

(Z)-2,2,5,5-Tetramethyl-3,4-diphenyl-3-hexene: a Cofacial Stilbene

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Abstract. $C_{22}H_{28}$, $M_r = 292.47$, orthorhombic, $Pbca$, $a = 18.154$ (2), $b = 16.973$ (2), $c = 12.081$ (1) Å, $V = 3722.7$ Å³, $Z = 8$, $D_x = 1.04$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.5$ cm⁻¹, $F(000) = 1280$, $T = 294$ (1) K, 5499 unique reflections, $R = 0.040$, $wR = 0.046$, $S = 1.34$ for 920 observed unique reflections. Steric repulsion of the vicinal *tert*-butyl groups forces them back into the geminal phenyl rings. In order to avoid further steric strain, the phenyl rings assume a cofacial or face-to-face relationship. The planes of both phenyl rings are perpendicular to the plane of the central double bond with a nearest point of contact at 2.65 Å. The central double bond is normal.

Introduction. As part of an investigation into the structural distortions caused by steric compression (Gano, Lenoir, Park & Roesner, 1987), both H atoms on the central double bond of (*Z*)-stilbene were replaced by *tert*-butyl groups to give (*Z*)-3,4-diphenyl-2,2,5,5-tetramethyl-3-hexene, (1), (Gano, Park, Subramaniam, Lenoir & Glieter, 1990). By analogy with other stilbenes, (1) was anticipated to show a twisted central double bond. For example, the central C=C bond is twisted about 37° in (*Z*)-stilbene (Bouwstra, Schouten & Kroon, 1984), and 3.9° in (*Z*)-2,3-diphenyl-2-butene (Fronczek, Swan, Corkern & Gandour, 1984) (Table 1). Contrary to expectation, the X-ray analysis showed the central C=C bond to be planar. Steric compression was, instead, relieved by deconjugation of the phenyl rings to form an unusual cofacial stilbene.

Experimental. Compound (1) was prepared as reported (Lenoir, Gano & McTague, 1986), and crystallized from methanol to provide colorless plates. The crystal used for data collection (0.26 × 0.24 × 0.08 mm) was mounted on a glass fiber at room temperature. Preliminary examination and data collection were carried out with Mo $K\alpha$ radi-

ation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 diffractometer.

Lattice parameters from 25 reflections, θ range 14–15°, hkl range $-1, -1, -1$ to 20, 18, 11. Three standard reflections, 57.5% intensity decrease owing to sublimation of the crystal. The measured intensities (ω - θ scans to $2\theta = 60.0^\circ$, coupling ratio of 1.5, 6616 total, 5499 unique, $R_{int} = 2.3\%$) were corrected for absorption ($\mu = 0.5$ cm⁻¹, transmission factors 0.98–1.00) and decay. The structure was solved by direct methods and refined on F by full-matrix least squares. In the final cycles, all of the non-H atoms were refined anisotropically and H atoms included as riding atoms with isotropic temperature factors equal to 1.3 times the U_{eq} of the atom to which they are bonded. The refinement converged with $R = 0.040$, $wR = 0.046$ and $S = 1.34$ for 199 variables and 920 reflections with $F_o^2 > 3.0\sigma(F_o^2)$. The low number of useful reflections was due to reduction in crystal volume caused by sublimation. Weighting scheme, $w = 4F_o^2/\sigma^2(F_o^2)$. $(\Delta/\sigma)_{max} = 0.02$. $\Delta\rho$ max. and min. = 0.09 (2) and -0.10 (2) e Å⁻³. The scattering factors for the neutral atoms and anomalous-scattering coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1). All calculations were carried out on a VAX 11/750 computer using *SDP/VAX* (Frenz, 1978). Final atomic coordinates are given in Table 2.† Bond lengths are given in Table 3. Perspective drawings of the molecule along with the atom numbering are shown in Fig. 1.

Discussion. Steric congestion can be relieved in stilbenes by twisting about the double bond, twisting about the phenyl rings, and elongation of bonds.

† Lists of calculated and observed structure factors, anisotropic thermal parameters, least-squares planes, bond lengths, bond angles and torsional angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53165 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Structural features of related stilbenes

	Angle (°)		Length (Å)			Reference
	11—3—4—17*	16—11—3—4*	3—4*	3—11*	2—3*	
(Z)-[(<i>o</i> -MeOPh)(CH ₃)C] ₂ =	-9.8	71.6	1.310	1.492	1.516	Fronczek, Swan, Corkern & Gandour (1984)
(Z)-[Ph(CH ₃)C] ₂ =	3.9	57.6	1.343	1.497	1.512	Fronczek, Oliver & Gandour (1984)
(Z)-(tert-BuPhC) ₂ = (1)	4.5	91.7	1.343	1.508	1.555	Bernstein (1975)
(E)-(PhHC) ₂ =†	180	5.0	1.318	1.466	—	Tirado-Rives, Fronczek & Gandour (1985)
(E)-[Ph(CH ₃)C] ₂ =	—	74.2	1.33	1.491	1.515	

* Numbering scheme as shown in Fig. 1.

