

H atoms were included using a riding model with $d(\text{C—H}) = 0.96 \text{ \AA}$ and $U_{\text{iso}} = 0.08 \text{ \AA}^2$. Structure solution and refinement used either our locally modified version of the *UCLA Crystallographic Package* (Strouse, 1981) or the *SHELXLT-Plus88* program set (Sheldrick, 1988).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HH1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(1Z,3Z)-1,4-Diphenyl-1,4-bis(*p*-tolylmethylthio)-1,3-butadiene

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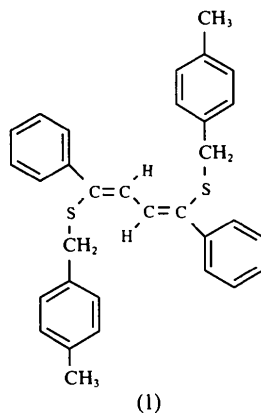
Abstract

The crystal structure of (1Z,3Z)-1,4-diphenyl-1,4-bis(*p*-tolylmethylthio)-1,3-butadiene (1), $\text{C}_{32}\text{H}_{30}\text{S}_2$, is described. Compound (1) has an *s-trans* conformation. The single bond length, C(2)—C(2'), in compound (1) of 1.432 (5) Å is shorter than the C(3)—C(4) single bond (1.48 Å) in 1,3-butadiene and the double-bond length, C(1)—C(2), of 1.350 (3) Å in compound (1) is comparable to that in 1,3-butadiene (1.34 Å). The short C—C single and double bonds in (1) may be attributed to delocalization (resonance) over the planar four-atom unit, hybridization changes, the presence of the S atoms, and/or other factors.

Comment

The addition of *p*-tolylmethanethiol to 1,4-diphenyl-1,3-butadiene may afford (1Z,3Z)-1,4-diphenyl-1,4-bis(*p*-tolylmethylthio)-1,3-butadiene (1), 2-(*p*-tolyl)-5-phenyl-3-(phenylmethyl)thiophene (Freeman, Lu & Rodriguez, 1993; Freeman, Lu, Zeng & Rodriguez, 1994), or (Z)-1,4-diphenyl-1-(*p*-tolylmethylthio)but-1-en-3-yne (Zschunke, Mugge, Hintzsche & Schroth, 1992) depending on the solvent system and the ratio of reactants. The reaction of thiols with polyalkynes is of interest in the synthesis of 1,2-dithiacyclohexa-3,5-dienes (1,2-dithiins) in general (Freeman, 1990; Freeman, Kim & Rodriguez, 1989, 1992; Koreeda & Yang, 1994) and of the bioactive thiarubins in particular (Balza, Lopez, Rodriguez & Towers, 1989; Freeman, Aregullin & Rodriguez, 1993; Freeman, Kim & Rodriguez, 1989; Rodriguez, Aregullin, Nishida, Uehara, Wrangham, Abramowski, Finlayson & Towers, 1985; Schroth, Billig & Reinhold, 1967; Schroth, Billig & Zschunke, 1969). In addition, the cycloaddition reactions of substituted dienes are of great synthetic and theoretical interest, and questions concerning the conformation and

delocalization of π electrons in 1,3-dienes are topics of considerable discussion and controversy (Bartell, 1978; Dewar & Gleicher, 1965; Fischer & Michl, 1987; Popov & Kogan, 1968; Marias, Sheppard & Stoicheff, 1962; Simmons, 1970; Wiberg, Rosenberg & Rablen, 1991).



In compound (1) the conformation of the 1,3-butadiene moiety is *trans*-planar. The planes of the two phenyl rings attached to C(1) and C(1') are both tilted 39.7° from the 1,3-butadiene plane. The single bond length, C(2)—C(2'), of 1.432 (5) Å in compound (1) is shorter than the C(3)—C(4) bond (1.48 Å) in 1,3-butadiene and the double-bond length, C(1)—C(2), of 1.350 (3) Å is comparable to that in 1,3-butadiene (1.34 Å). The short C—C single and double bonds in (1) may be attributed to delocalization (resonance) over the planar four-C-atom unit, hybridization changes, the presence of the S atoms, and/or other factors.

