Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O(1)	0.2365 (3)	0.2387 (3)	0.4128 (3)	3.6 (1)
O(2)	0.4921 (3)	−0.2801 (3)	0.1671 (3)	4.5 (1)
O(3)	0.2149 (4)	0.0306 (3)	0.5369 (2)	3.9 (1)
O(4)	0.3908 (4)	−0.4690 (3)	0.2621 (3)	4.8 (1)
C(1)	0.3188 (4)	−0.2545 (4)	0.2904 (3)	2.7 (1)
C(2)	0.3124 (5)	−0.3851 (4)	0.3138 (4)	3.6 (2)
C(3)	0.2265 (6)	−0.4297 (4)	0.3887 (4)	3.6 (2)
C(4)	0.1460 (5)	−0.3487 (4)	0.4441 (4)	3.0 (1)
C(5)	0.1508 (5)	−0.2161 (4)	0.4238 (3)	2.9 (1)
C(6)	0.2333 (4)	−0.1711 (4)	0.3473 (3)	2.5 (1)
C(7)	0.2362 (5)	−0.0304 (4)	0.3201 (3)	2.9 (1)
C(8)	0.1170 (5)	0.0439 (4)	0.3644 (3)	2.9 (1)
C(9)	0.0943 (5)	0.0090 (4)	0.4773 (3)	3.0 (1)
C(10)	0.0610 (5)	−0.1289 (4)	0.4872 (4)	3.5 (2)
C(11)	0.1311 (5)	0.1898 (4)	0.3469 (3)	3.2 (1)
C(12)	0.1650 (6)	0.2198 (4)	0.2341 (4)	4.4 (2)
C(13)	0.0012 (5)	0.2576 (5)	0.3780 (4)	4.2 (2)
C(14)	0.4142 (5)	−0.2093 (4)	0.2159 (4)	3.3 (1)
C(15)	0.0533 (6)	−0.4013 (5)	0.5238 (4)	4.6 (2)

Table 2. *Selected geometric parameters (Å, °)*

O(1)—C(11)	1.443 (6)	O(2)—C(14)	1.247 (6)
O(3)—C(9)	1.436 (6)	O(4)—C(2)	1.354 (6)
C(1)—C(2)	1.414 (6)	C(1)—C(6)	1.424 (6)
C(1)—C(14)	1.433 (6)	C(2)—C(3)	1.366 (7)
C(3)—C(4)	1.368 (7)	C(4)—C(5)	1.422 (6)
C(4)—C(15)	1.485 (7)	C(5)—C(6)	1.369 (6)
C(5)—C(10)	1.513 (7)	C(6)—C(7)	1.527 (6)
C(7)—C(8)	1.522 (6)	C(8)—C(9)	1.520 (6)
C(8)—C(11)	1.567 (6)	C(9)—C(10)	1.503 (6)
C(11)—C(12)	1.522 (7)	C(11)—C(13)	1.519 (7)
C(2)—C(1)—C(6)	117.8 (4)	C(6)—C(7)—C(8)	113.5 (3)
C(2)—C(1)—C(14)	120.3 (4)	C(7)—C(8)—C(9)	110.5 (4)
C(6)—C(1)—C(14)	121.9 (4)	C(7)—C(8)—C(11)	112.7 (4)
O(4)—C(2)—C(1)	120.3 (4)	C(9)—C(8)—C(11)	112.8 (4)
O(4)—C(2)—C(3)	118.4 (4)	O(3)—C(9)—C(8)	111.0 (3)
C(1)—C(2)—C(3)	121.2 (4)	O(3)—C(9)—C(10)	106.8 (4)
C(2)—C(3)—C(4)	120.6 (4)	C(8)—C(9)—C(10)	110.2 (4)
C(3)—C(4)—C(5)	120.2 (4)	C(5)—C(10)—C(9)	114.8 (4)
C(3)—C(4)—C(15)	118.8 (4)	O(1)—C(11)—C(8)	109.4 (4)
C(5)—C(4)—C(15)	120.9 (4)	O(1)—C(11)—C(12)	109.5 (4)
C(4)—C(5)—C(6)	119.6 (4)	O(1)—C(11)—C(13)	106.2 (4)
C(4)—C(5)—C(10)	118.8 (4)	C(8)—C(11)—C(12)	111.2 (4)
C(6)—C(5)—C(10)	121.6 (4)	C(8)—C(11)—C(13)	110.6 (4)
C(1)—C(6)—C(5)	120.6 (4)	C(12)—C(11)—C(13)	109.8 (4)
C(1)—C(6)—C(7)	118.2 (4)	O(2)—C(14)—C(1)	122.9 (4)
C(5)—C(6)—C(7)	121.2 (4)		

