C34 appeared to be disordered and were modelled with two equal-occupancy orientations.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *WinGX*-32 (Farrugia, 1999); software used to prepare material for publication: *enCIFer* (CCDC, 2003).

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