kind of crystals are obtained from a solution of dimethylformamide. It should be noted that another phase, obtained from water at room temperature, may be due to the presence of water and hydrogen bonding in the crystal.

Crystal data

$C_{16}H_{16}N_2O_6$
$M_r = 332.3$
Monoclinic
$P2_1/c$
$a = 7.8620\,(8)$ Å
$b = 19.526\,(2)$ Å
$c = 10.469\,(1)$ Å
$\beta = 105.15\,(1)°$
$V = 1551.3\,(3)$ Å^3
$Z = 4$
$D_x = 1.423$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 10–12°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Parallelepiped
$0.4 \times 0.3 \times 0.3$ mm
Translucent pale white

Data collection

Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
4965 measured reflections
4504 independent reflections
2981 reflections with $I_{\rm net} > 2\sigma(I_{\rm net})$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 29.96°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 27$
$l = -14 \rightarrow 14$
2 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.036$
$S = 1.526$
2967 reflections
282 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.1F]$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.279$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.167$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 0.26 (2)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected bond lengths (Å)*

C14—N10	1.382 (2)	N20—C23	1.390 (2)
C14—O12	1.204 (2)	N20—C25	1.460 (3)
O22—C24	1.204 (2)	N10—C15	1.462 (3)
C13—N10	1.389 (2)	O23—C26	1.396 (3)
C13—O11	1.205 (2)	O23—C27	1.421 (3)
O21—C23	1.205 (2)	O13—C16	1.403 (3)
N20—C24	1.390 (2)	O13—C17	1.411 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.2 *SORTRF* and *ADDREF* (Hall *et al.*, 1992). Program(s) used to solve structure: *Xtal*3.2 *GENTAN*. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2 *ORTEP*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA* and *CIFIO*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1219). Services for accessing these data are described at the back of the journal.

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Bond-length alternation in rigidized merocyanines

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Abstract

The two merocyanines 7-(4-dimethylaminophenyl)-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one [$C_{22}H_{25}NO$, (2)] and [2,3,4,4a,5,6,10,10a-octahydro-7-(5-piperidino-2-thienyl)-2-anthrylidene]methanedicarbonitrile [$C_{26}H_{27}N_3S$, (4)] show somewhat shortened single bonds [1.434 (4)–1.452 (4) Å in (2) and 1.421 (4)–1.425 (4) Å in (4)] and elongated double bonds [1.345 (4)–1.358 (4) Å in (2) and 1.355 (4)–1.365 (4) Å in (4)] compared to standard bond lengths in polyenes. A comparison of the merocyanines reveals that (4) exhibits a slightly smaller bond length alternation within the rigidized hexatriene moiety than (2), probably because of an increased ground-state polarization.

Comment

Photorefractive materials have a high potential for optical information processing and storage (Kippelen *et*

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al., 1997). Electro-optical (EO) chromophores are essential components of these materials. Design criteria have been developed (Würthner *et al.*, 1997; Marder *et al.*, 1997) for linear π-systems with donor and acceptor substituents (merocyanines). The linear polarizability, α, is of greater importance than the first-order hyperpolarizability, β. The α value is optimized when the ground and excited states of the molecule exhibit the same charge separation. In merocyanines this charge-resonance limit is established when each resonance structure – the neutral (polyene-like, with markedly alternating C—C single- and double-bond lengths) and the zwitterionic (with inverted patterns of bond lengths) – contributes 50%. Thus merocyanines that exist in the so-called 'cyanine limit' are particularly promising candidates. In this state, the bond length alternation is zero (Gorman & Marder, 1995).

Since only merocyanines with a rigidized polymethine chain are photochemically stable, we have prepared dyes such as (2) and (4). Other (mero)cyanines with sterically fixed polymethine chains are known (Slominskii *et al.*, 1975; Heilig & Lüttke, 1986; Cabrera *et al.*, 1994; Kippelen *et al.*, 1998), but their crystal structures have not been determined. The crystal structure of a derivative of (2) has been published recently (Shu *et al.*, 1998). In order to investigate and to correlate the bond-length alternation (BLA) of our (mero)cyanines with their linear and non-linear optical properties, we have carried out corresponding X-ray structure determinations.