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were found in a difference synthesis and included as fixed contributors with an overall isotropic temperature factor that refined to U_{iso} = 0.074 (4) Å². Programs used were: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). The refinement was by block-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Fisica e Quimica de Sao Carlos.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1016). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Conformation of Acyclic Derivatives of 1,1,4,4-Tetraphenyl-1,3-butadiene

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Abstract

The structures of three functionally different acyclic derivatives of 1,1,4,4-tetraphenyl-1,3-butadiene, dimethyl 2,3-bis(diphenylmethylene)-1,4-butanedioate, $C_{32}H_{26}O_4$, 2,3-bis(diphenylmethylene)-1,4-butanedioic acid diethanol solvate, $C_{30}H_{22}O_4.2C_2H_6O$, and 2,3-bis(bromomethyl)-1,1,4,4-tetraphenyl-1,3-butadiene, $C_{30}H_{24}Br_2$, have been determined characterizing the preferred conformational mode of this moiety in the solid state. The diphenylmethylene groups adopt a *syn* conformation with respect to the central bond of the butadiene segment, the C=C—C=C torsion angles about this bond varying within 48–49°. In the observed structures, two of the phenyl rings are almost parallel to one another and partly overlap. The different crystalline environments seem to have little effect on the overall molecular conformation.

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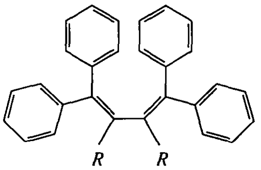
Comment

The 1,2-bis(diphenylmethylene)ethane fragment serves as an important building block in the synthesis of bulky hydrocarbons of constrained geometry. Characterization of its structural properties has been confined thus far to cyclic cyclobutane-type systems in which the two double bonds of the butadiene sequence are forced to be in a *syn* arrangement with varying degrees of torsion about the central bond of the butadiene moiety (*e.g.* Hart, Ward, Tanaka & Toda, 1982; Byrn, Maverick, Muscio, Trueblood & Jacobs, 1971; Iyoda *et al.*, 1986; Weber, Seichter, Goldberg, Will & Dasting, 1991). In a more recent study, we have incorporated this fragment into a less strained five-membered ring system, 3,4-bis(diphenylmethylene)succinimide (Toda, Tanaka, Stein & Goldberg, 1995). Torsion angles between 14 and 21° about the central =C—C= bond have been observed in the latter. It has also been shown that the proximity between the aryl rings in the optimized conformation enforces a helical twist of the molecular structure. The only other variant of the bis(diphenylmethylene)ethane structural element which has been previously determined is that of dianthronylidene-ethane, in which the observed conformation about the central =C—C= bond is *anti* (Becker, Karlsson & Pilotti, 1976; Becker, Sandros, Karlsson & Pilotti, 1978). The present study was undertaken in order to ellucidate the inherent conformational features of the tetraphenylbutadiene moiety in non-cyclic systems, (I)–(III), in a search for structural elements which can be useful in asymmetric synthesis. Crystallographic characterization of this moiety has not been reported as yet (Cambridge Structural Database, August 1994 version; Allen & Kennard, 1993).



