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rac- and *meso*-3,3′-Bis(3,5-dimethylphenyl)-3*H*,3′*H*-2,2′-biindenylidene-1,1′(2*H*,2′*H*)-dione

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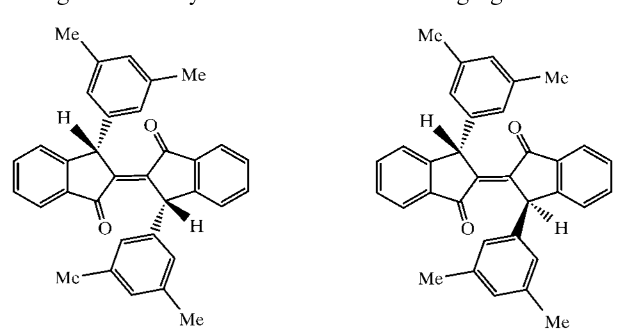
In the *rac* isomer of the title compound, $C_{34}H_{28}O_2$, the two $C-Ph_{dimethylphenyl}$ bond axes make an angle of 58.7 (1)°. There is no short contact between the two 3,5-dimethylphenyl rings, although the dihedral angle between them is 4.93 (7)°. The *meso* isomer has a center of symmetry at the middle of the C=C bond, and the two $C-Ph_{dimethylphenyl}$ bond axes are antiparallel to one another.

Comment

Organic photochromic compounds have received considerable attention in recent years because of their potential applications in many fields (Gemert, 1999). The title compounds, (I) and (II), respectively, were prepared during a study of crystal photochromism of 3,3′-diaryl-3*H*,3′*H*-2,2′-biindenylidene-1,1′-diones (Tanaka & Toda, 2000; Tanaka *et al.*, 2003). Compounds (I) and (II) are geometrical isomers, and they cannot be identified conclusively from spectroscopic data. The color of the crystals of both (I) and (II) changed from yellow to orange when they were irradiated with Hg light. This color



(I) (II)

changed back to yellow after 30 min for (I) but has been stable for (II) for more than six months. Electron-spin resonance (ESR) spectra suggest that the photochromism of these crystals is due to the biradical caused by breaking the π-bond at the center of the biindenylidene moiety. In the present study, X-ray structure analyses of (I) and (II) have been carried out in order to investigate their molecular structures and π–π interactions.

In (I), each indene system is approximately planar (Fig. 1). The dihedral angle between the C3/C4/C5 and C6–C11 planes is 3.12 (5)°, and that between the C12/C13/C14 and C15–C20 planes is 4.55 (6)°. The two indene systems are skewed with respect to each other by 13.29 (4)°. The two 3,5-dimethylphenyl rings are almost parallel, and the dihedral angle between the C21–C26 and C29–C34 planes is 4.93 (7)°. However, there is no intramolecular short contact between these rings. The shortest distance between the non-H atoms is 3.964 (4) Å for C27···C35, and the second shortest distance is 3.986 (3) Å for C22···C30. Selected geometric parameters are given in Table 1.

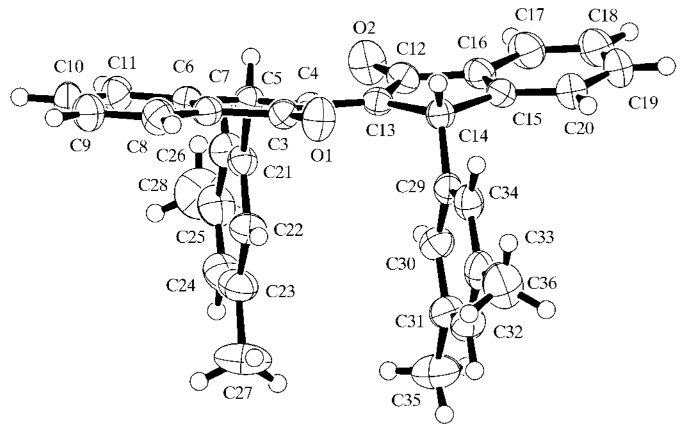


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids shown at the 50% probability level.