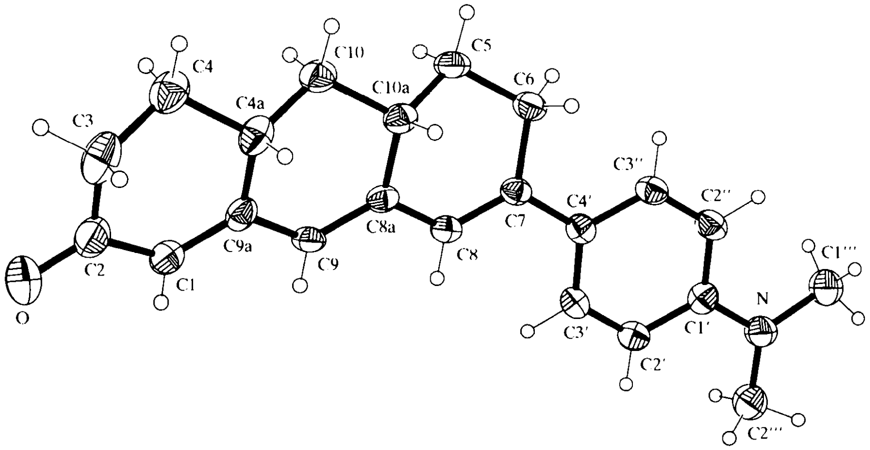


Fig. 1. Perspective view of (2). Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

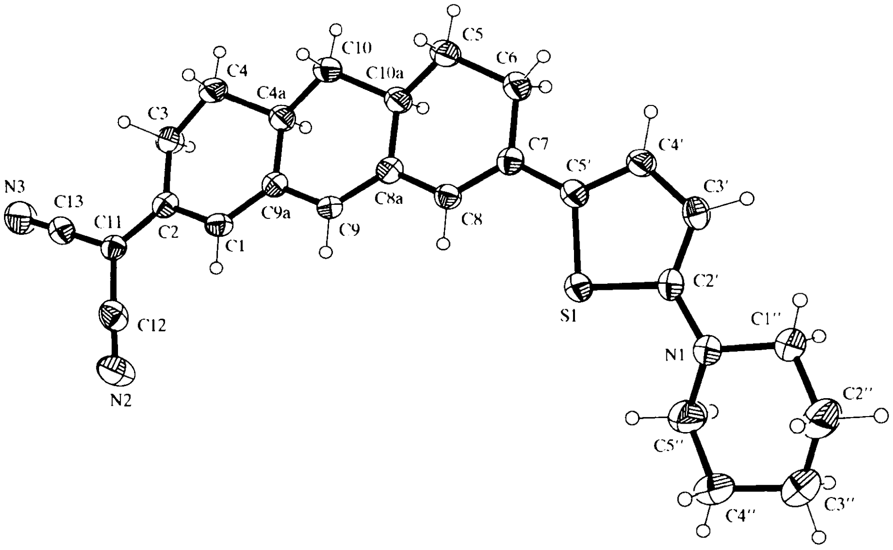
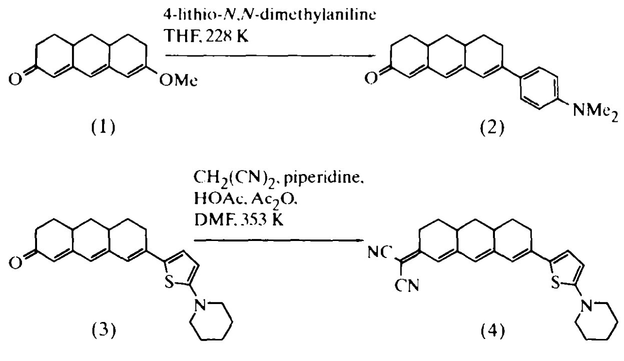


Fig. 2. Perspective view of (4). Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.