(I) $R = \mathrm{COOCH_3}$
(II) $R = \mathrm{COOH}$
(III) $R = \mathrm{CH_2Br}$

The molecular structures of the three compounds reveal consistent conformational features in the different crystalline environments. They are all characterized by a *C*2 symmetry, the two diphenylmethylene groups adopting, somewhat surprisingly, a *syn* arrangement with respect to the central C—C bond of the 1,3-butadiene residue (Figs. 1, 2 and 4). The C=C—C=C torsion angle ranges in the three structures from 48.1 (6) to 49.2 (2)° (Table 4). The inner phenyl groups are almost parallel to one another and overlap significantly (Fig. 3). This indicates that rotation of the bulky substituents about the =C—C= bond is sterically hindered, which introduces features of 'soft' chirality into the molecular structure (in solution the molecules equilibrate rapidly between inverted configurations). It also suggests that favourable aryl–aryl π–π interactions between the overlapping rings contribute significantly to the stabilization of the observed conformation (Klebe & Diederich, 1993; Burley & Petsko, 1986). Variation of packing forces in the crystal structures of (I)–(III) and the presence of extensive intermolecular hydrogen bonding in the ethanol solvate of (II) seem to have little effect on the molecular conformation of the title entity. The above results confirm the prochiral nature of the latter.

The structure of the diethanol solvate of (II) is of a particular interest. As can easily be seen in Fig. 3, the molecular constituents are topologically preorganized for polyester-type condensation, which can readily take place upon a suitable activation. For example, upon

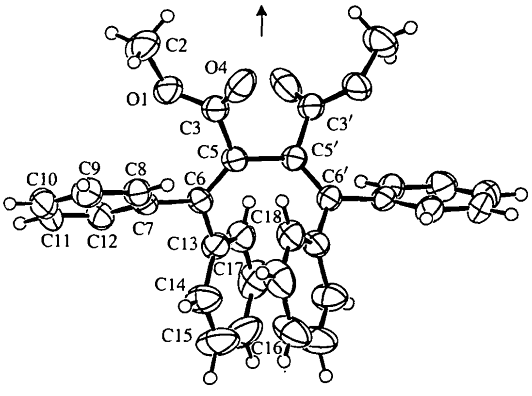


Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids for the non-H atoms. Molecules are located in the crystal on axes of twofold rotation at $\frac{1}{2}$, 0, $\frac{1}{4}$. The latter is represented by the dark arrow, and relates the primed atoms to the corresponding non-primed ones.

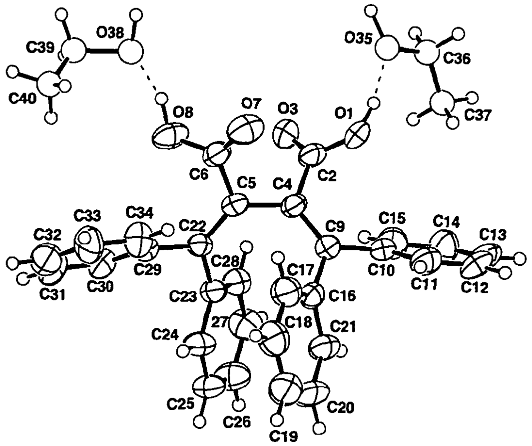


Fig. 2. Molecular structure of (II) showing 50% probability displacement ellipsoids for the non-H atoms. Atoms of the ethanol solvate are marked by circles of arbitrary size; the hydrogen bonds are marked by dashed lines.

