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

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

	x	y	z	U_{eq}
O(1)	0.2981 (2)	0.6408 (2)	0.8687 (2)	0.074 (1)
O(2)	0.4848 (2)	0.5308 (2)	0.8697 (2)	0.086 (1)
C(1)	0.5607 (2)	0.6403 (2)	0.8512 (2)	0.062 (1)
C(2)	0.5101 (2)	0.7421 (2)	0.8373 (2)	0.063 (1)
C(3)	0.3754 (2)	0.7363 (2)	0.8417 (2)	0.060 (1)
C(11)	0.6987 (2)	0.6384 (2)	0.8466 (2)	0.067 (1)
C(12)	0.7418 (3)	0.5332 (3)	0.8775 (3)	0.086 (1)
C(13)	0.8724 (4)	0.5328 (4)	0.8752 (3)	0.107 (1)
C(14)	0.9583 (4)	0.6338 (4)	0.8437 (3)	0.109 (1)
C(15)	0.9165 (3)	0.7364 (4)	0.8117 (3)	0.101 (4)
C(16)	0.7861 (3)	0.7391 (3)	0.8131 (3)	0.082 (1)
C(21)	0.2757 (2)	0.9040 (2)	1.0250 (2)	0.060 (1)
C(22)	0.1651 (3)	0.9046 (2)	1.0833 (2)	0.074 (1)
C(23)	0.1642 (3)	0.8829 (3)	1.2026 (3)	0.088 (1)
C(24)	0.2712 (4)	0.8601 (3)	1.2643 (3)	0.090 (1)
C(25)	0.3824 (3)	0.8613 (3)	1.2085 (2)	0.083 (1)
C(26)	0.3841 (3)	0.8833 (2)	1.0900 (2)	0.069 (1)
C(31)	0.3233 (2)	0.8465 (2)	0.8099 (2)	0.057 (1)
C(32)	0.3214 (2)	0.8690 (2)	0.6893 (2)	0.060 (1)
C(33)	0.2742 (2)	0.9700 (2)	0.6558 (2)	0.062 (1)
C(34)	0.2276 (2)	1.0501 (2)	0.7393 (2)	0.060 (1)
C(35)	0.2294 (2)	1.0252 (2)	0.8584 (2)	0.061 (1)
C(36)	0.2758 (2)	0.9252 (2)	0.8959 (2)	0.057 (1)
C(41)	0.3653 (2)	0.7819 (2)	0.5957 (2)	0.061 (1)
C(42)	0.2911 (3)	0.6598 (2)	0.5566 (2)	0.080 (1)
C(43)	0.3312 (4)	0.5780 (3)	0.4711 (3)	0.096 (1)
C(44)	0.4473 (4)	0.6178 (3)	0.4258 (3)	0.091 (1)
C(45)	0.5213 (3)	0.7377 (3)	0.4634 (2)	0.086 (1)
C(46)	0.4813 (3)	0.8213 (3)	0.5475 (2)	0.076 (1)
C(51)	0.1747 (2)	1.1566 (2)	0.7018 (2)	0.064 (1)
C(52)	0.1117 (3)	1.1466 (3)	0.5865 (3)	0.078 (1)
C(53)	0.0557 (3)	1.2426 (3)	0.5523 (3)	0.095 (1)
C(54)	0.0638 (3)	1.3504 (3)	0.6347 (4)	0.100 (1)
C(55)	0.1269 (3)	1.3626 (3)	0.7480 (4)	0.097 (1)
C(56)	0.1830 (3)	1.2677 (2)	0.7821 (3)	0.082 (1)

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

C(1)—C(2)	1.355 (3)	C(3)—C(31)	1.498 (3)
C(2)—C(3)	1.421 (3)	C(1)—O(2)	1.327 (3)
C(1)—C(11)	1.474 (3)	C(3)—O(1)	1.254 (3)
C(11)—C(1)—C(2)	125.1 (2)	C(1)—C(2)—C(3)	121.9 (2)
C(11)—C(1)—O(2)	114.4 (2)	C(2)—C(3)—O(1)	122.2 (2)
O(2)—C(1)—C(2)	120.5 (2)	C(31)—C(3)—O(1)	118.9 (2)

Programs used: *SHELXS*86 (Sheldrick, 1985) and *SHELXL* (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71706 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1058]

