O16	0.12907 (6)	0.67770 (5)	0.05336 (13)	0.0268 (3)
C17	0.03518 (8)	0.86878 (8)	0.15669 (18)	0.0288 (4)
C18	0.01514 (8)	0.89366 (8)	−0.1213 (2)	0.0304 (3)
C2	1/4	1/4	0.6847 (2)	0.0227 (4)
C21	0.28394 (7)	0.30885 (7)	0.59361 (16)	0.0215 (3)
C22	0.35723 (8)	0.30388 (8)	0.55471 (17)	0.0239 (3)
O22	0.39212 (6)	0.24824 (6)	0.58010 (15)	0.0335 (3)
C23	0.39409 (8)	0.36404 (8)	0.4753 (2)	0.0255 (4)
C24	0.35912 (9)	0.43620 (9)	0.49982 (17)	0.0233 (3)
C25	0.27962 (8)	0.42880 (8)	0.46599 (18)	0.0251 (3)
C26	0.24608 (8)	0.36683 (8)	0.54397 (17)	0.0221 (3)
O26	0.17696 (6)	0.37239 (6)	0.56006 (14)	0.0293 (3)
C27	0.37060 (8)	0.46200 (8)	0.66484 (18)	0.0289 (4)
C28	0.39077 (9)	0.49060 (9)	0.3884 (2)	0.0327 (4)

The data collection nominally covered over a sphere of reciprocal space, by a combination of six sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set was over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. Despite the excellent reflection profiles and promising $R_{\rm int}$ and $R_{\rm sigma}$ of 0.068 and 0.016, respectively, it was impossible to solve the structure in the tetragonal space group $P4_2/ncm$. As a result, the symmetry was lowered to the orthorhombic space group *Pccn*, for which the same extinction conditions are valid; $R_{\rm int}$ and $R_{\rm sigma}$ for this space group are only slightly better: 0.036 and 0.015, respectively. Now the structure could be solved with difficulty by direct methods using *SHELXS*86 (Sheldrick, 1990), but anisotropic refinement with *SHELXL*96 (Sheldrick, 1996*b*) by full-matrix least-squares methods remained stuck at $R1 = 0.21$, yielding non-sensible anisotropic displacement parameters. Taking into account our experiences with (1) (Bolte *et al.*, 1997), we assumed that this crystal was twinned also, and applying the twin law $(010/100/00\bar{1})$ provided the ultimate success ($R1$ dropped below 0.1). All H atoms could be located by difference Fourier synthesis. While the two hydroxyl H atoms were refined isotropically, the others were refined with fixed individual displacement parameters [$U({\rm H}) = 1.5U_{\rm eq}({\rm C}_{\rm methyl})$ or $U({\rm H}) = 1.2\,U_{\rm eq}({\rm C})$] using a riding model with C—H(methyl) = 0.98 or C—H(secondary) = 0.99 Å. The twin ratio refined to 0.424 (2).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1194). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1871–1873

Methyl 3′,6′-Bis(chloromethyl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate

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Abstract

The dihedral angle between the naphthalene ring systems in the title compound, $C_{26}H_{22}Cl_2O_4$, is 97.0 (1)°. The methoxycarbonyl group is disordered over two positions and is twisted out of the plane of the attached binaphthyl ring system in both cases. The molecules are joined together through weak C4′—H4′···O2 and C4′—H4′···O2*A*($-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$) hydrogen bonds, and by stacking interactions between the methoxycarbonyl groups along the **a** direction.

Comment

Chemists have long sought ways to control the molecular structure of synthetic high-molecular weight compounds at a level comparable to that realised in biological macromolecules. With such methods available, it may be possible to fine tune the properties of materials thus obtained.

One method discovered recently has already resulted in a new set of materials called starburst dendrimers as seen in numerous review articles (Stibor & Lellek, 1994; Tomalia, Naylor & Goddard, 1990; Mekelburger, Jaworek & Voegtle, 1992; Newkome, Moorefield & Baker, 1992; Tomalia & Durst, 1993; Issberner, Moors & Voegtle, 1994; Newkome & Moorefield, 1996; Bell, 1996). Starburst dendrimers, as highly ordered polymers, are believed to provide solutions to a wide variety of technological and ecological problems, from the removal of heavy metal pollutants from industrial waste to highly efficient drug-delivery systems and even the formation of artificial chemical cells and tissues (Tomalia & Durst, 1993; Newkome & Moorefield, 1996).

The extraordinary activity in the field of dendrimers and within chiral dendrimers in particular, prompted us to develop a modular preparative approach to inherently axially chiral dendrimers (Lellek & Stibor, 1997). One of the leading structures of our design is the title molecule, (I), shown with the atom-numbering scheme in Fig. 1.

