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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 3-Benzyl-5-phenyl-2-*p*-tolylthiophene

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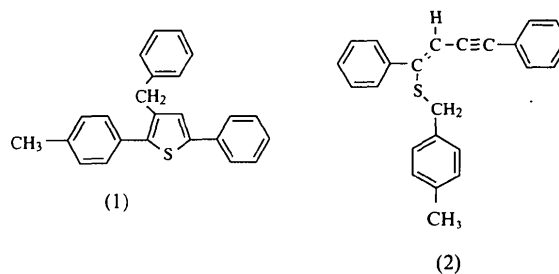
## Abstract

The crystal structure of 3-benzyl-5-phenyl-2-*p*-tolylthiophene, C<sub>24</sub>H<sub>20</sub>S, is described. The thiophene ring in the title compound is planar and its structural properties are very similar to those of thiophene.

There is steric repulsion between the *p*-tolyl ring at C(2) and the benzyl group on the adjacent atom, C(3).

## Comment

The addition of (*p*-tolyl)methanethiol to 1,4-diphenyl-1,3-butadiene in potassium hydroxide/dimethyl sulfoxide afforded 3-benzyl-5-phenyl-2-*p*-tolylthiophene, (1) (Freeman, Lu & Rodriguez, 1993), instead of the 1:1 nucleophilic addition product (*Z*)-1,4-diphenyl-1-(*p*-tolylmethylthio)but-1-en-3-yne, (2) (Zschunke, Mugge, Hintzsche & Schroth, 1992). The reaction of thiols with diynes is of interest in the synthesis of 1,2-dithiacyclohexa-3,5-dienes (1,2-dithiins) in general (Freeman, Aregullin & Rodriguez, 1993; Freeman, Kim & Rodriguez, 1989, 1992; Freeman, 1990) and of bioactive thiarubins in particular (Balza, Lopez, Rodriguez & Towers, 1989; Freeman, Kim & Rodriguez, 1989; Koreeda & Yang, 1994; Rodriguez, Aregullin, Nishida, Uehara, Wrangham, Abramowski, Finlayson & Towers, 1985; Schroth, Billig & Reinhold, 1967; Schroth, Billig & Zschunke, 1969). Disorder in crystals of thiophene derivatives is a general phenomenon (Gronowitz & Hornfeldt, 1990) and there are relatively few X-ray crystallographic studies of highly substituted thiophenes. The structural features of trisubstituted thiophenes are also of interest.



The thiophene ring in compound (1) is planar as are the phenyl rings. The structure of the thiophene ring in compound (1) is very similar to that of thiophene (Bak, Christensen, Hansen-Nygaard & Rastrup-Andersen, 1961; Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956; Harshbarger & Bauer, 1970). The C—S distances are 1.735 (2) and 1.731 (2) Å, respectively, and the C—S—C bond angle is 92.3 (1)°. The steric repulsion between the *p*-tolyl ring at C(2) and the benzyl group at the adjacent carbon, C(3), is minimized by the rotation of the *p*-tolyl group 56.1° from the thiophene plane. The benzene ring at C(5) deviates from the plane of the thiophene ring by 36.9°. In 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene (Meester, Maldar, Hosmane & Chu, 1986) the angle between the 4-

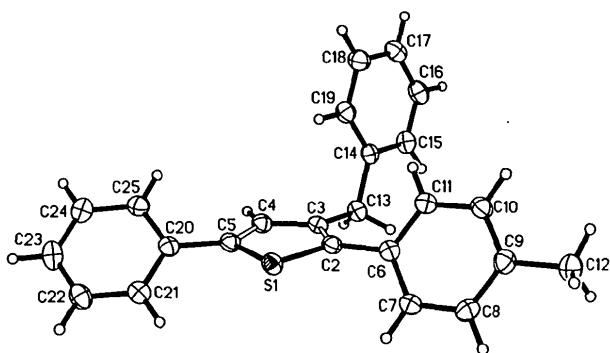


Fig. 1. ORTEP view (Johnson, 1976) of the molecular structure and atom numbering of 3-benzyl-5-phenyl-2-*p*-tolylthiophene. The displacement ellipsoids are drawn at 50% probability.

nitrophenyl and thiophene rings is 26.6°. The angle between the phenyl and thiophene rings in 2-amino-4-methyl-5-phenylthiophene-3-carboxamide is 54.9° (Joseph, Selladurai, Kannan & Parthasarathi, 1991).