† Favini, Simonetta, Sottocornola & Todeschini (1982).

Table 2. Positional parameters with *e.s.d.*'s in parentheses

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(8\pi^2/3) \times (U_{11} + U_{22} + U_{33})$.

	x	y	z	B(Å ²)
C1	0.4599 (2)	0.2567 (3)	0.1997 (5)	8.0 (1)
C2	0.4228 (2)	0.1982 (2)	0.1198 (3)	5.0 (1)
C3	0.3611 (2)	0.1517 (2)	0.1808 (3)	3.74 (9)
C4	0.3623 (2)	0.0884 (2)	0.2475 (3)	3.50 (8)
C5	0.4266 (2)	0.0359 (2)	0.2900 (3)	4.2 (1)
C6	0.4452 (2)	-0.0273 (2)	0.2014 (4)	6.5 (1)
C7	0.4811 (2)	0.1464 (2)	0.0633 (4)	7.7 (1)
C8	0.3898 (2)	0.2486 (3)	0.0247 (4)	10.7 (2)
C9	0.4965 (2)	0.0808 (2)	0.3251 (4)	6.0 (1)
C10	0.4039 (2)	-0.0110 (3)	0.3951 (4)	7.6 (1)
C11	0.2862 (2)	0.1875 (2)	0.1621 (3)	3.85 (9)
C12	0.2613 (2)	0.2475 (2)	0.2303 (4)	5.2 (1)
C13	0.1932 (2)	0.2820 (2)	0.2153 (4)	6.0 (1)
C14	0.1484 (2)	0.2566 (3)	0.1316 (4)	6.6 (1)
C15	0.1713 (2)	0.1975 (2)	0.0628 (4)	6.6 (1)
C16	0.2400 (2)	0.1633 (2)	0.0773 (3)	5.2 (1)
C17	0.2885 (2)	0.0590 (2)	0.2866 (3)	3.82 (9)
C18	0.2557 (2)	0.0884 (2)	0.3822 (3)	5.2 (1)
C19	0.1890 (2)	0.0602 (3)	0.4180 (4)	6.9 (1)
C20	0.1548 (2)	0.0013 (3)	0.3615 (5)	7.9 (1)
C21	0.1856 (2)	-0.0289 (2)	0.2670 (5)	7.4 (1)
C22	0.2528 (2)	0.0005 (2)	0.2296 (4)	5.4 (1)

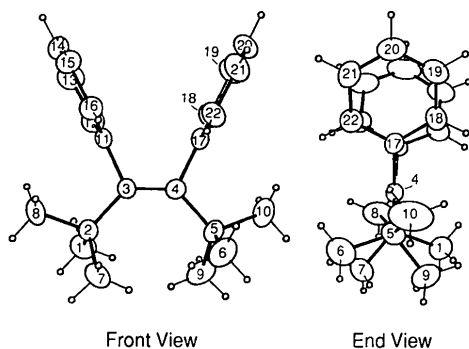


Fig. 1. Front and end views on (1) showing atom labeling. All labeled atoms are carbon.

Although (*E*)-stilbene is planar, most stilbenes show strain relief by a combination of these factors (see Table 1). Contrary to expectation, the strain introduced by the vicinal *tert*-butyl groups in (1) is not

Table 3. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

C1—C2	1.540 (6)	C11—C16	1.386 (5)
C2—C3	1.555 (5)	C12—C13	1.379 (5)
C2—C7	1.536 (6)	C13—C14	1.368 (6)
C2—C8	1.553 (6)	C14—C15	1.368 (6)
C3—C4	1.343 (5)	C15—C16	1.386 (6)
C3—C11	1.507 (5)	C17—C18	1.392 (5)
C4—C5	1.555 (5)	C17—C22	1.371 (5)
C4—C17	1.506 (5)	C18—C19	1.372 (6)
C5—C6	1.552 (5)	C19—C20	1.361 (6)
C5—C9	1.539 (5)	C20—C21	1.369 (7)
C5—C10	1.554 (6)	C21—C22	1.393 (6)
C11—C12	1.385 (5)		
C1—C2—C3	110.2 (3)	C9—C5—C10	104.2 (3)
C1—C2—C7	110.2 (3)	C3—C11—C12	120.1 (3)
C1—C2—C8	106.1 (4)	C3—C11—C16	122.4 (3)
C3—C2—C7	114.6 (3)	C12—C11—C16	117.4 (3)
C3—C2—C8	110.7 (3)	C11—C12—C13	121.8 (4)
C7—C2—C8	104.6 (3)	C12—C13—C14	119.7 (4)
C2—C3—C4	132.7 (3)	C13—C14—C15	120.0 (4)
C2—C3—C11	112.0 (3)	C14—C15—C16	120.2 (4)
C4—C3—C11	115.3 (3)	C11—C16—C15	120.9 (4)
C3—C4—C5	132.0 (3)	C4—C17—C18	121.5 (3)
C3—C4—C17	116.0 (3)	C4—C17—C22	120.2 (3)
C5—C4—C17	112.0 (3)	C18—C17—C22	118.3 (3)
C4—C5—C6	109.3 (3)	C17—C18—C19	121.0 (4)
C4—C5—C9	115.2 (3)	C18—C19—C20	120.0 (4)
C4—C5—C10	111.4 (3)	C19—C20—C21	120.4 (4)
C6—C5—C9	110.7 (3)	C20—C21—C22	119.6 (4)
C6—C5—C10	105.5 (3)	C17—C22—C21	120.7 (4)