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Methyl 3-(1,3-Benzothiazol-2-yldithio)-propanoate, $C_{11}H_{11}NO_2S_3$

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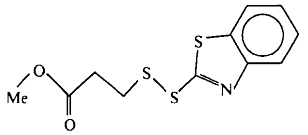
Abstract

The benzothiazole unit is similar to those found in other derivatives, *e.g.* bis(1,3-benzothiazol-2-yl) disulfide [Zingaro & Meyers (1980). *Cryst. Struct. Commun.* **9**, 1167–1172] or 2-methylthio-1,3-benzothiazole [Wheatley (1962). *J. Chem. Soc.* p. 3636]. The S atoms of the disulfide group and the condensed ring system are nearly coplanar (torsion angle τ_{NCSS} + 9.3°). The overall conformation of the title compound is almost linear.

Comment

3-(1,3-Benzothiazol-2-yldithio)propanoic acid methyl ester (1) may be prepared by condensation of 2-mercaptobenzothiazole with 2-(methoxycarbonyl)ethyl sulfenic acid, $HOS(CH_2)_2CO_2CH_3$ (Bachi, Gross & Frolow, 1982).



(1)

The structure determination of (1) was undertaken in order to analyse whether there is any interaction between the carboxyl group and the disulfide and benzothiazole units. This interaction is of interest with respect to the reactivity of (1) as an accelerator in rubber vulcanization. However, no such inter- or intramolecular interaction of the carboxyl group was found. The molecule of (1) adopts a stretched conformation. Most bond distances and valence angles are comparable to those of other benzothiazole derivatives. The ring system is planar and the two S atoms linked to the ring system are nearly coplanar with the ring plane, as with bis(1,3-benzothiazol-2-yl) disulfide (2) (Zingaro & Meyers, 1980) [the torsion angle τ_{NCSS} is +9.3 (3)° in (1) and +9.7 (3)° in (2)]. There are some differences between the values found for 2-mercaptobenzothiazole (3) (Radha, 1985) and those reported for (1). In (1), the C(5)—S(2) distance is remarkably longer [1.756 (3) Å in (1) *cf.* 1.657 (3) Å in (3)] and the C(5)—N—C(6) angle is smaller [109.5 (3)° in (1) *cf.* 116.7 (2)° in (3)]. This is consistent with the observation that the solid-state structure of (3) is that of the tautomer —NH—C(S)—, rather than —N=C(SH)— as the accepted nomenclature of (3) suggests.

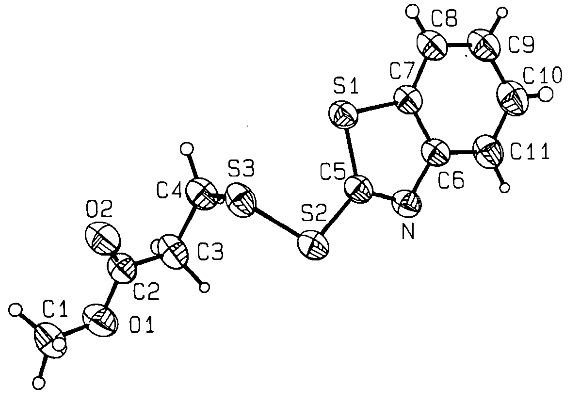


Fig. 1. Perspective view of $C_{11}H_{11}NO_2S_3$ with the numbering of the atoms.

Experimental

Crystal data

$C_{11}H_{11}NO_2S_3$
M_r = 285.41
Monoclinic
$P2_1/a$
a = 8.310 (2) Å
b = 16.473 (7) Å
c = 10.320 (5) Å
β = 113.60 (3)°
V = 1295 (1) Å^3
Z = 4
D_x = 1.47 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 4.3-17.6°
μ = 0.540 mm^{-1}
T = 293 K
Flattened
0.4 × 0.3 × 0.2 mm
Colourless
Crystal source: CH_2Cl_2 solution saturated at 293 K

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min}$ = 0.76, $T_{\max}$ = 1.13
2839 measured reflections
2751 independent reflections
2151 observed reflections [$I \geq 2\sigma(I)$]

$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 20$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 100 reflections
intensity variation: <1.5%

Refinement

Refinement on F
R = 0.0422
wR = 0.0422
S = 0.89
2151 reflections
186 parameters
Unit weights applied

