

1986). *SHELXS86* (Sheldrick, 1985) was used to solve the structure (using direct methods for C and B atoms). *SHELX76* (Sheldrick, 1976) was used to refine the structure. Molecular graphics were prepared using *SHELXTL/PC* (Sheldrick, 1990). Molecular-geometry calculations were carried out using *CALC* (Gould & Taylor, 1986).

We thank the EPSRC for support (TDM), the Callery Chemical Company for a generous gift of B₁₀H₁₄ and Dr R. O. Gould for helpful discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Gould, R. O. & Smith, D. E. (1986). *CADABS. Program for Data Reduction*. Univ. of Edinburgh, Scotland.
 Gould, R. O. & Taylor, P. (1986). *CALC. Program for Crystallographic Calculations*. Univ. of Edinburgh, Scotland.
 Kirillova, N. I., Klimova, T. V., Struchkov, Yu. T. & Stanko, V. I. (1979). *Izv. Akad. Nauk. SSSR Ser. Khim.* pp. 2481–2487.
 Kirillova, N. I., Klimova, T. V., Struchkov, Yu. T. & Stanko, V. I. (1981). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 600–604.
 Lewis, Z. G. & Welch, A. J. (1993). *Acta Cryst.* C49, 705–710.
 McGrath, T. D. & Welch, A. J. (1995a). *Acta Cryst.* C51, 646–649.
 McGrath, T. D. & Welch, A. J. (1995b). *Acta Cryst.* C51, 649–651.
 McGrath, T. D. & Welch, A. J. (1995c). *Acta Cryst.* C51, 654–657.
 Reid, B. D. (1992). PhD thesis, Univ. of Edinburgh, Scotland.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
 Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Zakharkin, L. I., Bregadze, V. I. & Okhlobytsin, O. Yu. (1965). *J. Organomet. Chem.* 4, 211–216.

Acta Cryst. (1995). C51, 654–657

Steric Effects in Heteroboranes. VI. 1-Ph-2-*i*-BuMe₂Si-1,2-*closo*-C₂B₁₀H₁₀

THOMAS D. MCGRATH AND ALAN J. WELCH†

Department of Chemistry, University of Edinburgh,
Edinburgh EH9 3JJ, Scotland

(Received 9 March 1994; accepted 3 August 1994)

Abstract

The new icosahedral *closo*-dicarbaborane 1-phenyl-2-(*tert*-butyldimethylsilyl)-1,2-dicarba-*closo*-dodecabor-

† Permanent address: Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland.

ane(12), C₁₄H₃₀B₁₀Si, has been prepared and its structure determined by a crystallographic study. Although some relief from steric crowding is achieved by a bending back of the cage-bound phenyl substituent, the bulk of the *tert*-butyldimethylsilyl group severely restricts any bending back of the silyl moiety. In consequence, some deformation of the cage has resulted. Most significantly, the C_{cage}—C_{cage} connectivity suffers a considerable extension: the C(1)—C(2) distance is 1.745 (6) Å, one of the longest observed in systems of this type.

Comment

In preceding contributions (McGrath & Welch, 1995a,b) we presented the molecular structures of 1-Ph-2-Me-1,2-*closo*-C₂B₁₀H₁₀ and 1-Ph-2-Br-1,2-*closo*-C₂B₁₀H₁₀, respectively, considered as possible (uncrowded and hence relatively undistorted) reference members of a series of 1-Ph-2-*R*-1,2-*closo*-C₂B₁₀H₁₀ carbaboranes in which the substituent *R* varies in steric requirement. The preceding paper (McGrath & Welch, 1995c) describes the structure of 1-Ph-2-Me₃Si-1,2-*closo*-C₂B₁₀H₁₀, which exhibits somewhat greater steric congestion. We now report the synthesis and molecular structure of the new carbaborane 1-Ph-2-*i*-BuMe₂Si-1,2-*closo*-C₂B₁₀H₁₀, (I), where intramolecular crowding to a greater degree is anticipated.

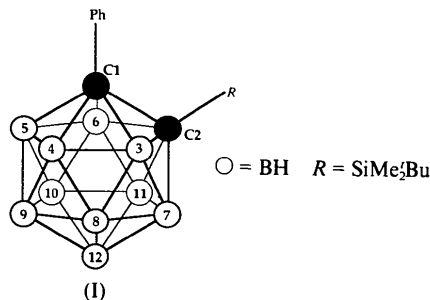


Fig. 1 shows a perspective view of a single molecule of the title compound and the atomic numbering scheme adopted. Note that for consistency we have again labelled the C_{cage} atom bearing the aryl moiety as C(1). The title compound crystallizes with no close intermolecular contacts.

