ORGANIC COMPOUNDS

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(1Z,3Z)-1,4-Diphenyl-1,4-bis(3-chlorophenylmethylthio)buta-1,3-diene

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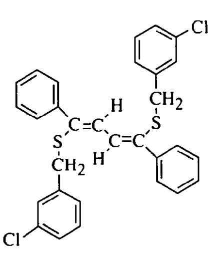
Abstract

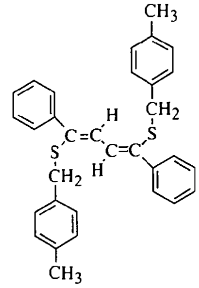
The crystal structure of the title compound, $C_{30}H_{24}Cl_2S_2$, (I), is described and compared with that of (1Z,3Z)-1,4-diphenyl-1,4-bis(*p*-tolylmethylthio)buta-1,3-diene, (II). The 1,3-butadiene moiety in compound (I) has a planar *s-trans* conformation with the planes of the two phenyl rings tilted 32.8° from the 1,3-butadiene plane. The relatively short C—C single-bond and the length of the C═C double bond of the butadiene moiety in (I) may be attributed to delocalization (resonance) over the planar four-carbon unit and to hybridization changes.

Comment

The addition of (3-chlorophenyl)methanethiol to 1,4-diphenylbuta-1,3-diyne affords (1Z,3Z)-1,4-diphenyl-1,4-bis(3-chlorophenylmethylthio)buta-1,3-diene, (I) (Freeman, Lu & Rodriguez, 1995; Freeman, Lu, Ziller & Rodriguez, 1995*a*; Koreeda & Yang, 1994*a*,*b*; Radeglia, Poleschner & Schroth, 1988; Schroth, Billig & Reinhold, 1967; Schroth, Billig & Zschunke, 1969), 2-(3-chlorophenyl)-5-phenyl-3-(phenylmethyl)-thiophene (Freeman, Lu & Rodriguez, 1993; Freeman, Lu, Zeng & Rodriguez, 1994, Freeman, Lu, Ziller & Rodriguez, 1995*b*) or (*Z*)-1,4-diphenyl-1-(3-chlorophenylmethylthio)but-1-en-3-yne (Freeman, Lu, Zeng & Rodriguez, 1994; Zschunke, Mugge, Hintzsche & Schroth, 1992) depending on the solvent system and the ratio of reactants. Compound (I) and its analogues are of interest in the synthesis of the 1,2-dithiacyclohexa-3,5-dienes (1,2-dithiins) (Block, Guo, Thiruvazhi & Toscano, 1995; Freeman, Kim & Rodriguez, 1989; Koreeda & Yang, 1994*a*,*b*; Schroth, Billig & Reinhold, 1967; Schroth, Billig & Zschunke, 1969) and the preparation and cycloaddition reactions of 1,3-dienes are of considerable synthetic and theoretical interest. The structure of the second stable conformer (*cis* or *gauche*), the nature of the hybridization changes, and the delocalization of π electrons in buta-1,3-diene are topics of considerable theoretical discussion (Bartell, 1978; Fischer & Michl, 1987; Marias, Sheppard & Stoicheff, 1962; Popov & Kogan, 1968; Simmons, 1970; Wiberg & Rosenberg, 1990; Wiberg, Rosenberg & Rablen, 1991).



(I)



(II)

Compound (I) has the *s-trans* conformation. The single-bond length C(2)—C(2′) in compound (I) [1.442 (5) Å] is comparable to the corresponding bond length in (1Z,3Z)-1,4-diphenyl-1,4-bis(*p*-tolylmethylthio)-buta-1,3-diene, (II) [1.432 (5) Å; Freeman, Lu, Ziller & Rodriguez, 1995*a*] but is shorter than the C(3)—C(4) single bond (1.48 Å) in 1,3-butadiene (Marias, Sheppard & Stoicheff, 1962). The value of the C═C double-bond lengths of the butadiene moiety in compound (I) [C(1)═C(2) 1.353 (4) Å] is comparable to those in (II) [1.350 (3) Å] and 1,3-butadiene (1.34 Å). The relatively short C—C single bond and the length of the double bond in (I) may be attributed to delocalization (resonance) in the conjugated system, hybridization changes

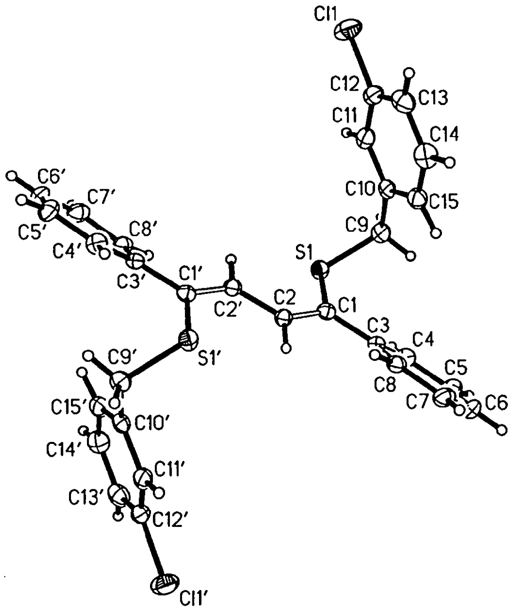


Fig. 1. Displacement ellipsoid plot (*SHELXTL-Plus*88; Sheldrick, 1988) of the molecular structure and atom numbering of (I). Ellipsoids are drawn at the 50% probability level.

