

C9	0.0322 (4)	1.0907 (3)	-0.1953 (4)	0.064 (2)
C10	0.0727 (4)	1.1791 (3)	-0.2537 (4)	0.078 (3)
C11	0.1802 (5)	1.1743 (3)	-0.3142 (4)	0.074 (2)
C12	0.2452 (4)	1.0812 (3)	-0.3172 (4)	0.063 (2)
C13	0.2042 (3)	0.9936 (3)	-0.2598 (3)	0.054 (2)
C14	-0.0239 (3)	0.6922 (3)	-0.0183 (3)	0.053 (2)
C15	0.0331 (4)	0.5939 (3)	-0.0136 (4)	0.073 (2)
C16	-0.0175 (5)	0.5066 (3)	-0.0690 (5)	0.083 (3)
C17	-0.1258 (5)	0.5153 (4)	-0.1303 (4)	0.088 (3)
C18	-0.1843 (4)	0.6119 (4)	-0.1361 (4)	0.082 (3)
C19	-0.1340 (3)	0.6981 (3)	-0.0806 (4)	0.067 (2)

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.200 (3)	C3—C7	1.565 (5)
O2—C4	1.218 (6)	C4—C5	1.497 (6)
C1—C2	1.484 (6)	C6—C8	1.501 (5)
C2—C3	1.523 (5)	C7—C14	1.505 (5)
C3—C4	1.540 (5)	Car—Car	1.375 (6)
C3—C6	1.550 (5)		
O1—C2—C1	121.8 (3)	O2—C4—C5	120.8 (3)
O1—C2—C3	119.6 (3)	C3—C4—C5	118.4 (4)
C1—C2—C3	118.5 (3)	C3—C6—C8	117.8 (3)
C2—C3—C4	109.3 (3)	C3—C7—C14	114.8 (3)
C2—C3—C6	107.4 (3)	C6—C8—C9	120.3 (3)
C2—C3—C7	111.8 (3)	C6—C8—C13	122.9 (3)
C4—C3—C6	112.3 (3)	C7—C14—C15	122.0 (3)
C4—C3—C7	106.9 (3)	C7—C14—C19	121.4 (3)
C6—C3—C7	109.1 (3)	Car—Car—Car	120.0 (4)
O2—C4—C3	120.8 (3)		

The original cell had the space-group symmetry  $Cc$  with  $a = 15.590$  (5),  $b = 12.620$  (4),  $c = 11.502$  (4) Å,  $\beta = 132.48$  (2)°. This cell was reduced by the matrix (001, 010,  $\bar{1}0\bar{1}$ ) to the reported  $Ia$  cell because of the large value of  $\beta$  ( $= 90 + 42.48^\circ$ ).

H atoms were refined riding on the parent C atoms at a distance of 0.95 Å. The rotational orientation of the methyl C1 and C5 H atoms was determined by the contour  $\Delta F$  map calculated through the plane defined by the methyl H atoms. The direction of the chiral axis was determined unequivocally by refinement of the chirality value  $\eta$  (Rogers, 1981).

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); *NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1116). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 'Stiff' *cis*-Stilbenes. (*Z*)-6,6'-Dimethyl-1,1'-biindanylidene and (*Z*)-4,4',7,7'-Tetramethyl-1,1'-biindanylidene

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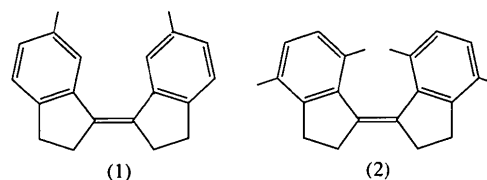
(Received 6 March 1995; accepted 20 April 1995)

## Abstract

The X-ray crystal structures of (*Z*)-6,6'-dimethyl-1,1'-biindanylidene,  $C_{20}H_{20}$  (1), and (*Z*)-4,4',7,7'-tetramethyl-1,1'-biindanylidene,  $C_{22}H_{24}$  (2), were determined at 90 K. The structure around the ethylene bond in (2) is distorted by steric congestion due to the methyl groups at C7 and C7'.