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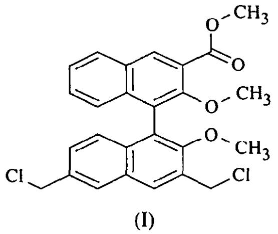

(I)

The dihedral angle between the two naphthalene rings is 97.0 (1)°, similar to other known crystal structures of methyl 1,1′-binaphthalene-3-carboxylates (Akimoto & Iitaka, 1969; Ondráček, Pakhomova, Hovorka & Ščigel, 1993; Ondráček, Pakhomova, Novotný, Hovorka & Ščigel, 1994) and indicates no orbital overlap between the two aromatic systems. The methoxycarbonyl group is disordered over two positions with site-occupancy factors of 0.8 and 0.2. The values of both torsion angles: C4—C3—C11—O3 [−20.3 (4)°] and C4—C3—C11—O3*A* [13.2 (11)°], indicate that the methoxycarbonyl moiety does not lie in the plane of the C1–C10 aromatic ring system. The chloromethyl groups are oriented on the same side of the C1′–C10′ aromatic plane in such a way that the short intramolecular contacts Cl1···C2′ [3.474 (3) Å], Cl1···C4′ [3.589 (3) Å], Cl2···C5′ [3.585 (3) Å] and Cl2···C7′ [3.499 (3) Å] are observed (for torsion angles, see Table 1).

The molecules are connected into ribbons along the *b* axis through weak C4′—H4′···O2 and C4′—H4′···O2*A*$(-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2})$ interactions [C4′···O2 3.397 (4), H4′···O2 2.46 (4) Å and C4′—H4′···O2 165 (3)°; C4′···O2*A* 3.08 (1), H4′···O2*A* 2.17 (4) Å and C4′—H4′···O2*A* 161 (3)°]. The ribbons form lateral contacts in the **a** direction *via* the stacking motif. It is interesting that no $\pi\cdots\pi$ interactions between naphthalene systems have been observed; inter-ribbon arrangement comprises a stacking of methoxycarbonyl groups. Separation between the planes through the atoms C11, O3, O2 and C11″, O3″, O2″$(-x+1, -y, -z+1)$ is 2.97 (1) Å, and for C11, O3*A*, O2*A* and C11″, O3*A*″, O2*A*″ is 3.04 (4) Å. Similar stacking interactions of methoxycarbonyl groups have been discussed in the literature (Filippakis, Leiserowitz & Schmidt, 1967).

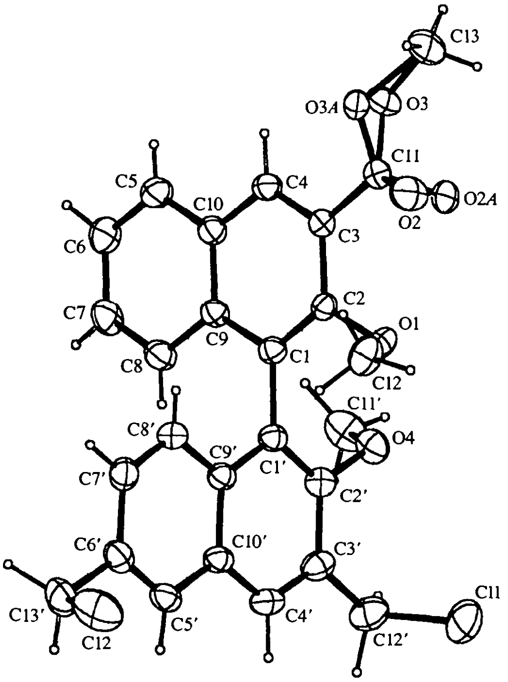

Fig. 1. View of the title molecule with the disordered methoxycarbonyl group and the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

A solution of methyl-3′-acetoxymethyl-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxylate (2.2 mg, 4.9 mmol) in anhydrous dichloromethane (20 ml) was treated consecutively with methoxymethylchloride (1.6 g, 24.8 mmol) at 253 K with vigorous stirring, then a solution of $SnCl_4$ (1.43 ml, 12.42 mmol) in 15 ml dichloromethane was added within 5 min. The reaction mixture was stirred for 30 min at this temperature then quenched by addition of 10 ml of a 5% solution of HCl. The organic layer was washed with 5 ml of water, 5 ml of a 3% solution of $NaHCO_3$, dried with $MgSO_4$, evaporated *in vacuo* and chromatographed on silica gel with a mixture of 97% toluene and 3% acetone. Recrystallization was from toluene–hexane.