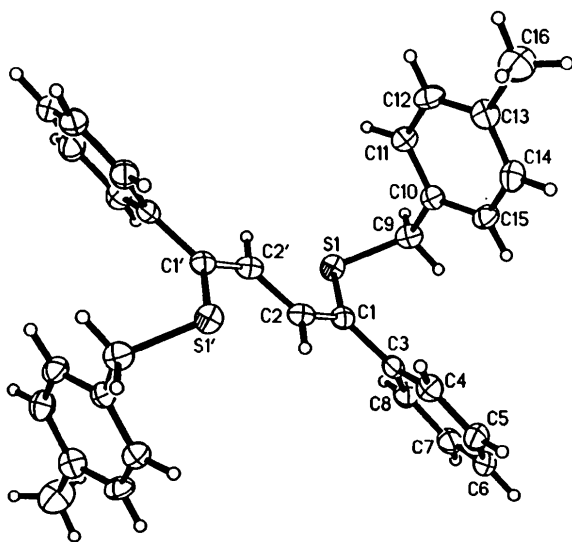


Fig. 1. Thermal ellipsoid plot of the molecular structure and atom numbering of (1). The displacement ellipsoids are drawn at the 50% probability level.

Experimental

(1*Z*,3*Z*)-1,4-Diphenyl-1,4-bis(*p*-tolylmethylthio)buta-1,3-diene was prepared by the reaction of *p*-tolylmethanethiol and 1,4-diphenylbuta-1,3-diene in ethanolic potassium hydroxide. Recrystallization was from 1:1 benzene/ethyl ethanoate.

Crystal data

C₃₂H₃₀S₂
M_r = 478.7
 Triclinic
P $\bar{1}$
a = 7.3431 (13) Å
b = 7.6239 (17) Å
c = 12.2209 (20) Å
 α = 78.411 (16)°
 β = 78.381 (14)°
 γ = 79.439 (15)°
V = 649.2 (2) Å³
Z = 1
D_x = 1.224 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 32 reflections
 θ = 11.0–15.0°
 μ = 0.213 mm⁻¹
T = 158 K
 Plate
 0.44 × 0.30 × 0.13 mm
 Colourless

Data collection

Siemens *R3m/V* diffractometer
 θ – 2θ scans
 Absorption correction: none
 1868 measured reflections
 1634 independent reflections
 1506 observed reflections
 [*F* > 3.0σ(*F*)]

*R*_{int} = 0.0105
 θ _{max} = 22.5°
h = 0 → 7
k = –8 → 8
l = –12 → 13
 2 standard reflections monitored every 98 reflections
 intensity variation: none