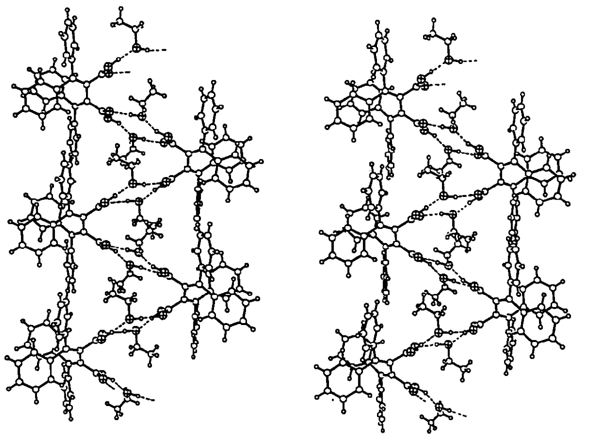


Fig. 3. Intermolecular arrangement in crystals of the ethanol solvate of (II), stereoviewed down the *b* axis (*a* is vertical), showing the continuous hydrogen-bonding (trilayered) regime in this structure. The partial overlap between the almost parallel inner phenyl rings in (II) is also visualized. O atoms are marked by crossed circles. The distances between the hydrogen-bonded atoms are: OH1···O35 (at 1 + *x*, *y*, *z*) 2.642 (5), OH8···O38 2.572 (5), OH35···O3 (at 1 − *x*, 1 − *y*, −*z*) 2.844 (5), and OH38···O7 (at 1 − *x*, 1 − *y*, −*z*) 2.763 (5) Å. The corresponding O—H···O angles are 164.9 (2), 160.3 (3), 160.1 (3) and 175.1 (2)°, respectively. The observed topological features are perfectly suited for a polyester-type condensation.

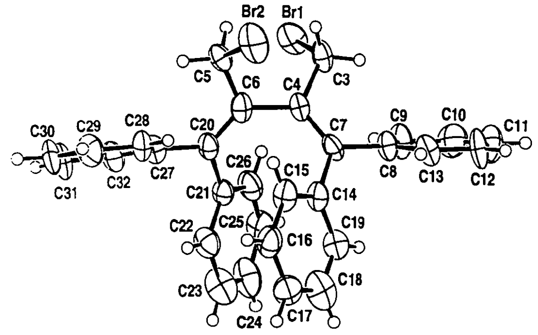


Fig. 4. Molecular structure of (III) showing 50% probability displacement ellipsoids for the non-H atoms.

heating above 424 K, formation of such oligoesters, accompanied by elimination of water and colour change of the solid to brown, occurs. Crystalline melting point of the solid material is only at 528 K.

Experimental

All three compounds represent synthetic intermediates used in efforts to prepare bis(diphenylmethylene)-substituted prochiral succinimide derivates (Toda *et al.*, 1995).

Compound (I)

Crystal data

$C_{32}H_{26}O_4$
$M_r = 474.55$
Monoclinic
$C2/c$
$a = 16.4510 (10)$ Å
$b = 9.4810 (10)$ Å
$c = 16.5770 (10)$ Å
$\beta = 102.340 (10)°$
$V = 2525.8 (3)$ Å^3
$Z = 4$
$D_x = 1.248$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.44–11.09°$
$\mu = 0.076$ mm^{-1}
$T = 295 (2)$ K
Elongated prism
$0.40 \times 0.25 \times 0.20$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2120 measured reflections
2057 independent reflections
1661 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0122$
$\theta_{\rm max} = 24.95°$
$h = -19 \rightarrow 19$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0497$
$wR(F^2) = 0.1436$
$S = 1.061$
2057 reflections
169 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.032$
$\Delta\rho_{\rm max} = 0.164$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.195$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.57351 (9)	0.18824 (15)	0.38818 (9)	0.0556 (4)
C2	0.6306 (2)	0.3022 (3)	0.4180 (2)	0.0780 (8)
C3	0.57560 (11)	0.1379 (2)	0.31374 (12)	0.0436 (5)
O4	0.61171 (10)	0.1951 (2)	0.26750 (10)	0.0668 (5)
C5	0.52538 (11)	0.0063 (2)	0.29301 (11)	0.0402 (5)
C6	0.52825 (11)	−0.0995 (2)	0.34827 (11)	0.0396 (5)
C7	0.59414 (12)	−0.1034 (2)	0.42483 (12)	0.0424 (5)
C8	0.67674 (12)	−0.0752 (2)	0.42291 (13)	0.0487 (5)
C9	0.73764 (14)	−0.0734 (3)	0.4939 (2)	0.0626 (6)
C10	0.7178 (2)	−0.1003 (3)	0.5683 (2)	0.0713 (7)
C11	0.6372 (2)	−0.1316 (3)	0.57189 (14)	0.0681 (7)
C12	0.57547 (14)	−0.1349 (2)	0.50077 (13)	0.0555 (6)
C13	0.46838 (12)	−0.2192 (2)	0.33497 (12)	0.0449 (5)
C14	0.49560 (14)	−0.3569 (2)	0.3512 (2)	0.0645 (7)
C15	0.4400 (2)	−0.4678 (3)	0.3387 (2)	0.0821 (8)
C16	0.3580 (2)	−0.4445 (3)	0.3125 (2)	0.0797 (8)
C17	0.32832 (14)	−0.3083 (3)	0.2981 (2)	0.0703 (7)
C18	0.38344 (13)	−0.1963 (2)	0.30897 (13)	0.0523 (6)