Gross intramolecular crowding is substantially reduced by the disposition of the trialkylsilyl group, which is oriented such that the *i*-Bu group is *anti* to the phenyl ring. Although this brings the *i*-Bu moiety close to the carbaborane polyhedron, this situation appears to be less serious than unfavourable steric interaction arising from proximity to the phenyl substituent.

The C(1)—C(11) distance in 1-Ph-2-*i*-BuMe₂Si-1,2-*closo*-C₂B₁₀H₁₀ is 1.493 (5) Å, essentially the same as in 1-Ph-2-Br-1,2-*closo*-C₂B₁₀H₁₀ [1.494 (7) Å], but slightly shorter than in the 2-Me [1.514 (5) Å] and 2-

Me₃Si [1.513 (4) Å] analogues. There is some asymmetry in the angles C(11)—C(1)—X: the angle C(11)—C(1)—C(2) is 121.5 (3)°, whereas the other four angles all lie in the range 118.7 (3)–119.6 (3)°, demonstrating a bending back of the phenyl group away from the silyl moiety. However, in contrast to the situation in the 2-Me₃Si analogue, there is no evidence for 'bend back' of the phenyl ring at C(11) in the present compound, evidenced by angles at C(11) which sum to 360° and the fact that C(1) lies within 0.001 Å of the plane of the ring (the equivalent displacement in the 2-Me₃Si analogue is 0.047 Å). Equally, there is no bend back of the silyl group in 1-Ph-2-'BuMe₂Si-1,2-*closo*-C₂B₁₀H₁₀ to give rise to a wide C(1)—C(2)—Si(1) angle. Instead, the phenyl group is twisted about C(1)—C(11) resulting in $\theta = 7.6^\circ$ (Lewis & Welch, 1993; McGrath & Welch, 1995c) [C(16) moving towards the silyl group] and the 'BuMe₂Si group appears to bend slightly towards B(3). The torsion angle C(11)—C(1)—C(2)—Si(1) is 2.9 (5)°.

In the title compound, the single most important deformation by which the C₂B₁₀ polyhedron avoids overcrowding appears to be lengthening of the C(1)—C(2) bond to 1.745 (6) Å, the same as the hitherto longest reported C_{cage}—C_{cage} distance in an aryl 1,2-*closo*-dicarbododecaborane species with (simple) σ -bonded substituents (Lindeman, Khotina, Teplyakov, Struchkov & Korshak, 1988). The chemically most closely related analogue is 1-Ph-2-Me₃Si-1,2-*closo*-

C₂B₁₀H₁₀ (McGrath & Welch, 1995c) in which C(1)—C(2) is only 1.708 (4) Å. As C(1)—C(2) is stretched in the present compound it appears that the B(3)···B(6) distance shortens, being 2.838 (7) Å compared with 2.847 (6), 2.865 (10) and 2.845 (5) Å in the 2-Me, 2-Br and 2-Me₃Si analogues, respectively (McGrath & Welch, 1995a,b,c). This situation resembles that in *pseudocloso*-MC₂B₉ complexes (Lewis & Welch, 1992) and species whose geometries appear to be intermediate between *closo* and *pseudocloso* (Cowie, Reid, Watmough & Welch, 1994). However, detailed analysis of the deformation of the cage in the present case is not straightforward. In an icosahedron, torsion angles involving opposite edges of the type 1—2···9—12, 4—8···6—11 *etc.* are ideally 180°. We have calculated all 15 such unique angles in the present compound and the two which deviate most are C(1)—B(6)···B(8)—B(12) [177.5 (4)°] and C(2)—B(6)···B(8)—B(9) [−177.4 (4)°]. These equate, effectively, to rotations of the C(1)—B(6) and C(2)—B(6) edges such that C(1)—C(2) is extended and B(3)···B(6) is reduced. A further consequence of these apparent rotations is an asymmetry in certain chemically equivalent connectivities, *e.g.* C(1)—B(6) is less than C(1)—B(3) and C(2)—B(6) is quite significantly shorter than C(2)—B(3). Further analysis of this and related structures is outside the intended scope of this contribution, but will be published elsewhere.