relieved by twisting of the central double bond. All atoms attached to the double bond are within 0.035 Å of a common plane (Fig. 1, end view). In addition, the C=C bond length is normal, 1.343 (5) Å compared with related stilbenes (see Table 1). The dominant steric repulsion occurred between the vicinal *tert*-butyl groups. That repulsion (see Fig. 2) opened the *tert*-Bu—C=C angle and forced the *tert*-butyl groups back into the phenyl rings. The phenyl groups responded by rotating out of the way so that their planes became perpendicular, 86.9 and 85.1°, to the plane of the central bond (Fig. 1, front view). Thus, (1) is an extreme example of strain relief by deconjugation. The phenyl rings are forced together in a cofacial or face-to-face relationship. The closest point of approach of the rings, C(11)—C(17), is 2.65 Å, much less than the normal 3.4 Å van der Waals distance for aromatic rings, yet

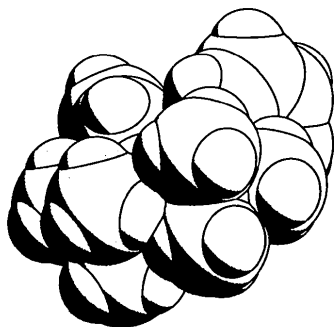


Fig. 2. Space-filling model of (I) showing the steric congestion between the *tert*-butyl groups which opened the *tert*-Bu—C=C angle.

the rings remain planar, within 0.01 Å of a common plane, and there was no pyramidalization at C(11) or C(17) (Tirado-Rives, Fronczek & Gandour, 1985). As often happens in hydrocarbons, additional strain relief was obtained by stretching the *tert*-Bu—C bonds to 1.556 (5) Å.

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2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one and 5,6,7,8-Tetrachloro-3a,9a-dihydro-2,3,3a,9a-tetraphenylcyclopenta[2,3-*b*][1,4]benzodioxin-1-one-toluene (2/1): Compounds of Photochemical Interest

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Abstract. (I) $C_{29}H_{20}O$, $M_r = 384.45$, monoclinic, $C2/c$, $a = 26.16$ (2), $b = 8.38$ (1), $c = 21.57$ (2) Å, $\beta = 119.5$ (2)°, $V = 4115.6$ Å³, $Z = 8$, $D_x = 1.24$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 4.9$ cm⁻¹, $F(000) = 1616$, $T = 293$ K, $R = 0.063$ for 1789 reflexions. (IIIa) $C_{35}H_{20}Cl_4O_3 \cdot 0.5C_7H_8$, $M_r = 676.42$, monoclinic, $P2_1/a$, $a = 18.26$ (2), $b = 10.50$ (1), $c = 17.74$ (2) Å, $\beta = 109.6$ (1)°, $V = 3204.2$ Å³, $Z = 4$, $D_x = 1.40$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.5418$ Å, $\mu = 35.2$ cm⁻¹, $F(000) = 1394$, $T = 293$ K, $R = 0.079$ for 2461 reflexions. The mechanisms of photolytic ring closure in tetraphenylcyclopentadienone (I) and its adduct (IIIa) with tetrachloro-*o*-benzoquinone are still in doubt. In the crystal the non-bonded C···C distances of the atoms linked during photolysis are 3.264 (6) Å

(I) and 3.208 (7) Å (IIIa). Packing-energy calculations suggest that the observed structures are stabilized by lattice forces and that the phenyl groups are further from coplanarity with the central ring in the free molecule.

Introduction. The photochemical behaviour of tetraphenylcyclopentadienone (I) and its derivatives is complicated by apparent hydrogen-abstraction reactions (Toshima & Moritani, 1967) as well as *cis*-stilbene-type cyclization to phenanthrocyclopentenones (II) (Moritani, Toshima, Nakagawa & Yakushiji, 1967). High yields of (II) can be obtained by the irradiation of adducts (III) of tetraaryl substituted cyclopentadienones (Horspool, 1969, 1971).