Compound (II)

Crystal data

$C_{30}H_{22}O_4.2C_2H_6O$
$M_r = 538.64$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
$a = 10.300$ (8) Å
$b = 16.004$ (2) Å
$c = 17.788$ (3) Å
$\beta = 92.06$ (3)°
$V = 2930.3$ (24) Å^3
$Z = 4$
$D_x = 1.221$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 8.65$–11.12°
$\mu = 0.077$ mm^{-1}
$T = 295$ (2) K
Prism
0.45 × 0.40 × 0.30 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4630 measured reflections
4385 independent reflections
2968 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0139$
$\theta_{\rm max} = 25.01$°
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 90 min
intensity decay: 13%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0832$
$wR(F^2) = 0.2181$
$S = 1.510$
4375 reflections
341 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.352$
$\Delta\rho_{\rm max} = 0.308$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.375$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.9250 (3)	0.4086 (2)	0.14275 (15)	0.0587 (8)
C2	0.8935 (4)	0.4834 (3)	0.1661 (2)	0.0463 (10)
O3	0.9185 (3)	0.5462 (2)	0.1325 (2)	0.0699 (10)
C4	0.8177 (4)	0.4853 (2)	0.2359 (2)	0.0422 (9)
C5	0.7070 (4)	0.5446 (2)	0.2305 (2)	0.0438 (10)
C6	0.6285 (4)	0.5370 (3)	0.1588 (2)	0.0483 (10)
O7	0.6110 (3)	0.4696 (2)	0.1290 (2)	0.0664 (9)
O8	0.5896 (3)	0.6070 (2)	0.1288 (2)	0.0635 (9)
C9	0.8498 (4)	0.4383 (2)	0.2970 (2)	0.0416 (9)
C10	0.9743 (4)	0.3908 (2)	0.3042 (2)	0.0447 (10)
C11	0.9782 (5)	0.3089 (3)	0.3258 (2)	0.0571 (11)
C12	1.0930 (6)	0.2659 (3)	0.3346 (2)	0.060 (2)
C13	1.2062 (6)	0.3055 (4)	0.3222 (3)	0.067 (2)
C14	1.2057 (5)	0.3868 (4)	0.3032 (3)	0.068 (2)
C15	1.0907 (5)	0.4303 (3)	0.2942 (3)	0.0637 (12)
C16	0.7690 (4)	0.4325 (2)	0.3642 (2)	0.0465 (10)
C17	0.6379 (5)	0.4167 (3)	0.3589 (2)	0.0611 (12)
C18	0.5674 (5)	0.4104 (3)	0.4238 (3)	0.078 (2)
C19	0.6247 (6)	0.4193 (4)	0.4932 (3)	0.083 (2)
C20	0.7538 (6)	0.4354 (3)	0.4997 (2)	0.0762 (15)
C21	0.8271 (4)	0.4425 (3)	0.4356 (2)	0.0590 (12)
C22	0.6792 (4)	0.6029 (2)	0.2828 (2)	0.0399 (9)
C23	0.7711 (4)	0.6262 (2)	0.3457 (2)	0.0428 (9)
C24	0.7290 (5)	0.6370 (3)	0.4180 (2)	0.0626 (12)
C25	0.8119 (6)	0.6631 (4)	0.4752 (2)	0.060 (2)
C26	0.9372 (6)	0.6801 (3)	0.4615 (3)	0.067 (2)
C27	0.9814 (4)	0.6714 (3)	0.3908 (3)	0.0630 (13)
C28	0.8988 (4)	0.6442 (3)	0.3329 (2)	0.0534 (11)
C29	0.5511 (4)	0.6450 (2)	0.2842 (2)	0.0442 (9)
C30	0.5424 (4)	0.7291 (3)	0.2994 (2)	0.0579 (11)
C31	0.4237 (6)	0.7674 (3)	0.3027 (3)	0.0738 (15)
C32	0.3124 (5)	0.7238 (4)	0.2917 (3)	0.069 (2)
C33	0.3177 (5)	0.6408 (4)	0.2766 (3)	0.071 (2)
C34	0.4366 (5)	0.6013 (3)	0.2731 (3)	0.0651 (13)
O35	0.0683 (4)	0.4127 (2)	0.0225 (2)	0.0876 (12)
C36	0.2012 (9)	0.4015 (5)	0.0305 (4)	0.136 (3)
C37	0.2567 (10)	0.4034 (6)	0.1010 (7)	0.167 (4)
O38	0.4382 (4)	0.6015 (2)	0.0107 (2)	0.0979 (14)
C39	0.3604 (14)	0.6760 (6)	0.0036 (4)	0.196 (5)
C40	0.2752 (14)	0.6842 (9)	0.0495 (9)	0.226 (6)