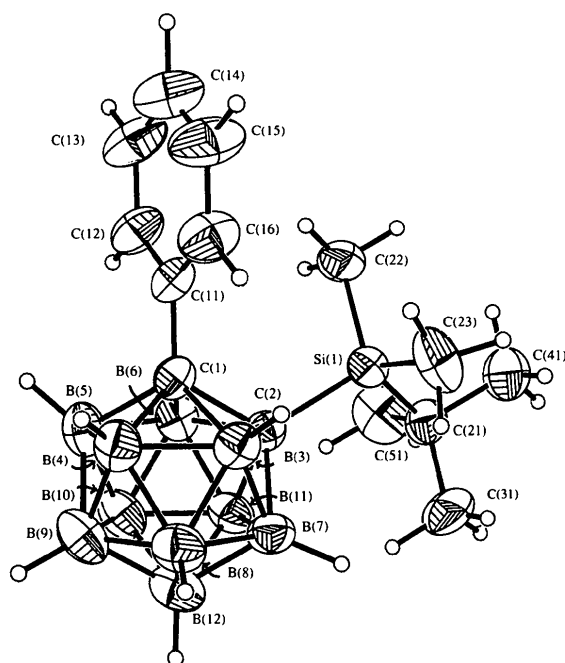


Fig. 1. A perspective view of 1-Ph-2-'BuMe₂Si-1,2-*closo*-C₂B₁₀H₁₀ with displacement ellipsoids at the 50% probability level for non-H atoms. H atoms are represented by spheres with arbitrary radii of 0.1 Å.

Experimental

Typically, 1-Ph-1,2-*closo*-C₂B₁₀H₁₁ (0.500 g, 2.27 mmol) (Reid, 1992) was dissolved in benzene (25 ml) and cooled to 273 K. MeLi (4.20 mmol, 3.0 ml of a 1.4 M solution in Et₂O) was added dropwise, and the mixture allowed to warm to room temperature. A solution of an excess of 'BuMe₂SiCl (0.800 g, 5.31 mmol) in benzene (5 ml) was added dropwise, and the mixture was heated to reflux for 44 h. Removal of volatiles *in vacuo* yielded an off-white waxy solid. The product was extracted into CH₂Cl₂ (5 × 50 ml) and the extract filtered and evaporated to yield the crude title compound as a white powder. The pure product was separated from unreacted PhC₂B₁₀H₁₁ by fractional crystallization (colourless blocks were obtained by slow diffusion of H₂O into a MeOH solution at 277 K); or, more reliably, by preparative thin-layer chromatography [silica gel; eluent CH₂Cl₂/*n*-hexane (1:19); product *R_f* = 0.7, PhC₂B₁₀H₁₁ *R_f* = 0.5]. Yield 0.231 g, 0.69 mmol, 31% (not optimized). Found: 49.25% C; 8.24% H. Calculated for C₁₄H₃₀B₁₀Si: 50.26% C; 9.04% H. IR (CH₂Cl₂): ν_{CH} = 2980, ν_{BH} = 2565 cm^{−1}. NMR (298 K, CDCl₃): δ (¹H) 7.65–7.26 (5H, C₆H₅), 0.90 [9H, Me₂SiC(CH₃)₃], −0.25 p.p.m. [6H, (CH₃)₂Si'Bu]; δ (¹¹B) 2.91 (1B), −2.13 (1B), −6.68 (4B), −8.54 (2B), −11.16 (2B) p.p.m. Crystals were obtained by the slow diffusion of water into a methanol solution at 277 K.

Crystal data

C₁₄H₃₀B₁₀Si
M_r = 334.58

Mo K α radiation
 λ = 0.71069 Å

Triclinic

$P\bar{1}$
 $a = 9.3854$ (19) Å
 $b = 10.2938$ (26) Å
 $c = 13.061$ (5) Å
 $\alpha = 68.607$ (25)°
 $\beta = 70.281$ (24)°
 $\gamma = 64.998$ (17)°
 $V = 1039.3$ (5) Å³
 $Z = 2$
 $D_x = 1.069$ Mg m⁻³

Cell parameters from 25 reflections
 $\theta = 7-12^\circ$
 $\mu = 0.103$ mm⁻¹
 $T = 293$ (1) K
 Block
 $0.45 \times 0.4 \times 0.35$ mm
 Colourless