## Comment

In the course of our studies on the unusually short ethylene bond of (*E*)-stilbenes and the large amplitude torsional motion in their crystals (Ogawa *et al.*, 1988; Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992), we have recently reported the structures of 'stiff' stilbenes, *i.e.* (*E*)-1,1'-biindanylidene, and discussed the length of the central ethylene bond (Ogawa, Harada & Tomoda, 1995). We report here the crystal structures of the *cis* isomers of two of these stiff stilbenes, namely, (*Z*)-6,6'-dimethyl-1,1'-biindanylidene, (1), and (*Z*)-4,4',7,7'-tetramethyl-1,1'-biindanylidene, (2).



Each of the molecules has a crystallographic twofold axis through the center of the ethylene bond. The  $\pi$  systems are non-planar. The dihedral angle between the

best least-squares plane of the phenyl group (C4–C9) and the plane formed by the ethylene C1=C1<sup>i</sup> bond [symmetry code: (i) 1–x, y,  $\frac{3}{2}$ –z for compound (1), 1–x, y,  $\frac{1}{2}$ –z for (2)] and atom C8 is 14.3 (3) in (1) and 28.1 (2)<sup>o</sup> in (2). The ethylene bond is significantly twisted. The dihedral angle between the plane formed by atoms C8, C1 and C2, and that formed by atoms C8<sup>i</sup>, C1<sup>i</sup> and C2<sup>i</sup> is 5.7 (1)<sup>o</sup> in compound (1) and 17.2 (1)<sup>o</sup> in (2). The greater degree of non-planarity of the  $\pi$  system in (2) is attributed to the increased steric congestion around the ethylene bond, which is caused by the methyl groups at C7 and C7<sup>i</sup>.

The cyclopentene rings adopt envelope conformations in which the four C atoms C1, C8, C9 and C3 are nearly in the same plane. The distance between this plane and atom C2 is larger in (2) [0.491 (3) Å] than in (1) [0.256 (4) Å], reflecting the greater non-planarity of the  $\pi$  system in (2).

The ethylene bond length in (2) [1.356 (2) Å] is, however, equal to that in (1) [1.356 (3) Å], and also to that of the *E* isomer of (1) [1.358 (3) Å] (Ogawa, Harada & Tomoda, 1995). The results clearly show that relief of the steric congestion is not achieved by elongation of the ethylene bond, but instead by a twisting of the bond in both compounds (1) and (2).

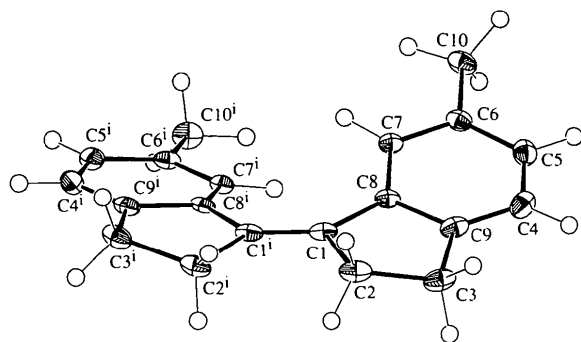


Fig. 1. The molecular structure of (1) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

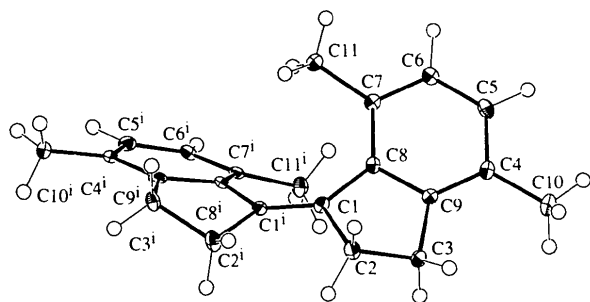


Fig. 2. The molecular structure of (2) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

## Experimental

Compounds (1) and (2) were isolated from the binary mixture containing the corresponding *E* isomers prepared according to Ogawa, Harada & Tomoda (1995). Compound (1) was recrystallized from methanol and pentane, and compound (2) was recrystallized from ethanol.