The sterically fixed hexatriene units of (2) (Fig. 1) and (4) (Fig. 2) are planar with a mean deviation of 0.040 and 0.012 Å, respectively. As can be seen from Tables 1 and 2, the conjugated chains in (2), and even in the more polarized dye (4), remain strongly polyenic.

The N atom of the *N*,*N*-dimethylamino group in (2) can be considered as nearly planar, lying 0.094 (3) Å out of the plane defined by C1′, C1‴ and C2‴. As expected for the piperidino substituent, N1 in (4) is more pyramidalized lying 0.294 (4) Å from the plane of C1″, C5″ and C2′.

The (hetero)aromatic rings are nearly planar with mean deviations from planarity of 0.005 in (2) and 0.006 Å in (4). The small interplanar angles between the rings and the polymethinic chain, 15.9 (3) for (2) and 16.9 (3)° for (4), do not disturb the conjugation within the whole chromophore. The thiophene ring in (4) exhibits bond lengths that are nearly the same as those in unsubstituted thiophene (C2—C3 1.368 and C3—C4 1.424 Å; Harshbarger & Bauer, 1970) and thus possesses only little quinoid character. This is further evidence for a more polyene-like ground state and is consistent with electro-optical absorption measurements (Wortmann *et al.*, 1998).

The fact that (4) is 'bent' about C7—C5′, rather than exhibiting a linear ring sequence with the thiophene ring rotated by *ca* 180° about this bond, may be associated with an interaction between H8 (at C8) and S1. This interaction leads to a five-membered intramolecular ring consisting of C8—H, C8, C7, C5′, S1 [corresponding to the descriptor *S*(5) (Bernstein *et al.*, 1995)]. The S—H distance (2.670 Å) is shorter than the corresponding values in several oligoene-linked thiophenes, given here with Cambridge Structural Database refcodes (Allen & Kennard, 1993): 2.813–2.876 Å in TDTHEY (Ruban & Zobel, 1975), TTHBUD and TDTHTR (Buschmann & Ruban, 1978), and is nearly the same as in a thiatricarbocyanine (2.713 and 2.745 Å, DETZCI; Potenza *et al.*, 1978). Similarly, the angle C8—H8···S1 (108.0°) is more consistent with those within the cyanine (105.7 and 106.6°) than those in the above-mentioned thiophene derivatives (102.5–104.4°).

The three annelated six-membered rings adopt half-boat conformations with C4, C10 and C5 lying out of the planes of the other corresponding five atoms by 0.614 (4)–0.616 (5) Å in (2) and 0.591 (6)–0.596 (5) Å in (4). The mean deviation from planarity for the five nearly coplanar C atoms varies from 0.006 to 0.063 Å in (2) and 0.009 to 0.035 Å in (4). As expected, the deviations from planarity in the rings bearing the (hetero)aromatic substituents are significantly greater. These values do not differ greatly from those in 6,6-diphenyl-2,3,4,4a,5,6,10,10a-octahydroanthracen-2-one [KAZJIE (Zimmerman & Lamers, 1989): C4, C10 and C5 lying 0.637, 0.629 and 0.656 Å out of the planes; mean deviations from planarity for the corresponding planes 0.007, 0.014 and 0.026 Å].

Experimental

Ketone (2) was obtained by treatment of the vinylogous ester (1) (400 mg, 1.74 mmol) (Heilig & Lüttke, 1987) in tetrahydrofuran (20 ml) at 228 K with a solution of 4-lithio-*N*,*N*-dimethylaniline prepared from 4-bromo-*N*,*N*-dimethylaniline (710 mg, 3.55 mmol), ^{n}BuLi (2.67 ml, 4.26 mmol) (15%, hexane) and tetramethylenediamine (0.64 ml, 4.26 mmol) in diethyl ether (15 ml). Aqueous workup, column chromatography (SiO_2; toluene, chloroform, ethyl acetate 3:3:1) and recrystallization from toluene gave (2) in 50% yield as a yellow solid (278 mg, m.p. 540 K). Orange tablets were grown from chloroform solution by slow evaporation.

