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4,5,12,13-Tetraacetyl[2.2]paracyclophane

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Key indicators

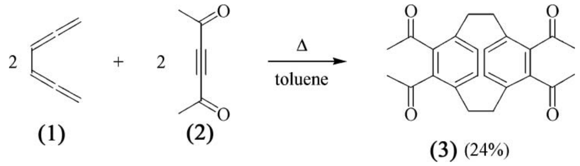
Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.132
Data-to-parameter ratio = 21.1

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

The title compound, $C_{24}H_{24}O_4$, crystallizes with two independent molecules, both with crystallographic inversion symmetry. The acetyl groups are rotated out of the ring planes, with the O atoms directed towards the inside of the molecules. Two C—H···O and one C—H···π interaction link the molecules into layers parallel to the *ac* plane.

Comment

Tetrasubstituted [2.2]paracyclophanes are readily obtained by cycloaddition of triple-bond dienophiles carrying two electron-withdrawing groups to 1,2,4,5-hexatetraene, (1) (Hopf *et al.*, 1981), and are useful substrates for further transformations in the cyclophane field (Hopf & Kleinschroth, 1978). In order to prepare the tetraketone, (3), we added 3-hexyne-2,5-dione, (2), to the bisallene, (1). Here, we report the solid-state structure of (3).



Compound (3) crystallizes with two independent molecules, both of which display crystallographic inversion symmetry (Fig. 1). A least-squares fit of the two parts of the asymmetric unit (excluding H atoms) gives an r.m.s. deviation of 0.09 Å. In both molecules, the acetyl groups are rotated appreciably out of their parent ring planes, with the O atoms directed towards the inside of the molecules (torsion angles are given in Table 1). Similar effects were observed in 4-acetyl- and 4,13-diacetyl[2.2]paracyclophane, with absolute C—C—C═O torsion angles of 136.6° (Jones *et al.*, 1993) and 141.8° (Jones *et al.*, 2002).

Bond lengths and angles display the moderate distortions typical of cyclophanes (Table 1), *e.g.* the bridge single bonds are lengthened. The rings show the usual flattened boat form, whereby the bridgehead atoms C3, C6, C3′ and C6′ lie 0.167 (2), 0.164 (2), 0.174 (2) and 0.163 (2) Å, respectively, out of the planes of the other four ring atoms.

The molecular packing involves four C—H···O interactions (Table 2) and a C—H···π interaction from C12—H12*A* to the centroid of C4′/C5′/C7′/C8′, with H···π = 2.63 Å and an angle of 150°. This latter interaction represents an important topological distinction between the two independent molecules. The molecules are linked into layers parallel to the *ac* plane (Fig. 2) at $y \simeq 0, \frac{1}{2}$, *etc.* by this contact and the two shortest C—H···O interactions; the two longest H···O contacts link the layers.

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Experimental

A mixture of 1,2,4,5-hexatetraene, (1) (0.85 g, 10.9 mmol), and 3-hexyne-2,5-dione, (2) (1.0 g, 9.1 mmol), in toluene (50 ml) was heated at 348 K for 20 h. The solvent was then removed and the solid residue purified by column chromatography (ethyl acetate–hexane 2:3) to give (3) as yellow plates (yield 0.42 g, 24%). The spectroscopic data agree with the proposed structure (Narayanan, 2005). Large single crystals were obtained by liquid diffusion of pentane into a dichloromethane solution of (3). On cutting, the regular tablets shattered into irregular fragments.