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and other factors (Bartell, 1978). The C(2)—H(2) bond distance is 0.968 (34) Å while the range of C—H bond distances in the phenyl rings is 0.873 (30)–0.987 (30) Å and the range in the 3-chlorophenyl rings is 0.874 (29)–0.940 (35) Å. The planes of the two phenyl rings attached to C(1) and C(1′) in compound (I) are both tilted 32.8° from the 1,3-butadiene plane. In (II), the tilt angle is 39.7° (Freeman, Lu, Ziller & Rodriguez, 1995*a*).

Experimental

(1*Z*,3*Z*)-1,4-Diphenyl-1,4-bis(3-chlorophenylmethylthio)buta-1,3-diene, (I), was prepared from the reaction of (3-chlorophenyl)methanethiol and 1,4-diphenylbuta-1,3-diyne in ethanolic potassium hydroxide (Freeman, Lu & Rodriguez, 1992). Recrystallization was from 1:9 benzene/methanol.

Crystal data

$C_{30}H_{24}Cl_2S_2$
$M_r = 519.5$
Monoclinic
$P2_1/n$
$a = 13.0354\ (8)$ Å
$b = 6.3471\ (5)$ Å
$c = 15.8833\ (14)$ Å
$\beta = 107.217\ (6)^\circ$
$V = 1255.25\ (17)$ Å^3
$Z = 2$
$D_x = 1.374$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 10$–14°
$\mu = 0.435$ mm^{-1}
$T = 168$ K
Plate
0.50 × 0.40 × 0.07 mm
Pale yellow

Data collection

Siemens *R*3*m*/*V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2564 measured reflections
2125 independent reflections
1987 observed reflections [$F > 3\sigma(F)$]

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25^\circ$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 7$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 98 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.043$
$wR = 0.064$
$S = 1.61$
1987 reflections
202 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(|F_o|) + 0.001(|F_o|)^2]$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.13054 (18)	0.1473 (4)	1.02846 (15)	0.0185 (7)
C(2)	0.03029 (19)	0.0853 (4)	1.02566 (15)	0.0191 (7)
C(3)	0.18342 (19)	0.3280 (4)	1.08330 (15)	0.0190 (8)
C(4)	0.2952 (2)	0.3340 (4)	1.12240 (17)	0.0243 (8)
C(5)	0.3429 (2)	0.5038 (4)	1.17412 (18)	0.0292 (9)
C(6)	0.2825 (2)	0.6687 (4)	1.18908 (17)	0.0284 (9)
C(7)	0.1713 (2)	0.6638 (4)	1.15198 (17)	0.0258 (9)
C(8)	0.1236 (2)	0.4971 (4)	1.09933 (16)	0.0208 (8)
C(9)	0.2640 (2)	0.1920 (4)	0.91809 (17)	0.0237 (8)
C(10)	0.1853 (2)	0.2944 (4)	0.84015 (16)	0.0217 (8)
C(11)	0.1588 (2)	0.2008 (4)	0.75697 (18)	0.0251 (9)
C(12)	0.0891 (2)	0.3027 (4)	0.68604 (17)	0.0259 (8)
C(13)	0.0433 (2)	0.4945 (5)	0.6949 (2)	0.0295 (9)
C(14)	0.0698 (2)	0.5871 (5)	0.77767 (19)	0.0311 (10)
C(15)	0.1398 (2)	0.4886 (4)	0.84938 (18)	0.0258 (9)
S(1)	0.20599 (5)	−0.00494 (9)	0.97433 (4)	0.0226 (2)
Cl(1)	0.06061 (6)	0.18837 (13)	0.58142 (4)	0.0390 (3)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.353 (4)	C(1)—C(3)	1.481 (3)
C(1)—S(1)	1.772 (3)	C(2)—C(2′)	1.442 (5)
C(3)—C(4)	1.405 (3)	C(3)—C(8)	1.394 (4)
C(4)—C(5)	1.386 (4)	C(5)—C(6)	1.372 (4)
C(6)—C(7)	1.394 (4)	C(7)—C(8)	1.377 (3)
C(9)—C(10)	1.502 (3)	C(9)—S(1)	1.825 (3)
C(10)—C(11)	1.396 (4)	C(10)—C(15)	1.395 (4)
C(11)—C(12)	1.381 (3)	C(12)—C(13)	1.381 (4)
C(12)—Cl(1)	1.750 (3)	C(13)—C(14)	1.387 (4)
C(14)—C(15)	1.380 (4)		
C(2)—C(1)—C(3)	121.4 (2)	C(2)—C(1)—S(1)	119.6 (2)
C(3)—C(1)—S(1)	118.6 (2)	C(1)—C(2)—C(2′)	126.8 (3)
C(1)—C(3)—C(4)	121.5 (5)	C(1)—C(3)—C(8)	121.0 (2)
C(4)—C(3)—C(8)	117.5 (2)	C(3)—C(4)—C(5)	120.5 (2)
C(4)—C(5)—C(6)	121.0 (2)	C(5)—C(6)—C(7)	119.2 (2)
C(6)—C(7)—C(8)	120.0 (3)	C(3)—C(8)—C(7)	121.7 (2)
C(10)—C(9)—S(1)	114.8 (2)	C(9)—C(10)—C(11)	120.9 (2)
C(9)—C(10)—C(15)	120.3 (2)	C(11)—C(10)—C(15)	118.8 (2)
C(10)—C(11)—C(12)	119.4 (2)	C(11)—C(12)—C(13)	122.0 (3)
C(11)—C(12)—Cl(1)	118.9 (2)	C(13)—C(12)—Cl(1)	119.1 (2)
C(12)—C(13)—C(14)	118.4 (2)	C(13)—C(14)—C(15)	120.6 (3)
C(10)—C(15)—C(14)	120.8 (3)	C(1)—S(1)—C(9)	103.5 (1)