A similar procedure afforded ketone (3) in 14% yield. To a solution of (3) (170 mg, 0.47 mmol) in dry *N*,*N*-dimethylformamide (20 ml buffered with *ca* 0.1 ml HOAc and 0.05 ml Ac_2O), piperidine (0.6 ml, 6.1 mmol) and malonitrile (120 mg, 1.82 mmol) were added in five portions over 44 h at 353 K. Merocyanine (4) was obtained as dark blue microcrystals (m.p. 511–513 K) in 51% yield (98 mg) after aqueous workup, column chromatography (SiO_2; chloroform) and extraction with boiling ethanol. Slow evaporation of a dichloromethane solution gave dark blue metallic prisms (red in transmitted light).

Data for compound (2): ^{1}H NMR: δ (p.p.m.) = 7.42–7.45 (*AA′* of *AA′XX′*, 2H, 3′,3″-H), 6.68–6.72 (*XX′* of *AA′XX′*, 2H, 2′,2″-H), 6.58 (*d*, *J* = 2.1 Hz, 1H, 8-H), 6.09 (*s*, 1H, 9-H), 5.80 (*s*, 1H, 1-H), 2.99 (*s*, 6H, 1‴, 2‴-H), 2.77 (*ddd*, *J* = 17.6, 4.9, 2.2 Hz, 1H, 6-H_{eq}), 2.38–2.60 (*m*, 5H, 3-H_{eq}, 4-$H_{ax\ or\ eq}$, 4a-H, 6-H_{ax}, 10a-H), 1.97–2.12 (*m*, 3H, 4-$H_{ax\ or\ eq}$, 5-H_{eq}, 10-H_{eq}), 1.74 (*dddd*, *J* = 14.0, 13.0, 11.8, 4.9 Hz, 1H, 3-H_{ax}), 1.48 (*dq*, *J* = 12.8, 4.9 Hz, 1H, 5-H_{ax}), 1.28 (*q*, *J* = 12.4 Hz, 1H, 10-H_{ax}). ^{13}C NMR: δ (p.p.m.) = 199.9 (*s*, C-2), 160.4, 150.3 (*s*, C-8a,9a), 150.5 (*s*, C-1′), 144.5 (*s*, C-7), 127.7 (*s*, C-4′), 126.3 (*d*, C-3′,3″), 123.4 (*d*, C-9), 122.2 (*d*, C-1), 121.6 (*d*, C-8), 112.1 (*d*, C-2′,2″), 40.3 (*q*, C-1‴,C2‴), 38.0 (*t*, C-3), 37.1 (*t*, C-10), 36.1, 35.9 (*d*, C-4a,10a), 30.4 (*d*, C-4), 30.1 (*t*, C-5), 27.7 (*t*, C-6). MS, *m/z* (%): 319 (100) (M^+). UV/vis ($CHCl_3$) λ_{max} (log ε): 424 nm (4.64). Analysis calculated for $C_{22}H_{25}NO$: C 82.72, H 7.89, N 4.39%; found: C 82.81, H 8.00, N 4.24%.