## Experimental

3-Benzyl-5-phenyl-2-*p*-tolylthiophene, (1), was prepared from the reaction of phenylmethanethiol and 1,4-diphenyl-1,3-butadiene. Recrystallization was from 1:9 benzene/methanol.

### Crystal data

C<sub>24</sub>H<sub>20</sub>S

*M<sub>r</sub>* = 340.5

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 5.9314 (8) Å

*b* = 18.920 (3) Å

*c* = 15.866 (2) Å

β = 91.474 (12)°

*V* = 1779.9 (4) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.270 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10.0–14.0°

μ = 0.176 mm<sup>-1</sup>

*T* = 168 K

Prism

0.44 × 0.43 × 0.33 mm

Colourless

### Data collection

Syntex *P*2<sub>1</sub> diffractometer

θ–2θ scans

Absorption correction:  
none

3587 measured reflections

2984 independent reflections

2749 observed reflections

[*F* > 3σ(*F*)]

*R*<sub>int</sub> = 0.0094

θ<sub>max</sub> = 22.5°

*h* = 0 → 7

*k* = 0 → 22

*l* = –18 → 18

2 standard reflections

monitored every 98

reflections

intensity variation: none

### Refinement

Refinement on *F*

*R* = 0.043

*wR* = 0.055

*S* = 2.23

2749 reflections

227 parameters

Δρ<sub>max</sub> = 0.36 e Å<sup>-3</sup>

Δρ<sub>min</sub> = –0.25 e Å<sup>-3</sup>

Extinction correction: see  
text

Extinction coefficient:

0.0008 (2)

H atom treatment: see text  
*w* = 1/[σ<sup>2</sup>(*F*) + 0.0003*F*<sup>2</sup>]  
(Δ/σ)<sub>max</sub> = 0.001

Atomic scattering factors  
from *International Tables*  
for *X-ray Crystallography*  
(1974, Vol. IV)

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
S(1)	0.0703 (1)	0.8390 (1)	0.6458 (1)	0.0243 (2)
C(2)	0.1693 (3)	0.9134 (1)	0.6988 (1)	0.0225 (6)
C(3)	0.0757 (8)	0.9738 (1)	0.6659 (1)	0.0227 (6)
C(4)	–0.0801 (3)	0.9592 (1)	0.5983 (1)	0.0248 (7)
C(5)	–0.1023 (3)	0.8889 (1)	0.5794 (1)	0.0238 (6)
C(6)	0.3287 (3)	0.9055 (1)	0.7711 (1)	0.0226 (6)
C(7)	0.5338 (4)	0.8696 (1)	0.7635 (1)	0.0252 (7)
C(8)	0.6809 (4)	0.8626 (1)	0.8321 (1)	0.0281 (7)
C(9)	0.6291 (4)	0.8901 (1)	0.9107 (1)	0.0279 (7)
C(10)	0.4235 (4)	0.9248 (1)	0.9184 (1)	0.0278 (7)
C(11)	0.2767 (4)	0.9332 (1)	0.8500 (1)	0.0258 (7)
C(12)	0.7898 (4)	0.8817 (2)	0.9855 (2)	0.0417 (9)
C(13)	0.1422 (4)	1.0477 (1)	0.6932 (1)	0.0261 (7)
C(14)	–0.0119 (4)	1.0849 (1)	0.7539 (1)	0.0227 (6)
C(15)	0.0516 (4)	1.1513 (1)	0.7848 (1)	0.0290 (7)
C(16)	–0.0819 (4)	1.1873 (1)	0.8408 (1)	0.0320 (7)
C(17)	–0.2828 (4)	1.1577 (1)	0.8669 (1)	0.0319 (8)
C(18)	–0.3470 (4)	1.0924 (1)	0.8364 (1)	0.0318 (7)
C(19)	–0.2121 (4)	1.0560 (1)	0.7807 (1)	0.0270 (7)
C(20)	–0.2488 (4)	0.8568 (1)	0.5137 (1)	0.0235 (6)
C(21)	–0.1798 (4)	0.7985 (1)	0.4665 (1)	0.0263 (7)
C(22)	–0.3157 (4)	0.7720 (1)	0.4017 (1)	0.0316 (7)
C(23)	–0.5222 (4)	0.8033 (1)	0.3823 (2)	0.0350 (8)
C(24)	–0.5948 (4)	0.8598 (1)	0.4299 (2)	0.0326 (7)
C(25)	–0.4606 (4)	0.8863 (1)	0.4954 (1)	0.0279 (7)