Symmetry code: (′) $-x, -y, 2-z$.

Cell refinement: Churchill, Lashewyez & Rottella (1977). Data reduction: *UCLA Crystallographic Computing Package* (Strouse, 1981), *SHELXTL-Plus*88 (Sheldrick, 1988). Program(s) used to solve structure: *SHELXTL-Plus*88. Program(s) used to refine structure: *SHELXTL-Plus*88. Molecular graphics: *SHELXTL-Plus*88. Software used to prepare material for publication: *SHELXTL-Plus*88.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-(3a*R**,6*S**,7*S**,14a*R**)-2,3,3a,7,8,9,10,11,12,13,14,14a-Dodecahydro-1*H*,6*H*-3a,6-epoxy-7,14a-methanocyclopentacyclotridecen-15-one

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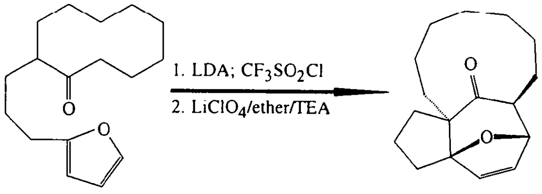
Abstract

The fused-ring system of the title compound, $C_{17}H_{24}O_2$, limits its conformational freedom. The five-membered cyclopentane and furan rings adopt envelope conformations, the tetrahydropyranone ring a boat conformation and the cyclodecanone ring a cyclodecane boat–chair–boat conformation.

Comment

As part of a continuing program involving the study of the intramolecular [4+3] cycloaddition reaction of allylic cations and dienes (Harmata, Gamlath, Barnes & Jones, 1995; Harmata, Elahmad & Barnes, 1994, 1995; Harmata & Herron, 1993*a*,*b*,*c*; Harmata & Elahmad, 1993; Harmata & Gamlath, 1988; Harmata, Gamlath & Barnes, 1990, 1993; Harmata, Fletcher & Claassen, 1991), we had occasion to study the reaction of the oxyallylic species generated from ketone (I) *via* chlorination and oxyallyl generation under conditions introduced by Föhlisch (Harmata, Elahmad & Barnes, 1995; Kaiser & Föhlisch, 1990, and references therein). The cycloaddition products were isolated as a 19:1 mixture in 59% yield. The major product (II) was isolated, crystallized from hexanes and its structure determined.



(I) (II)

Most interesting is the conformation of the tetrahydropyranone portion of the molecule, which is a boat with the methylene chain derived from cyclodecanone occupying both axial and equatorial positions at the 2 and 6 positions of the tetrahydropyranone. Vinter & Hoffman (1974) speculated that a minor product in the intermolecular [4+3] cycloaddition of cyclodecenyl oxyallyl to furan possessed this structure. Our isolation and structure determination of (II) supports their conjecture and their conclusion that cyclodecenyl oxyallylic cations are sickle shaped.

The bond lengths and angles fall within expected limits. The boat conformation of the tetrahydropyran-

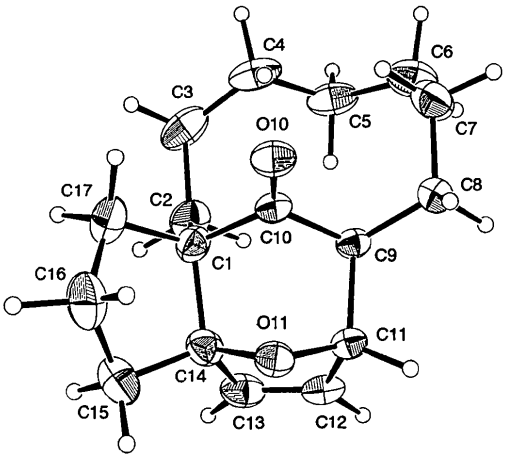


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids.

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