Data for compound (4): ^{1}H NMR: δ (p.p.m.) = 6.97 (*d*, *J* = 4.2 Hz, 1H, 4′-H), 6.46 (*s*, 1H, 1-H), 6.30 (*s*, 1H, 8-H), 6.06 (*s*, 1H, 9-H), 5.97 (*d*, *J* = 4.2 Hz, 1H, 3′-H), 3.24 (*t*, *J* = 5.5 Hz, 4H, 1″,5″-H), 2.95–2.99 (*m*, 1H, 3-H_{eq}), 2.78 (*ddd*, *J* = 17.5, 4.7, 2.2 Hz, 1H, 6-H_{eq}), 2.45–2.52 (*m*, 4H, 3-H_{ax}, 4a-H, 6-H_{ax}, 10a-H), 1.93–2.02 (*m*, 3H, 4-H_{eq}, 5-H_{eq}, 10-H_{eq}), 1.69–1.74 (*m*, 4H, 2″,4″-H), 1.59–1.64 (*m*, 2H, 3″-H), 1.41–1.51 (*m*, 2H, 4-H_{ax}, 5-H_{ax}), 1.24 (*q*, J = 12.4 Hz, 1H, 10-H_{ax}). ^{13}C NMR: δ (p.p.m.) = 169.1 (*s*, C-2), 161.6 (*s*, C-2′), 159.5, 154.1 (*s*, C-8a,9a), 141.9 (*s*, C-7), 128.4 (*s*, C-5′), 127.4 (*d*, C-4′), 122.9 (*d*, C-9), 119.3 (*d*, C-8), 118.5 (*d*, C-1), 115.0, 114.2 (*s*, C-12,13), 104.4 (*d*, C-3′), 72.0 (*s*, C-11), 51.5 (*t*, C-1″,5″), 36.8 (*t*, C-10), 36.4 (*d*, C-4a), 36.2 (*d*, C-10a), 29.5 (*t*, C-3, C-5), 28.9 (*t*, C-4), 27.3 (*t*, C-6), 25.0 (*t*, C-2″,4″), 23.7 (*t*, C-3″). MS, *m/z* (%): 413 (100) (M^+). UV/vis ($CHCl_3$) λ_{max} (log ε): 582 nm (4.71). Analysis calculated for $C_{26}H_{27}N_3S$: C 75.51, H 6.58, N 10.16%; found: C 75.33, H 6.63, N 10.00%.

400 MHz ^{1}H- and 100 MHz ^{13}C-NMR spectra were run on a Bruker AM 400 instrument using $CDCl_3$ with tetramethylsilane (^{1}H) or with the solvent signal (^{13}C) as internal standards. The degree of substitution of the C atoms was determined by DEPT 135° experiments. Further assignments were made with the help of H,H, CH-COSY and C,H-COLOC spectra. Additional information was obtained by comparison with similar compounds (Doering & Kitagawa, 1991).

Compound (2)

Crystal data

$C_{22}H_{25}NO$
M_r = 319.43
Monoclinic
$P2_1/n$
a = 7.733 (2) Å
b = 6.295 (2) Å
c = 34.222 (5) Å
β = 95.32 (3)°
V = 1658.6 (7) Å^3
Z = 4
D_x = 1.279 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10.0–11.5°
μ = 0.077 mm^{-1}
T = 143 (2) K
Tablet
0.60 × 0.28 × 0.24 mm
Orange

Data collection

Stoe Stadi-4 diffractometer
ω scans
Absorption correction: none
3500 measured reflections
2927 independent reflections
1645 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

θ_{max} = 25.01°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = -40 \rightarrow 5$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.150
S = 1.028
2927 reflections
219 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.2937P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å) for (2)*

N—C1′	1.374 (4)	C9—C9a	1.434 (4)
C1—C9a	1.354 (4)	C1′—C2″	1.399 (4)
C1—C2	1.452 (4)	C1′—C2′	1.407 (4)
C7—C8	1.345 (4)	C2′—C3′	1.378 (4)
C7—C4′	1.478 (4)	C3′—C4′	1.392 (4)
C8—C8a	1.443 (4)	C4′—C3″	1.399 (4)
C8a—C9	1.358 (4)	C2″—C3″	1.380 (4)

Compound (4)