Table 2. Selected geometric parameters (Å, °)

S(1)—C(2)	1.735 (2)	S(1)—C(5)	1.731 (2)
C(2)—C(3)	1.368 (3)	C(2)—C(6)	1.475 (3)
C(3)—C(4)	1.424 (3)	C(3)—C(13)	1.513 (3)
C(4)—C(5)	1.368 (3)	C(5)—C(20)	1.471 (3)
C(6)—C(7)	1.401 (3)	C(6)—C(11)	1.398 (3)
C(7)—C(8)	1.384 (3)	C(8)—C(9)	1.392 (3)
C(9)—C(10)	1.393 (3)	C(9)—C(12)	1.511 (3)
C(10)—C(11)	1.384 (3)	C(13)—C(14)	1.518 (3)
C(14)—C(15)	1.397 (3)	C(14)—C(19)	1.384 (3)
C(15)—C(16)	1.385 (3)	C(16)—C(17)	1.390 (3)
C(17)—C(18)	1.377 (3)	C(18)—C(19)	1.390 (3)
C(20)—C(21)	1.401 (3)	C(20)—C(25)	1.398 (3)
C(21)—C(22)	1.384 (3)	C(22)—C(23)	1.388 (3)
C(23)—C(24)	1.385 (3)	C(24)—C(25)	1.387 (3)
C(2)—S(1)—C(5)	92.3 (1)	S(1)—C(2)—C(3)	111.3 (2)
S(1)—C(2)—C(6)	119.8 (2)	C(3)—C(2)—C(6)	128.9 (2)
C(2)—C(3)—C(4)	112.0 (2)	C(2)—C(3)—C(13)	124.1 (2)
C(4)—C(3)—C(13)	123.7 (2)	C(3)—C(4)—C(5)	114.2 (2)
S(1)—C(5)—C(4)	110.2 (2)	S(1)—C(5)—C(20)	122.4 (2)
C(4)—C(5)—C(20)	127.4 (2)	C(2)—C(5)—C(7)	121.6 (2)
C(2)—C(6)—C(11)	120.4 (2)	C(7)—C(6)—C(11)	118.1 (2)
C(6)—C(7)—C(8)	120.7 (2)	C(7)—C(8)—C(9)	121.3 (2)
C(8)—C(9)—C(10)	118.0 (2)	C(8)—C(9)—C(12)	120.9 (2)
C(10)—C(9)—C(12)	121.1 (2)	C(9)—C(10)—C(11)	121.3 (2)
C(6)—C(11)—C(10)	120.7 (2)	C(3)—C(13)—C(14)	117.0 (2)
C(13)—C(14)—C(15)	118.6 (2)	C(13)—C(14)—C(19)	123.1 (2)
C(15)—C(14)—C(19)	118.3 (2)	C(14)—C(15)—C(16)	121.0 (2)
C(15)—C(16)—C(17)	120.1 (2)	C(16)—C(17)—C(18)	119.3 (2)
C(17)—C(18)—C(19)	120.6 (2)	C(14)—C(19)—C(18)	120.8 (2)
C(5)—C(20)—C(21)	121.9 (2)	C(5)—C(20)—C(25)	119.6 (2)
C(21)—C(20)—C(25)	118.5 (2)	C(20)—C(21)—C(22)	120.6 (2)
C(21)—C(22)—C(23)	120.3 (2)	C(22)—C(23)—C(24)	119.6 (2)
C(23)—C(24)—C(25)	120.5 (2)	C(20)—C(25)—C(24)	120.5 (2)

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 thiarubines 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