Compound (III)

Crystal data

$C_{30}H_{24}Br_2$
$M_r = 544.31$
Monoclinic
$P2/n$
$a = 14.643$ (4) Å
$b = 8.8890$ (10) Å
$c = 19.682$ (4) Å
$\beta = 105.22$ (2)°
$V = 2472.0$ (9) Å^3
$Z = 4$
$D_x = 1.463$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.10$–10.73°
$\mu = 3.26$ mm^{-1}
$T = 295$ (2) K
Prism
0.30 × 0.30 × 0.20 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3879 measured reflections
3753 independent reflections
2534 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0273$
$\theta_{\rm max} = 24.97$°
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.1013$
$wR(F^2) = 0.2224$
$S = 1.522$
3753 reflections
289 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 1.667$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.115$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (III)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br1	0.31955 (8)	0.39662 (12)	0.62140 (6)	0.0565 (4)
Br2	0.06790 (8)	0.78465 (14)	0.62631 (6)	0.0616 (4)
C3	0.2986 (7)	0.5992 (11)	0.6548 (5)	0.041 (2)
C4	0.2744 (6)	0.7101 (11)	0.5946 (4)	0.033 (2)
C5	0.1032 (6)	0.6350 (11)	0.5639 (5)	0.037 (2)
C6	0.1870 (6)	0.6821 (10)	0.5379 (5)	0.038 (2)
C7	0.3321 (7)	0.8317 (12)	0.5983 (5)	0.040 (2)
C8	0.4241 (6)	0.8430 (11)	0.6525 (5)	0.036 (2)
C9	0.4943 (7)	0.7337 (12)	0.6566 (6)	0.050 (3)
C10	0.5814 (8)	0.7452 (16)	0.7071 (7)	0.068 (4)
C11	0.5978 (8)	0.8605 (18)	0.7525 (7)	0.070 (4)
C12	0.5304 (8)	0.9686 (14)	0.7494 (5)	0.058 (3)
C13	0.4462 (7)	0.9598 (13)	0.6997 (5)	0.048 (3)
C14	0.3104 (6)	0.9606 (11)	0.5488 (5)	0.036 (2)