Si(1)—C(23)	1.868 (6)	B(5)—B(10)	1.756 (8)
C(1)—C(2)	1.745 (6)	B(6)—B(10)	1.774 (8)
C(1)—B(3)	1.733 (7)	B(6)—B(11)	1.755 (7)
C(1)—B(4)	1.710 (7)	B(7)—B(8)	1.772 (8)
C(1)—B(5)	1.700 (7)	B(7)—B(11)	1.755 (8)
C(1)—B(6)	1.717 (7)	B(7)—B(12)	1.775 (8)
C(1)—C(11)	1.493 (5)	B(8)—B(9)	1.778 (9)
C(2)—B(3)	1.752 (7)	B(8)—B(12)	1.779 (9)
C(2)—B(6)	1.714 (7)	B(9)—B(10)	1.762 (9)
C(2)—B(7)	1.715 (7)	B(9)—B(12)	1.761 (9)
C(2)—B(11)	1.694 (7)	B(10)—B(11)	1.757 (8)
B(3)—B(4)	1.770 (8)	B(10)—B(12)	1.759 (9)
B(3)—B(7)	1.756 (7)	B(11)—B(12)	1.772 (8)
B(3)—B(8)	1.739 (8)	C(21)—C(31)	1.517 (8)
B(4)—B(5)	1.781 (8)	C(21)—C(41)	1.544 (8)
B(4)—B(8)	1.757 (8)	C(21)—C(51)	1.537 (8)
C(2)—Si(1)—C(21)	111.7 (2)	B(7)—B(8)—B(12)	60.0 (3)
C(2)—Si(1)—C(22)	110.6 (2)	B(9)—B(8)—B(12)	59.3 (3)
C(2)—Si(1)—C(23)	106.3 (2)	B(4)—B(9)—B(5)	59.9 (3)
C(21)—Si(1)—C(22)	108.4 (2)	B(4)—B(9)—B(8)	59.0 (3)
C(21)—Si(1)—C(23)	109.4 (2)	B(5)—B(9)—B(10)	59.5 (3)
C(22)—Si(1)—C(23)	110.4 (3)	B(8)—B(9)—B(12)	60.3 (4)
C(2)—C(1)—B(3)	60.5 (3)	B(10)—B(9)—B(12)	59.9 (4)
C(2)—C(1)—B(6)	59.4 (3)	B(5)—B(10)—B(6)	60.5 (3)
C(2)—C(1)—C(11)	121.5 (3)	B(5)—B(10)—B(9)	60.7 (3)
B(3)—C(1)—B(4)	61.9 (3)	B(6)—B(10)—B(11)	59.6 (3)
B(3)—C(1)—C(11)	119.6 (3)	B(9)—B(10)—B(12)	60.0 (4)
B(4)—C(1)—B(5)	62.9 (3)	B(11)—B(10)—B(12)	60.5 (3)
B(4)—C(1)—C(11)	118.7 (3)	C(2)—B(11)—B(6)	59.6 (3)
B(5)—C(1)—B(6)	62.7 (3)	C(2)—B(11)—B(7)	59.6 (3)
B(5)—C(1)—C(11)	119.1 (3)	B(6)—B(11)—B(10)	60.7 (3)
B(6)—C(1)—C(11)	119.1 (3)	B(7)—B(11)—B(12)	60.4 (3)
Si(1)—C(2)—C(1)	120.9 (3)	B(10)—B(11)—B(12)	59.8 (3)
Si(1)—C(2)—B(3)	117.4 (3)	B(7)—B(12)—B(8)	59.8 (3)
Si(1)—C(2)—B(6)	121.2 (3)	B(7)—B(12)—B(11)	59.3 (3)
Si(1)—C(2)—B(7)	120.2 (3)	C(1)—B(4)—B(3)	59.7 (3)
Si(1)—C(2)—B(11)	123.4 (3)	C(1)—B(4)—B(5)	58.3 (3)
C(1)—C(2)—B(3)	59.4 (3)	B(3)—B(4)—B(8)	59.1 (3)
C(1)—C(2)—B(6)	59.5 (3)	B(5)—B(4)—B(9)	59.7 (3)
B(3)—C(2)—B(7)	60.9 (3)	B(8)—B(4)—B(9)	60.2 (3)
B(6)—C(2)—B(11)	62.0 (3)	C(1)—B(5)—B(4)	58.8 (3)
B(7)—C(2)—B(11)	62.0 (3)	C(1)—B(5)—B(6)	59.1 (3)
C(1)—B(3)—C(2)	60.1 (3)	B(4)—B(5)—B(9)	60.4 (3)
C(1)—B(3)—B(4)	58.4 (3)	B(6)—B(5)—B(10)	60.2 (3)
C(2)—B(3)—B(7)	58.5 (3)	B(9)—B(5)—B(10)	59.8 (3)
B(4)—B(3)—B(8)	60.1 (3)	C(1)—B(6)—C(2)	61.1 (3)
B(7)—B(3)—B(8)	60.9 (3)	B(8)—B(12)—B(9)	60.3 (4)
C(1)—B(6)—B(5)	58.2 (3)	B(9)—B(12)—B(10)	60.1 (4)
C(2)—B(6)—B(11)	58.5 (3)	B(10)—B(12)—B(11)	59.7 (3)
B(5)—B(6)—B(10)	59.2 (3)	C(1)—C(11)—C(12)	119.2 (3)
B(10)—B(6)—B(11)	59.7 (3)	C(1)—C(11)—C(16)	120.8 (3)
C(2)—B(7)—B(3)	60.6 (3)	C(12)—C(11)—C(16)	120.0 (3)
C(2)—B(7)—B(11)	58.5 (3)	Si(1)—C(21)—C(31)	114.8 (4)
B(3)—B(7)—B(8)	59.1 (3)	Si(1)—C(21)—C(41)	106.2 (3)
B(8)—B(7)—B(12)	60.2 (3)	Si(1)—C(21)—C(51)	111.2 (4)
B(11)—B(7)—B(12)	60.3 (3)	C(31)—C(21)—C(41)	108.1 (4)
B(3)—B(8)—B(4)	60.8 (3)	C(31)—C(21)—C(51)	109.5 (4)
B(3)—B(8)—B(7)	60.0 (3)	C(41)—C(21)—C(51)	106.6 (4)
B(4)—B(8)—B(9)	60.8 (3)		