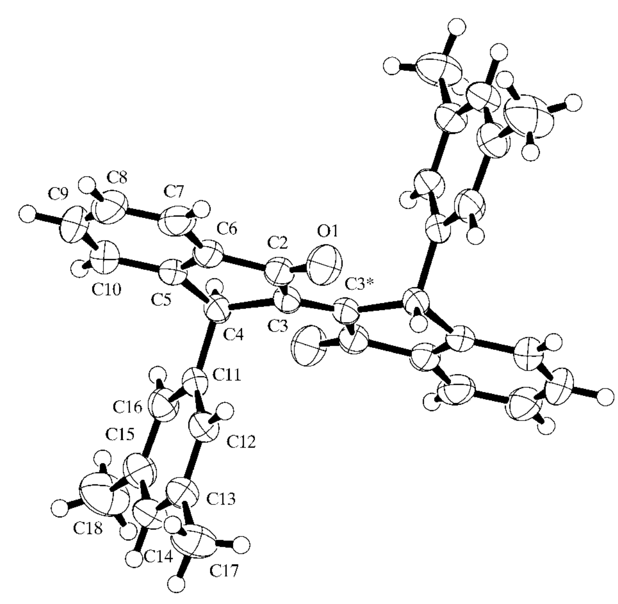


Figure 2
A view of the molecular structure of (II), with displacement ellipsoids shown at the 50% probability level.

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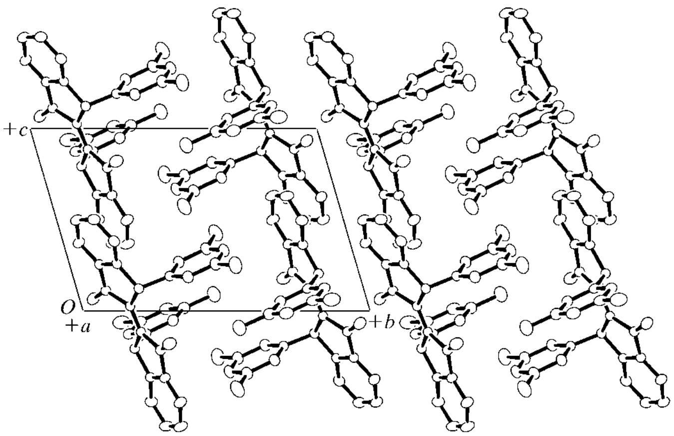

Figure 3
The crystal structure of (I), projected along *a*.

The *meso* isomer, (II), has a center of symmetry (Fig. 2). Each indene system is twisted slightly, and the dihedral angle between the C2/C3/C4 and C5–C10 planes is 11.31 (7)°. The puckering of the five-membered ring can also be seen from the C—C—C—C torsion angles of the ring, which range from −9.1 (2) to 10.5 (2)° (Table 2). Non-planarity of the five-membered rings in the biindenylidene moiety was also observed in crystals of 2,2′-biindenylidene-1,3,1′,3′-tetraone (Khodorkovsky *et al.*, 1994), the torsion angles in the five-membered rings ranging between −18.8 and 18.1°.

The densities of (I) and (II) indicate that the *meso* isomer has a slightly lower packing efficiency than the *rac* isomer. The more flexible space around the molecule might be preferable for photochromism. In crystals of (I), a pair of molecules related by a center of symmetry exhibit π–π interactions between the rings of the biindenylidene moieties, with a C3···C3^{i} distance of 3.479 (4) Å, a C8···C13^{i} distance of 3.480 (3) Å and a C9···C15^{i} distance of 3.283 (3) Å [symmetry code: (i) $-x$, $-y$, $-z$; Fig. 3]. In (II), π–π stacking is observed between the terminal phenyl rings of the biindenylidene moieties, which leads to the formation of columns along *c* (Fig. 4), the shortest distance being 3.409 (3) Å for C6···C8($1-x$, $-y$, $2-z$).

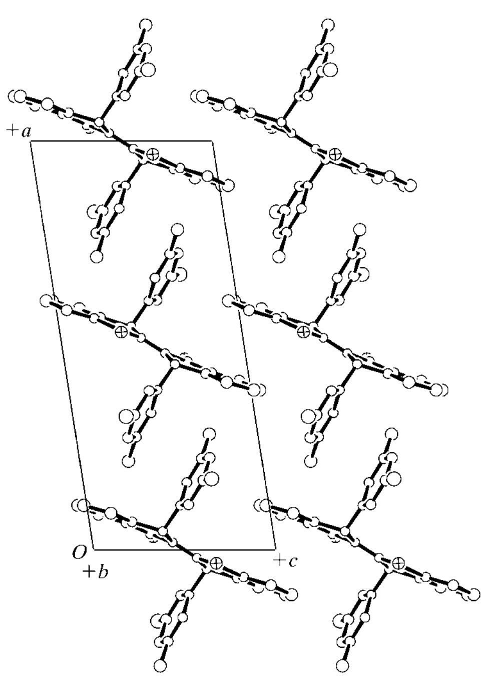

Figure 4
The crystal structure of (II), projected along *b*.