Refinement

Refinement on *F*²
R = 0.043
wR = 0.049
S = 1.42
 1506 reflections
 214 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.0005F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	0.2962 (1)	0.7042 (1)	0.4776 (1)	0.0274 (3)
C(1)	0.2440 (3)	0.9388 (3)	0.4228 (2)	0.0228 (10)
C(2)	0.0778 (4)	1.0342 (4)	0.4615 (2)	0.0257 (11)
C(3)	0.3938 (4)	1.0257 (4)	0.3414 (2)	0.0249 (10)
C(4)	0.3486 (4)	1.1654 (4)	0.2534 (2)	0.0300 (11)
C(5)	0.4860 (4)	1.2530 (4)	0.1806 (3)	0.0352 (12)
C(6)	0.6729 (5)	1.2030 (4)	0.1943 (3)	0.0380 (13)
C(7)	0.7219 (4)	1.0610 (5)	0.2791 (3)	0.0365 (12)
C(8)	0.5840 (4)	0.9733 (4)	0.3512 (3)	0.0298 (11)
C(9)	0.3678 (4)	0.6136 (4)	0.3454 (3)	0.0293 (11)
C(10)	0.2165 (4)	0.6468 (3)	0.2741 (2)	0.0247 (10)
C(11)	0.0557 (4)	0.5642 (4)	0.3104 (3)	0.0280 (11)
C(12)	–0.0786 (4)	0.5861 (4)	0.2415 (3)	0.0309 (11)
C(13)	–0.0588 (4)	0.6940 (4)	0.1353 (2)	0.0316 (11)
C(14)	0.0985 (4)	0.7809 (4)	0.1005 (3)	0.0327 (11)
C(15)	0.2342 (4)	0.7584 (4)	0.1681 (2)	0.0295 (11)
C(16)	–0.2042 (6)	0.7186 (6)	0.0594 (3)	0.0513 (16)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S(1)—C(1)	1.779 (3)	S(1)—C(9)	1.827 (3)
C(1)—C(2)	1.350 (3)	C(1)—C(3)	1.483 (3)
C(2)—C(2')	1.432 (5)	C(3)—C(4)	1.398 (4)
C(3)—C(8)	1.403 (4)	C(4)—C(5)	1.379 (4)
C(5)—C(6)	1.389 (5)	C(6)—C(7)	1.390 (4)
C(7)—C(8)	1.379 (4)	C(9)—C(10)	1.502 (4)
C(10)—C(11)	1.391 (4)	C(10)—C(15)	1.396 (4)
C(11)—C(12)	1.388 (5)	C(12)—C(13)	1.386 (4)
C(13)—C(14)	1.387 (4)	C(13)—C(16)	1.513 (6)
C(14)—C(15)	1.384 (5)		
C(1)—S(1)—C(9)	100.1 (1)	S(1)—C(1)—C(2)	120.0 (2)
S(1)—C(1)—C(3)	117.7 (2)	C(2)—C(1)—C(3)	122.1 (2)
C(1)—C(2)—C(2')	127.3 (3)	C(1)—C(3)—C(4)	120.7 (2)
C(1)—C(3)—C(8)	121.4 (2)	C(4)—C(3)—C(8)	117.9 (2)
C(3)—C(4)—C(5)	121.1 (3)	C(4)—C(5)—C(6)	120.0 (3)
C(5)—C(6)—C(7)	120.0 (3)	C(6)—C(7)—C(8)	119.7 (3)
C(3)—C(8)—C(7)	121.2 (3)	S(1)—C(9)—C(10)	114.1 (2)
C(9)—C(10)—C(11)	121.1 (2)	C(9)—C(10)—C(15)	121.1 (3)
C(11)—C(10)—C(15)	117.7 (3)	C(10)—C(11)—C(12)	121.1 (3)
C(11)—C(12)—C(13)	121.1 (3)	C(12)—C(13)—C(14)	117.9 (3)
C(12)—C(13)—C(16)	121.5 (3)	C(14)—C(13)—C(16)	120.6 (3)
C(13)—C(14)—C(15)	121.5 (3)	C(10)—C(15)—C(14)	120.7 (3)

The structure was solved using direct methods (*SHELXTL-Plus88*; Sheldrick, 1988) and the *UCLA Crystallographic Package* (Strouse, 1981). H atoms were located and included with isotropic temperature factors.

We thank the National Institutes of Health (AI 24779) and the National Science Foundation (grant CHE-90-15849) for support of this research. Funds for the purchase of the Siemens *R3m/V* diffractometer system were made available from the National Science Foundation under grant CHE-85-14495.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: HH1054). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*tert*-butylsulfonyl) Disulfide

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Abstract

The crystal structure of bis(*tert*-butylsulfonyl) disulfide, $\text{C}_8\text{H}_{18}\text{O}_4\text{S}_4$, is described and compared with oxides of other polysulfanes. The $\text{SO}_2\text{—S}$ bond distance is longer than that of S—S and there is considerable double-bond character along the S—O bonds.

Comment

The oxidation of polysulfanes and the structures of the resulting oxides are of considerable interest (Block & Bayer, 1990; Block & Weidner, 1966; Folkins & Harpp, 1993; Freeman, 1984; Freeman & Angeletakis, 1983; Freeman, Ma & Lin, 1993; Oae, 1991). Although the crystal structures of sulfonyl derivatives of disulfides (thiosulfonates; Dawson, Mathieson & Robertson, 1948; Wahl, Bordner, Harpp & Gleason, 1973), two trisulfides [bis(arylsulfonyl) sulfides; Mathieson & Robertson, 1949], one tetrasulfide [bis(methylsulfonyl) disulfide; Sörum & Foss, 1949; Sörum, 1953], and one pentasulfide [bis(arylsulfonyl) trisulfide; Dawson, Mathieson & Robertson, 1948] have been determined, there is a