Crystal data

$C_{26}H_{27}N_3S$
M_r = 413.57
Monoclinic
$C2/c$
a = 32.972 (7) Å
b = 8.046 (2) Å
c = 19.647 (4) Å
β = 122.371 (15)°
V = 4402.0 (17) Å^3
Z = 8
D_x = 1.248 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 44 reflections
θ = 10.0–11.5°
μ = 0.165 mm^{-1}
T = 143 (2) K
Prism
0.44 × 0.38 × 0.30 mm
Metallic blue

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
5987 measured reflections
3885 independent reflections
2392 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

θ_{max} = 25.03°
$h = -39 \rightarrow 32$
$k = -9 \rightarrow 4$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.145
S = 1.026
3885 reflections
271 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 4.5674P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å) for (4)*

S1—C5′	1.742 (3)	C8—C8a	1.421 (4)
S1—C2′	1.742 (3)	C8a—C9	1.357 (4)
N1—C2′	1.380 (4)	C9—C9a	1.421 (4)
C1—C9a	1.365 (4)	C2′—C3′	1.369 (5)
C1—C2	1.425 (4)	C3′—C4′	1.405 (4)
C7—C8	1.355 (4)	C4′—C5′	1.370 (4)
C7—C5′	1.452 (4)		

Methyl groups were refined as rigid groups allowed to rotate but not tip from the starting position obtained from difference Fourier synthesis. Other H atoms were included with a riding model starting from calculated positions.

Because the crystals diffracted weakly, an extensive system of restraints to components of displacement parameters was employed; for the same reason the final $R(F)$ values are high.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*) for (2); *XSCANS* (Fait, 1991) for (4). Cell refinement: *DIF*4 for (2); *XSCANS* for (4). Data reduction: *REDU*4 (Stoe & Cie, 1992*b*) for (2); *XSCANS* for (4). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1290). Services for accessing these data are described at the back of the journal.

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(±)-6,6′-Dinitro-1,1′-binaphthyl 2,2′-diacetate

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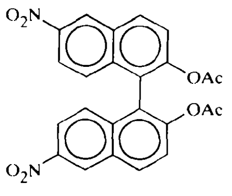
Abstract

The title compound, $C_{24}H_{16}N_2O_8$, is a twofold symmetric ether with two acetyl groups attached to the O atoms of the 1,1′-bi-2-naphthol. The molecular structure confirms that the nitro substituents are at the 6,6′ positions.

Comment

Optically active 1,1′-bi-2-naphthol and its derivatives are excellent ligands for chiral catalysts and have a C_2 symmetry axis (Narasaka, 1991; Mikami & Motoyama, 1995). Metal complexes of these molecules have been used for enantioselective reactions such as aldol reactions, Michael additions (Shibasaki & Sasai, 1996; Keller *et al.*, 1997) and Diels–Alder reactions (Mikami *et al.*, 1994; Markó *et al.*, 1996). Phosphorus amidites derived from 1,1′-bi-2-naphthol are particularly effective in the asymmetric copper-catalyzed conjugate addition of Et_2Zn to enones (Feringa *et al.*, 1997). The title compound, (I), is a derivative of 1,1′-bi-2-naphthol.



(I)

The monoclinic unit cell contains four discrete units of the title compound. Between the molecules, weak hydrogen bonding is observed (Berkovitch-Yellin & Leiserowitz, 1984; Steiner, 1997). The C—H···O distance for C2—H2···O4($\frac{1}{2}+x, -y, 1+z$) is 3.290 (3) Å [C14—H14···O3($\frac{1}{2}+x, -y, z$) 3.194 (3), C18—H18···O8($x, \frac{1}{2}-y, z-\frac{1}{2}$) 3.244 (2), C19—H19···O5($x-1, \frac{1}{2}-y, \frac{1}{2}+z$) 3.407 (3), C24—H24″···O1($x-1, y, z$) 3.146 (3) and C7—H7···O7($x, y, z-1$) 3.255 (2) Å]. The torsion angle between the two naphthyl fragments is 72.08 (6)°.

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