Experimental

Compounds (I) and (II) were synthesized according to the method reported by Tanaka & Toda (2000). The isomers were separated by repeated recrystallization of the crude reaction products from dichloromethane solution. Crystals of (I) and (II) suitable for X-ray study were grown from dichloromethane solutions. For (I), m.p. 509–515 K; IR: 1686 (C═O), 1604 (C═C) cm^{-1}; UV: λ nm^{-1} (ε) 241 (9600), 302 (24000); ^{1}H NMR: δ 2.25 (12H, *s*, CH_3), 5.74 (2H, *s*, CH), 6.83–7.76 (14H, *m*, Ph). For (II), m.p. 529–532 K; IR: 1685 (C═O), 1600 (C═C) cm^{-1}; UV: λ nm^{-1} (ε) 241 (9900), 294 (24200); ^{1}H NMR: δ 2.22 (12H, *s*, CH_3), 5.88 (2H, *s*, CH), 6.75–7.75 (14H, *m*, Ph).

Compound (I)

Crystal data

$C_{34}H_{28}O_2$
$M_r = 468.59$
Triclinic, $P\overline{1}$
$a = 11.392$ (2) Å
$b = 13.9700$ (18) Å
$c = 9.2771$ (13) Å
$\alpha = 97.705$ (11)°
$\beta = 109.950$ (12)°
$\gamma = 109.492$ (11)°
$V = 1256.0$ (4) Å^3
$Z = 2$
$D_x = 1.239$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.4$–14.4°
$\mu = 0.08$ mm^{-1}
$T = 298$ K
Plate, yellow
0.50 × 0.25 × 0.10 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
6275 measured reflections
5773 independent reflections
3911 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -18 \rightarrow 6$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.154$
$S = 1.03$
5773 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.2455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C3	1.211 (2)	C5—C21	1.526 (2)
O2—C12	1.213 (2)	C12—C13	1.509 (3)
C3—C4	1.508 (3)	C12—C16	1.470 (2)
C3—C7	1.478 (2)	C13—C14	1.521 (2)
C4—C5	1.519 (2)	C14—C15	1.523 (3)
C4—C13	1.337 (2)	C14—C29	1.520 (3)
C5—C6	1.518 (3)		
C3—C4—C13—C12	−166.8 (2)	C5—C4—C13—C14	−173.6 (2)
C3—C4—C13—C14	9.5 (3)	C3—C7—C6—C5	4.3 (2)
C5—C4—C13—C12	10.1 (3)	C4—C5—C6—C7	−5.2 (2)

Compound (II)

Crystal data

$C_{34}H_{28}O_2$
$M_r = 468.59$
Monoclinic, $P2_1/a$
$a = 19.230$ (2) Å
$b = 8.0506$ (10) Å
$c = 8.4461$ (11) Å
$\beta = 98.802$ (10)°
$V = 1292.2$ (3) Å^3
$Z = 2$
$D_x = 1.204$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–12.8°
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Needle, yellow
0.5 × 0.2 × 0.2 mm

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
3542 measured reflections
2969 independent reflections
1870 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 10$
$l = -10 \rightarrow 4$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.054$
$wR(F^2) = 0.195$
$S = 1.21$
2969 reflections
164 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0887P)^2 + 0.4121P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

O1—C2	1.222 (3)	C3—C4	1.523 (3)
C2—C3	1.508 (3)	C4—C5	1.527 (3)
C2—C6	1.467 (3)	C4—C11	1.531 (2)
C3—C3^{ii}	1.336 (4)		
C2—C3—C4—C5	10.5 (2)	C4—C3—C2—C6	−9.1 (2)

Symmetry code: (ii) $1-x, -y, 1-z$.

All H atoms were positioned geometrically and fixed, with U_{iso}(H) values equal to $1.2U_{eq}$(parent atom). Some methyl H-atom positional parameters were modified further on the basis of difference density maps.

For both compounds, data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1639). Services for accessing these data are described at the back of the journal.

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