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(*E*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene, $C_{22}H_{28}$

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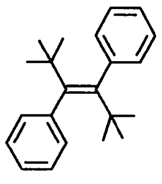
Abstract

In the title compound, an unusually short central $\mathrm{C}{=}\mathrm{C}$ bond observed at room temperature is shown to be an artifact by a measurement at low temperature. The phenyl planes are perpendicular to the plane of the double bond.

Comment

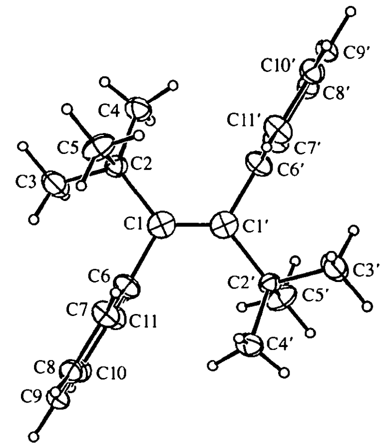
The structure of the title compound, (1), has prompted numerous investigations of this molecule and its derivatives (Bellucci, Chiappe, Bianchini, Lenoir & Herges, 1995; Gano & Gano, 1994; Gano, Jacob & Roesner, 1991; Gano, Jacob, Sekher, Subramaniam, Eriksson & Lenoir, 1996; Gano, Park, Pinkerton & Lenoir, 1990; Gano, Park, Subramaniam, Lenoir & Gleiter, 1991; Laali, Gano, Lenoir & Gundlach, 1994). Although a structure appeared for its *Z* isomer some time ago (Gano, Park, Pinkerton & Lenoir, 1991), difficulties preparing acceptable crystals, which are not unusual with (*E*)-stilbenes, limited reports, until now, to a disordered structure (Ermer, 1977; Pilati & Simonetta, 1982) and a highly brominated derivative (Gano, Kirschbaum & Sekher, 1996). Suitable crystals were obtained by slow evaporation of a methanol solution. The triclinic cell contains two independent molecules (Fig. 1) which are located on inversion centers.



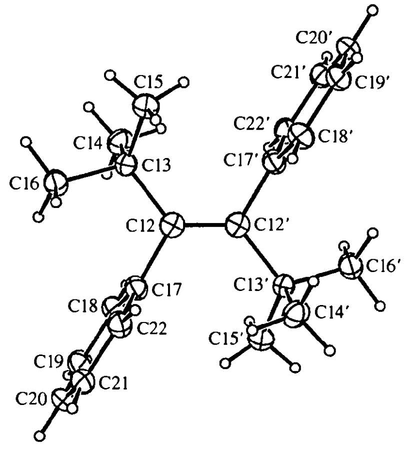
(1)

Although (*E*)-stilbene is planar in its crystalline form or at very low temperatures (Waldeck, 1991), in (1), the phenyl groups rotate out of the molecular plane to avoid steric repulsion of the *tert*-butyl groups. As seen in Fig. 1, the rings are perpendicular to the plane defined by the central $\mathrm{C}{=}\mathrm{C}$ bond and its attached atoms: C1′—C1—C6—C7 93.2 (2), C1′—C1—C6—C11 −89.3 (2), C12′—C12—C17—C18 −96.8 (2) and C12′—C12—C17—C22 87.5 (2)°; C1′ = C1($-x$, $-y$, $-z$) and C12′ = C12($1-x$, $1-y$, $1-z$)].

Rotation of the phenyl groups so they are not in conjugation with the $\mathrm{C}{=}\mathrm{C}$ bond might be expected



Molecule *A*



Molecule *B*

Fig. 1. *ORTEP* plots (50% probability) showing the two independent molecules of the title compound. Both molecules are viewed perpendicular to the plane defined by the atoms in the central $\mathrm{C}{=}\mathrm{C}$ bond and its substituents.

to affect bond lengths; this is not the case. The phenyl–alkene bonds are at the upper end of the 1.48–1.52 Å stilbene range, C1—C6 1.518 (3) and C12—C17 1.508 (2) Å. Bond lengths within the rings are in the normal range, 1.379 (3)–1.400 (3) Å. As expected, the *tert*-butyl–alkene bond is relatively long: C1—C2 1.574 (2) and C12—C13 1.568 (3) Å. Cleavage of this weakest C—C bond is the characteristic dominant fragmentation observed in the mass spectra of this class of compounds (Gano, Sekher, Weber & Lenoir, 1996).

The crystal packing shows planes of molecules built up with close *tert*-butyl–phenyl contacts. The three methyl groups of a *tert*-butyl group sit on the face of the phenyl group on an adjacent molecule like a three-legged stool sitting on the floor. Simultaneously, the *tert*-butyl group on the adjacent molecule interacts in the same manner with the phenyl group on the first molecule. These planes of molecules, which extend parallel to the *a* and *b* axes, fit into one another through edge-to-face interactions of their phenyl groups.