Crystal data

$C_{24}H_{24}O_4$
$M_r = 376.43$
Monoclinic, $P2_1/c$
$a = 8.0251$ (8) Å
$b = 14.8898$ (14) Å
$c = 15.5679$ (16) Å
$\beta = 93.163$ (4)°
$V = 1857.4$ (3) Å^3
$Z = 4$
$D_x = 1.346$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 133$ (2) K
Irregular tablet, pale yellow
0.45 × 0.25 × 0.15 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: none
14863 measured reflections
5422 independent reflections
3718 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\rm max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.132$
$S = 1.00$
5422 reflections
257 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.589 (2)	C1′—C2′	1.5881 (18)
C6$^{\rm i}$—C1—C2	112.99 (11)	C6′$^{\rm ii}$—C1′—C2′	113.56 (11)
C3—C2—C1	112.50 (11)	C3′—C2′—C1′	112.11 (11)
C8—C3—C4	117.07 (12)	C8′—C3′—C4′	117.13 (12)
C7—C6—C5	116.80 (12)	C7′—C6′—C5′	117.43 (12)
C5—C4—C9—O1	−46.88 (18)	C5′—C4′—C9′—O1′	−54.95 (18)
C4—C5—C11—O2	128.21 (14)	C4′—C5′—C11′—O2′	128.92 (14)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C10′—H10*D*⋯O1	0.98	2.63	3.6033 (18)	176
C1—H1*A*⋯O1′	0.99	2.67	3.4770 (17)	139
C12′—H12*E*⋯O2$^{\rm iii}$	0.98	2.55	3.4701 (18)	156
C12—H12*C*⋯O1′$^{\rm iv}$	0.98	2.45	3.3586 (18)	154

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

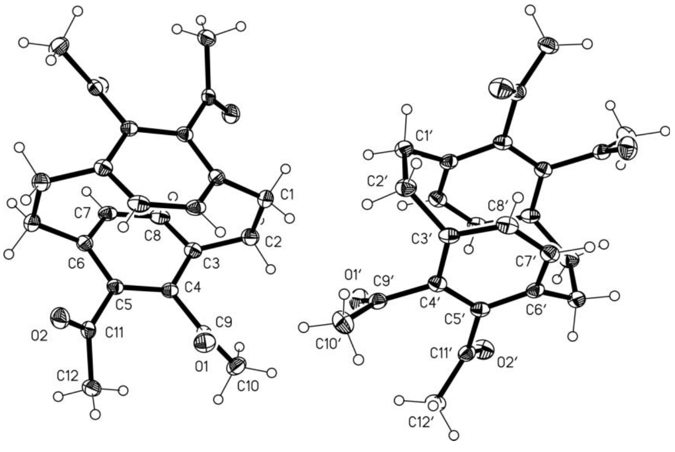

Figure 1
The two independent molecules of the title compound in the crystal structure. Only the asymmetric unit is numbered. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by $-x, 1-y, -z$ and $1-x, -y, -z$ for the unprimed and primed molecules, respectively.

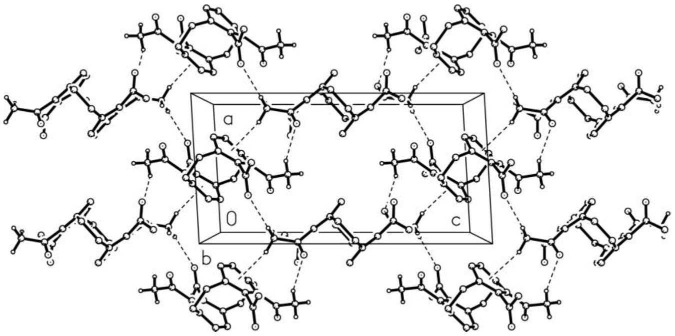

Figure 2
A packing diagram of the layer at $y \simeq 0$, involving the two shortest C—H⋯O interactions and the C—H⋯π contact (dashed lines).

Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups (C—H = 0.98 Å and H—C—H = 109.5°) allowed to rotate but not tip. Other H atoms were included using a riding model, with C—H = 0.95 Å (sp^2 C—H) or 0.98 Å (sp^3 CH_2). $U_{\rm iso}$(H) values were fixed at 1.2 times the equivalent isotropic *U* value of the parent C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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