C15	0.2197 (7)	1.0246 (11)	0.5274 (5)	0.045 (3)
C16	0.1994 (8)	1.1442 (13)	0.4795 (6)	0.058 (3)
C17	0.2714 (9)	1.2025 (12)	0.4532 (6)	0.059 (3)
C18	0.3580 (10)	1.1464 (15)	0.4768 (6)	0.069 (4)
C19	0.3795 (7)	1.0273 (12)	0.5240 (5)	0.048 (3)
C20	0.1784 (6)	0.6911 (10)	0.4691 (5)	0.037 (2)
C21	0.2619 (6)	0.7059 (10)	0.4373 (5)	0.035 (2)
C22	0.2557 (7)	0.8065 (13)	0.3826 (5)	0.052 (3)
C23	0.3338 (8)	0.8244 (15)	0.3529 (6)	0.064 (3)
C24	0.4116 (8)	0.7345 (16)	0.3752 (6)	0.062 (3)
C25	0.4154 (7)	0.6328 (15)	0.4272 (6)	0.059 (3)
C26	0.3423 (7)	0.6204 (12)	0.4589 (5)	0.048 (3)
C27	0.0872 (7)	0.6856 (10)	0.4147 (5)	0.038 (2)
C28	0.0125 (7)	0.7834 (12)	0.4181 (5)	0.043 (2)
C29	−0.0712 (7)	0.7785 (13)	0.3651 (6)	0.052 (3)
C30	−0.0839 (7)	0.6805 (15)	0.3108 (5)	0.053 (3)
C31	−0.0115 (8)	0.5847 (14)	0.3055 (5)	0.055 (3)
C32	0.0713 (7)	0.5876 (12)	0.3576 (5)	0.045 (3)

Table 4. *Selected geometric parameters for* (I), (II) *and* (III) *(°, Å)*

(I)*		(II)		(III)	
Torsion angles about the central bond					
C6/C5/C5′/C6′	49.2 (2)	C9/C4/C5/C22	48.1 (6)	C7/C4/C6/C20	48.2 (15)
C3/C5/C5′/C3′	50.1 (2)	C2/C4/C5/C6	46.7 (7)	C3/C4/C6/C5	43.1 (12)
Dihedral angle between the overlapping inner phenyl rings					
C13–C18 and C13′–C18′	9.60 (7)	C16–C21 and C23–C28	10.5 (1)	C14–C19 and C21–C26	14.5 (3)
Shortest interatomic distance between overlapping inner phenyl rings					
C13···C13′	3.206 (3)	C16···C23	3.118 (5)	C14···C21	3.103 (13)

* The primed atoms are related to the corresponding non-primed atoms by a twofold rotation at $\frac{1}{2}, 0, \frac{1}{4}$.

Compound (I) crystallized as a pure material and provided the most precise structural results. The molecules are located in the crystal on twofold rotational axes of crystallographic symmetry. Somewhat less precise results were obtained for compounds (II) and (III). (II) crystallized as a diethanol solvate. The ethyl residues of the solvate are located in loosely packed regions of the structure and reveal partial disorder. Moreover, the crystals of this compound were slightly 'damaged' by X-rays during the diffraction experiment, most probably due to some polyester-type condensation which occurs in the solid upon prolonged X-ray irradiation. (III) contains two heavy Br atoms. The absorption effects on the diffraction data in this case were initially corrected for by an empirical absorption correction method (Walker & Stuart, 1983). However, since the latter is not acceptable by the journal any longer and the relevant information on the analyzed crystal was lost, the presented results are based on uncorrected data. In spite of the fact that the final electron density maps show somewhat high residual peaks and deep troughs in the vicinity of the two heavy atoms (diffraction ripples), and that there is a slight increase in the e.s.d. values of the refined parameters, the two sets of results (*i.e.* either empirically corrected or uncorrected for absorption effects) are almost the same. Thus, most of the atomic parameters obtained from the two refinements, and the covalent parameters of the resulting structural model, differ by less than 2σ.

For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CADINT*, local program; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93, *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dihydromorphine-6-*O*-sulfate

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Abstract

The synthesis of 3-*O*-acetyl-7,8-dihydromorphine-6-*O*-sulfate [IUPAC: (5α,6α)-3-acetoxy-4,5-epoxy-17-methyl-6-morphinaniosulfate], $C_{19}H_{23}NO_7S$, which has important analgesic properties, has been confirmed crystallographically. In the solid state, the zwitterions are linked into chains by N—H···O hydrogen bonds.

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