Although the phenyl–alkene angles are the trigonal value, C1′—C1—C6 120.0 (1) and C12′—C12—C17 120.4 (2)°, the *tert*-butyl–alkene angle is opened presumably due to the steric repulsion from the remote phenyl group, C1′—C1—C2 127.0 (2) and C12′—C12—C13 126.6 (2)°. This close proximity of the phenyl group is reflected in the large upfield shift of the *tert*-butyl resonances in the proton NMR spectrum, $\delta = 0.65$.

Considerable controversy has surrounded the observations of unusually short central C═C bonds in stilbenes and 1,2-diphenylethanes (Kahr *et al.*, 1995; Ogawa, Harada & Tomoda, 1995; Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992; Saito & Ikemoto, 1996). Low-temperature measurements demonstrated this can be attributed to large amplitude vibrations. Although the structure of (1) differs significantly from its planar parent, the same effect was observed here. Measurements of (1) at room temperature gave one short and one long C═C bond, 1.317 (3) and 1.335 (3) Å for C1—C1′ and C12—C12′, respectively. As in other stilbenes, these values in molecules *A* and *B*, respectively, increased to normal C═C bond lengths of 1.331 (2) and 1.347 (2) Å, respectively, at 140 K. The difference in bond length observed at room temperature, 0.018 (2) Å, remains at low temperatures, 0.016 (2) Å.

Experimental

The title compound was prepared as reported by Lenoir & Burghard (1980) and recrystallized from methanol by very slow evaporation at room temperature over a three-week period.

Crystal data

$C_{22}H_{28}$
$M_r = 292.47$
Triclinic
$P\overline{1}$
$a = 6.291\ (2)$ Å
$b = 8.259\ (2)$ Å
$c = 18.054\ (3)$ Å
$\alpha = 96.53\ (1)^\circ$
$\beta = 91.39\ (2)^\circ$
$\gamma = 112.06\ (2)^\circ$
$V = 861.4\ (7)$ Å^3
$Z = 2$
$D_x = 1.13$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–16°
$\mu = 0.059$ mm^{-1}
$T = 140$ K
Irregular
0.60 × 0.50 × 0.10 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.97$, $T_{\max} = 1.00$
3702 measured reflections
3374 independent reflections

2658 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 25.97^\circ$
$h = 0 \rightarrow 7$
$k = -10 \rightarrow 9$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 50 min
intensity decay: 2.4%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.066$
$S = 2.5$
2658 reflections
311 parameters
All H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.07$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C1—C2	1.574 (2)	C12—C13	1.568 (3)
C1—C1$^{\rm i}$	1.331 (2)	C12—C12$^{\rm ii}$	1.347 (2)
C1—C6	1.518 (3)	C12—C17	1.508 (2)
C2—C1—C6	112.9 (1)	C13—C12—C17	112.9 (1)
C1$^{\rm i}$—C1—C2	127.0 (2)	C12$^{\rm ii}$—C12—C13	126.6 (2)
C1$^{\rm i}$—C1—C6	120.0 (1)	C12$^{\rm ii}$—C12—C17	120.4 (2)
C1$^{\rm i}$—C1—C2—C5	−91.6 (2)	C12$^{\rm ii}$—C12—C13—C14	82.3 (2)
C1$^{\rm i}$—C1—C6—C7	93.2 (2)	C12$^{\rm ii}$—C12—C17—C18	−96.8 (2)
C1$^{\rm i}$—C1—C6—C11	−89.3 (2)	C12$^{\rm ii}$—C12—C17—C22	87.5 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989) (direct methods). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF VAX MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1316). Services for accessing these data are described at the back of the journal.

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(+)-Camphorsulfonylimine

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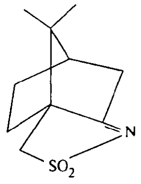
Abstract

The norbornane ring system in the title molecule, 8,8-dimethyl-3,3a,4,5,6,7-hexahydro-3a,6-methanobenz[*c*]isothiazole *S*,*S*-dioxide, $C_{10}H_{15}NO_2S$, is regular with normal bond lengths and angles. The bridgehead bond angle is 92.5 (2)°. The five-membered ring of the sulfonylimine moiety adopts a flattened envelope conformation. The crystal structure is stabilized by weak C—H···O hydrogen bonds.

Comment

Camphor derivatives are important chiral auxiliaries or catalysts for stereoselective synthesis (Oppolzer, 1987). The crystal structure determination of the title compound, (I), was carried out in order to elucidate the molecular conformation.



(I)

The bond lengths and angles of the camphor ring system are comparable to those in related molecules (Bear & Trotter, 1975; Garcia *et al.*, 1988). The six-membered ring of the norbornane ring system has a fairly symmetrical boat conformation, with atoms C3 and C7 displaced by −0.852 (3) and −0.845 (2) Å, respectively, from the best plane through atoms C1, C2, C5 and C6. The bridgehead bond angle (C3—C4—C7) of 92.5 (2)° is typical of norbornane derivatives. The two five-membered rings formed by the bridging atom C4 (C1—C2—C3—C4—C7 and C3—C5—C6—C7—C4) adopt envelope conformations with ΔC_s(C4) asymmetry parameters (Nardelli, 1983*a*) equal to 0.007 (2) and 0.015 (2), respectively. The angles between the

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