Crystal data

$C_{26}H_{22}Cl_2O_4$
$M_r = 469.34$
Monoclinic
$P2_1/n$
$a = 8.584\ (1)$ Å
$b = 16.066\ (3)$ Å
$c = 16.097\ (2)$ Å
$\beta = 92.93\ (1)°$
$V = 2217.0\ (6)$ Å^3
$Z = 4$
$D_x = 1.406$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.54187$ Å
Cell parameters from 20 reflections
$\theta = 48$–$50°$
$\mu = 2.90$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.88 × 0.49 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: semi-empirical, based on ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.33$, $T_{\max} = 0.36$
8369 measured reflections
4125 independent reflections

3684 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 70.83°$
$h = 0 \rightarrow 10$
$k = -19 \rightarrow 19$
$l = -19 \rightarrow 19$
2 standard reflections frequency: 120 min intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.203$

$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.70$ e Å^{-3}

$S = 1.054$
4120 reflections
394 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1171P)^2 + 0.9778P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0023 (5)
Scattering factors from *SHELXL*93

Table 1. *Selected geometric parameters (Å, °)*

Cl1—C12′	1.804 (4)	O2*A*—C11	1.253 (12)
Cl2—C13′	1.816 (4)	O3*A*—C11	1.235 (13)
O2—C11	1.232 (4)	O3*A*—C13	1.601 (14)
O3—C11	1.333 (4)	C1—C1′	1.504 (3)
O3—C13	1.432 (4)	C3—C11	1.490 (3)
C11—O3—C13	116.0 (3)	O2*A*—C11—C3	114.1 (6)
C11—O3*A*—C13	110.9 (9)	O3—C11—C3	113.2 (2)
O2—C11—O3	121.3 (3)	C3′—C12′—Cl1	111.9 (2)
O2—C11—C3	125.1 (3)	C6′—C13′—Cl2	111.3 (2)
O3*A*—C11—C3	110.6 (7)		
C12—O1—C2—C1	−95.0 (3)	C2—C1—C1′—C2′	−85.5 (3)
C13—O3*A*—C11—O2*A*	−14.8 (19)	C11′—O4—C2′—C1′	−92.1 (3)
C13—O3—C11—O2	−2.0 (6)	C4′—C3′—C12′—Cl1	−100.3 (3)
C4—C3—C11—O2	152.0 (3)	C5′—C6′—C13′—Cl2	96.9 (3)
C4—C3—C11—O2*A*	−135.3 (8)		

All H-atom parameters were refined except those of H135 where only the H-atom *U* value was refined. C—H distances are in the range 0.78 (3)–1.02 (4) Å and $U_{\rm iso}$ values are in the range 0.044 (7)–0.15 (2) Å^2 for the refined H atoms. Atoms O2/O2*A* and O3/O3*A* have occupancies of 0.801 (9)/0.199 (9).

Data collection: *SDP* (B. A. Frenz & Associates Inc., 1982). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1060). Services for accessing these data are described at the back of the journal.

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A 2:1 Co-Crystal of Hydroquinone and 3,5-Bis(2-pyridyl)-1,2,4-triazole

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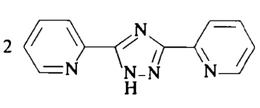
Abstract

The title compound, $2C_{12}H_9N_5.C_6H_6O_2$, exhibits a three-dimensional hydrogen-bonded network of N—H···N, C—H···N, O—H···N, C—H···O, C—H···π and π···π interactions.

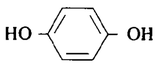
Comment

Recently, the synthesis and physical properties of a series of ruthenium(II)–polypyridyl complexes containing triazole ligands with pendant phenol (Hage, Haasnoot, Reedijk *et al.*, 1990) and hydroquinone (Wang *et al.*, 1993) moieties have been reported. In these studies, crystallographic, spectroscopic and electrochemical evidence was obtained for the presence of intermolecular hydrogen bonding in these complexes involving the hydroxy groups and the free N atoms of the triazole rings. On the basis of these results, we believe that a systematic investigation of the hydroquinone–pyridyl-triazole solid-state systems will lead to the development of new materials with interesting electron- and proton-transfer properties.

The bond lengths and angles for the bis(pyridyl)-triazole (Hbpt) moieties are consistent with those found for the coordinated species in the mono- and binuclear ruthenium complexes $[Ru(bpy)_2(bpt)]PF_6.0.5H_2O$ and $[Ru(bpy)_2(bpt)](CF_3SO_3).4H_2O$ (Hage *et al.*, 1989; Hage, Haasnoot, Nieuwenhuis *et al.*, 1990).



Hbpt



Hydroquinone