### Compound (1)

#### Crystal data

C<sub>20</sub>H<sub>20</sub>

*M<sub>r</sub>* = 260.38

Monoclinic

*C*2/*c*

*a* = 11.263 (1) Å

*b* = 18.507 (2) Å

*c* = 7.449 (1) Å

$\beta$  = 110.379 (9)<sup>o</sup>

*V* = 1455.5 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.188 Mg m<sup>-3</sup>

Cu *K* $\alpha$  radiation

$\lambda$  = 1.54184 Å

Cell parameters from 25 reflections

$\theta$  = 38.6–40.0<sup>o</sup>

$\mu$  = 0.47 mm<sup>-1</sup>

*T* = 90 K

Rectangular

0.30 × 0.25 × 0.20 mm

Colorless

#### Data collection

Rigaku AFC-6A diffractometer

$\theta/2\theta$  scans

Absorption correction: none

1185 measured reflections

1082 independent reflections

978 observed reflections

[*I* > 2 $\sigma$ (*I*)]

*R*<sub>int</sub> = 0.015

$\theta_{\max}$  = 59.93<sup>o</sup>

*h* = –4 → 12

*k* = –4 → 20

*l* = –8 → 7

3 standard reflections

monitored every 100

reflections

intensity decay: none

#### Refinement

Refinement on *F*

*R* = 0.052

*wR* = 0.066

*S* = 3.275

978 reflections

131 parameters

All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0002F^2]$

( $\Delta/\sigma$ )<sub>max</sub> = 0.46

$\Delta\rho_{\max}$  = 0.309 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = –0.415 e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Tables

2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (1)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C1	0.5632 (2)	0.4583 (1)	0.7672 (3)	0.0158 (9)
C2	0.6365 (2)	0.5292 (1)	0.7975 (3)	0.021 (1)
C3	0.7768 (2)	0.5093 (1)	0.8925 (3)	0.023 (1)
C4	0.8843 (2)	0.3843 (1)	0.8945 (3)	0.023 (1)
C5	0.8669 (2)	0.3113 (1)	0.8496 (3)	0.022 (1)
C6	0.7453 (2)	0.2820 (1)	0.7673 (3)	0.017 (1)
C7	0.6408 (2)	0.3272 (1)	0.7339 (3)	0.015 (1)
C8	0.6563 (2)	0.4002 (1)	0.7870 (3)	0.0147 (9)
C9	0.7795 (2)	0.4288 (1)	0.8620 (3)	0.019 (1)
C10	0.7282 (2)	0.2031 (1)	0.7153 (3)	0.023 (1)

Table 2. Selected geometric parameters (Å, °) for (1)

C1–C2	1.524 (3)	C4–C9	1.389 (3)
C1–C8	1.474 (3)	C5–C6	1.400 (3)
C1–C1 <sup>i</sup>	1.356 (3)	C6–C7	1.393 (3)

C2—C3	1.535 (3)	C6—C10	1.507 (3)
C3—C9	1.509 (3)	C7—C8	1.401 (3)
C4—C5	1.389 (3)	C8—C9	1.406 (3)
C2—C1—C8	106.5 (2)	C7—C6—C10	120.7 (2)
C2—C1—C1'	120.4 (2)	C6—C7—C8	120.8 (2)
C8—C1—C1'	133.1 (2)	C1—C8—C7	131.4 (2)
C1—C2—C3	106.2 (2)	C1—C8—C9	109.5 (2)
C2—C3—C9	103.8 (2)	C7—C8—C9	119.0 (2)
C5—C4—C9	119.6 (2)	C3—C9—C4	128.2 (2)
C4—C5—C6	121.1 (2)	C3—C9—C8	111.3 (2)
C5—C6—C7	118.9 (2)	C4—C9—C8	120.5 (2)
C5—C6—C10	120.4 (2)		
C8—C1—C2—C3	-16.4 (2)	C1—C2—C3—C9	15.0 (2)
C2—C1—C8—C9	11.3 (2)	C2—C3—C9—C8	-8.6 (3)
C1 <sup>i</sup> —C1—C8—C7	17.0 (4)	C2—C1—C1 <sup>i</sup> —C2 <sup>i</sup>	6.7 (3)
C1 <sup>i</sup> —C1—C8—C9	-167.6 (2)	C8—C1—C1 <sup>i</sup> —C8 <sup>i</sup>	4.3 (4)

Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .**Compound (2)***Crystal data*C<sub>22</sub>H<sub>24</sub>M<sub>r</sub> = 288.43

Monoclinic

C2/c

a = 11.604 (3) Å

b = 7.754 (2) Å

c = 18.146 (2) Å

β = 102.71 (1)°

V = 1592.6 (6) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.203 Mg m<sup>-3</sup>*Data collection*

Rigaku AFC-6A diffractometer

θ/2θ scans

Absorption correction:

none

1105 measured reflections

1015 independent reflections

969 observed reflections

[I &gt; 2σ(I)]

*Refinement*

Refinement on F

R = 0.054

wR = 0.073

S = 2.52

969 reflections

148 parameters

All H-atom parameters

refined

w = 1/[σ<sup>2</sup>(F) + 0.0006F<sup>2</sup>]Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C1	0.5269 (2)	0.3026 (2)	0.2872 (1)	0.0107 (9)
C2	0.5409 (2)	0.4669 (3)	0.3344 (1)	0.015 (1)
C3	0.5307 (2)	0.4013 (3)	0.41305 (9)	0.013 (1)
C4	0.6223 (2)	0.1187 (3)	0.47791 (9)	0.012 (1)
C5	0.6730 (2)	-0.0387 (2)	0.4650 (1)	0.014 (1)
C6	0.6799 (2)	-0.0902 (3)	0.39265 (9)	0.012 (1)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

C7	0.6332 (2)	0.0088 (2)	0.3286 (1)	0.011 (1)
C8	0.5764 (2)	0.1631 (3)	0.34060 (9)	0.0098 (9)
C9	0.5770 (2)	0.2194 (2)	0.41442 (9)	0.010 (1)
C10	0.6205 (2)	0.1790 (3)	0.5567 (1)	0.016 (1)
C11	0.6528 (2)	-0.0459 (3)	0.2527 (1)	0.015 (1)

Table 4. Selected geometric parameters (Å, °) for (2)

C1—C2	1.524 (3)	C4—C10	1.508 (3)
C1—C8	1.482 (2)	C5—C6	1.392 (3)
C1—C1'	1.356 (2)	C6—C7	1.398 (2)
C2—C3	1.544 (3)	C7—C8	1.405 (3)
C3—C9	1.508 (3)	C7—C11	1.506 (3)
C4—C5	1.397 (3)	C8—C9	1.408 (2)
C4—C9	1.396 (2)		
C2—C1—C8	105.3 (1)	C6—C7—C8	116.7 (2)
C2—C1—C1'	121.9 (2)	C6—C7—C11	119.7 (2)
C8—C1—C1'	132.7 (2)	C8—C7—C11	123.5 (2)
C1—C2—C3	102.9 (2)	C1—C8—C7	130.4 (2)
C2—C3—C9	102.9 (1)	C1—C8—C9	108.4 (2)
C5—C4—C9	116.5 (2)	C7—C8—C9	120.5 (2)
C5—C4—C10	121.6 (2)	C3—C9—C4	127.3 (2)
C9—C4—C10	121.8 (2)	C3—C9—C8	110.3 (1)
C4—C5—C6	121.5 (2)	C4—C9—C8	122.3 (2)
C5—C6—C7	122.3 (2)		
C8—C1—C2—C3	-30.9 (2)	C1—C2—C3—C9	29.2 (2)
C2—C1—C8—C9	20.7 (2)	C2—C3—C9—C8	-17.9 (2)
C1 <sup>i</sup> —C1—C8—C7	33.9 (4)	C2—C1—C1 <sup>i</sup> —C2 <sup>i</sup>	20.2 (3)
C1 <sup>i</sup> —C1—C8—C9	-156.1 (2)	C8—C1—C1 <sup>i</sup> —C8 <sup>i</sup>	12.9 (4)

Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .

The low-temperature experiments were carried out using a Cryostream (Oxford Cryosystems) open-flow gas cryostat (Cosier & Glazer, 1986).

For both compounds, data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *Xtal3.2 DIFDAT ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994) for (1); *Xtal3.2 GEN-TAN* for (2). For both compounds, program(s) used to refine structures: *Xtal3.2 CRYLSQ*; molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal3.2*; software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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