Data collection

CAD-4 diffractometer
 $\omega-2\theta$ scans
 Absorption correction: none
 3895 measured reflections
 3650 independent reflections
 2707 observed reflections
 $[F \geq 2.0\sigma(F)]$

$R_{\text{int}} = 0.0089$
 $\theta_{\text{max}} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 15$
 2 standard reflections
 frequency: 480 min
 intensity decay: <1%

Refinement

Refinement on F
 $R = 0.0836$
 $wR = 0.0939$
 $S = 1.351$
 2707 reflections
 230 parameters
 $w = 1/[\sigma^2(F) + 0.000930F^2]$

$\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

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

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

	x	y	z	U_{eq}
Si(1)	0.33786 (13)	0.73901 (13)	0.73148 (10)	0.0527 (9)
C(1)	0.2108 (4)	0.4874 (4)	0.7440 (3)	0.046 (3)
C(2)	0.1788 (4)	0.6754 (4)	0.7173 (3)	0.046 (3)
B(3)	0.2301 (6)	0.5959 (5)	0.6062 (4)	0.052 (4)
B(4)	0.1369 (6)	0.4604 (5)	0.6532 (4)	0.063 (4)
B(5)	0.0316 (6)	0.4580 (6)	0.7953 (4)	0.065 (4)
B(6)	0.0655 (5)	0.5899 (5)	0.8336 (4)	0.051 (3)
B(7)	0.0806 (6)	0.7707 (5)	0.6083 (4)	0.058 (4)
B(8)	0.0516 (6)	0.6379 (6)	0.5687 (4)	0.069 (4)
B(9)	-0.0758 (6)	0.5550 (7)	0.6852 (5)	0.078 (5)
B(10)	-0.1175 (6)	0.6332 (6)	0.7962 (5)	0.069 (4)
B(11)	-0.0224 (5)	0.7659 (5)	0.7488 (4)	0.057 (4)
B(12)	-0.1089 (6)	0.7452 (7)	0.6569 (5)	0.076 (5)
C(12)	0.3453 (3)	0.3001 (3)	0.8985 (2)	0.065 (4)
C(13)	0.4803 (3)	0.1896 (3)	0.9371 (2)	0.092 (5)
C(14)	0.6264 (3)	0.1486 (3)	0.8609 (2)	0.098 (5)
C(15)	0.6376 (3)	0.2180 (3)	0.7461 (2)	0.092 (5)
C(16)	0.5027 (3)	0.3284 (3)	0.7075 (2)	0.071 (4)
C(11)	0.3565 (3)	0.3695 (3)	0.7837 (2)	0.051 (3)
C(21)	0.2428 (5)	0.9294 (5)	0.7605 (4)	0.068 (4)
C(22)	0.4384 (6)	0.6052 (5)	0.8473 (4)	0.081 (4)
C(23)	0.4871 (5)	0.7477 (6)	0.5939 (4)	0.091 (5)
C(31)	0.1446 (7)	1.0499 (5)	0.6770 (5)	0.097 (5)
C(41)	0.3834 (6)	0.9745 (6)	0.7546 (5)	0.095 (5)
C(51)	0.1392 (6)	0.9225 (6)	0.8807 (5)	0.099 (5)

Table 2. Selected geometric parameters (Å, °)

Si(1)—C(2)	1.947 (4)	B(4)—B(9)	1.788 (9)
Si(1)—C(21)	1.902 (5)	B(5)—B(6)	1.779 (8)
Si(1)—C(22)	1.849 (5)	B(5)—B(9)	1.777 (9)

The C atoms of the phenyl ring were constrained to form a regular hexagon (C—C = 1.395 Å); cage, methyl and phenyl H atoms were set in idealized positions (C—H 1.08, B—H = 1.10 Å). All H atoms were refined with a common isotropic displacement parameter [$U_{\text{iso}} = 0.093$ (3) Å² at convergence].

Data reduction and corrections for Lorentz and polarization effects were performed using *CADABS* (Gould & Smith, 1986). *SHELXS86* (Sheldrick, 1985) was used to solve the structure (using direct methods for Si, C and B atoms). *SHELX76* (Sheldrick, 1976) was used to locate cage H atoms (by difference Fourier syntheses) and refine the structure. Molecular graphics were prepared using *SHELXTL/PC* (Sheldrick, 1990). Molecular-geometry calculations were made using *CALC* (Gould & Taylor, 1986).

We thank the EPSRC for support (TDM) and the Callery Chemical Company for a generous gift of B₁₀H₁₄.

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.

References

- Cowie, J., Reid, B. D., Watmough, J. M. S. & Welch, A. J. (1994). *J. Organomet. Chem.* **481**, 283–293.
- Gould, R. O. & Smith, D. E. (1986). *CADABS. Program for Data Reduction*. Univ. of Edinburgh, Scotland.
- Gould, R. O. & Taylor, P. (1986). *CALC. Program for Crystallographic Calculations*. Univ. of Edinburgh, Scotland.
- Lewis, Z. G. & Welch, A. J. (1992). *J. Organomet. Chem.* **430**, C45–C50.
- Lewis, Z. G. & Welch, A. J. (1993). *Acta Cryst.* **C49**, 705–710.
- Lindeman, S. V., Khotina, I. A., Teplyakov, M. M., Struchkov, Yu. T. & Korshak, V. V. (1988). *Makromol. Chem.* **189**, 471–493.
- McGrath, T. D. & Welch, A. J. (1995a). *Acta Cryst.* **C51**, 646–649.
- McGrath, T. D. & Welch, A. J. (1995b). *Acta Cryst.* **C51**, 649–651.
- McGrath, T. D. & Welch, A. J. (1995c). *Acta Cryst.* **C51**, 651–654.
- Reid, B. D. (1992). PhD thesis, Univ. of Edinburgh, Scotland.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). **C51**, 657–659

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

FILLMORE FREEMAN, HENGYAO LU AND JOSEPH W. ZILLER

Department of Chemistry, University of California, Irvine, California 92717, USA

ELOY RODRIGUEZ

Phytochemistry and Toxicology Laboratory, Department of Developmental and Cell Biology, University of California, Irvine, California 92717, USA

(Received 2 November 1992; accepted 5 July 1994)

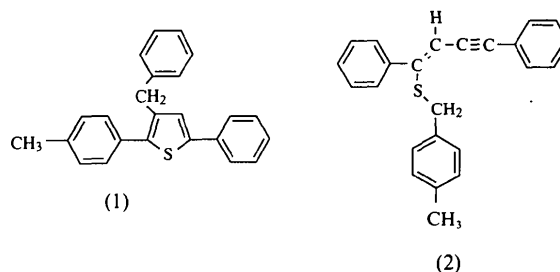
Abstract

The crystal structure of 3-benzyl-5-phenyl-2-*p*-tolylthiophene, C₂₄H₂₀S, 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-butadiyne 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-