$(\Delta/\sigma)_{\max}$ = 0.006
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.26 e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968)

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	$U_{\rm eq}$
S(1)	0.36113 (11)	0.06147 (5)	0.56517 (9)	0.0416 (3)
S(2)	0.16876 (13)	0.10191 (6)	0.25022 (10)	0.0514 (3)
S(3)	−0.00849 (12)	0.03763 (6)	0.29833 (11)	0.0518 (3)
O(1)	−0.5127 (4)	0.1650 (2)	0.0406 (3)	0.0627 (9)
O(2)	−0.4400 (3)	0.05201 (16)	0.1700 (3)	0.0598 (9)
N	0.4740 (4)	0.16231 (16)	0.4257 (3)	0.0408 (9)
C(1)	−0.6739 (6)	0.1258 (3)	−0.0530 (5)	0.0727 (2)
C(2)	−0.4070 (5)	0.1204 (2)	0.1484 (4)	0.0449 (11)
C(3)	−0.2470 (5)	0.1672 (2)	0.2379 (4)	0.0517 (12)
C(4)	−0.1168 (5)	0.1169 (2)	0.3569 (4)	0.0501 (12)
C(5)	0.3460 (4)	0.1141 (2)	0.4147 (3)	0.0389 (10)
C(6)	0.6002 (4)	0.1608 (2)	0.5640 (3)	0.0374 (10)
C(7)	0.5623 (4)	0.1087 (2)	0.6556 (3)	0.0381 (10)
C(8)	0.6760 (5)	0.1020 (2)	0.7973 (4)	0.0475 (11)
C(9)	0.8264 (5)	0.1478 (3)	0.8440 (4)	0.0572 (14)
C(10)	0.8663 (5)	0.1998 (3)	0.7542 (5)	0.0561 (14)
C(11)	0.7538 (5)	0.2068 (2)	0.6145 (4)	0.0485 (12)

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

S(1)—C(5)	1.738 (3)	S(1)—C(7)	1.738 (3)
S(2)—C(5)	1.756 (3)	S(2)—S(3)	2.0290 (15)
S(3)—C(4)	1.820 (4)	O(1)—C(2)	1.328 (5)
O(1)—C(1)	1.452 (6)	O(2)—C(2)	1.202 (4)
N—C(5)	1.294 (5)	N—C(6)	1.391 (4)
C(2)—C(3)	1.502 (6)	C(3)—C(4)	1.517 (5)
C(6)—C(7)	1.402 (4)	C(6)—C(11)	1.392 (5)
C(7)—C(8)	1.391 (5)	C(8)—C(9)	1.371 (6)
C(9)—C(10)	1.395 (7)	C(10)—C(11)	1.373 (6)
C(5)—S(1)—C(7)	88.02 (15)	C(5)—S(2)—S(3)	103.47 (12)
S(2)—S(3)—C(4)	102.07 (14)	C(2)—O(1)—C(1)	115.8 (3)
C(5)—N—C(6)	109.5 (3)	C(3)—C(2)—O(1)	110.8 (3)
C(3)—C(2)—O(2)	125.7 (3)	O(1)—C(2)—O(2)	123.4 (4)
C(4)—C(3)—C(2)	112.3 (3)	S(3)—C(4)—C(3)	114.2 (3)
S(1)—C(5)—S(2)	122.5 (2)	S(1)—C(5)—N	117.7 (2)
S(2)—C(5)—N	119.7 (2)	N—C(6)—C(7)	114.9 (3)
N—C(6)—C(11)	125.1 (3)	C(7)—C(6)—C(11)	120.0 (3)
S(1)—C(7)—C(6)	109.9 (2)	S(1)—C(7)—C(8)	129.1 (3)
C(6)—C(7)—C(8)	121.1 (3)	C(7)—C(8)—C(9)	117.7 (3)
C(8)—C(9)—C(10)	122.0 (4)	C(9)—C(10)—C(11)	120.4 (4)
C(6)—C(11)—C(10)	118.9 (4)		
C(5)—S(2)—S(3)—C(4)	82.9 (2)	N—C(6)—C(7)—S(1)	−0.7 (4)
S(1)—C(5)—S(2)—S(3)	11.3 (2)	C(6)—C(7)—S(1)—C(5)	0.3 (3)
N—C(5)—S(2)—S(3)	−170.7 (3)	C(8)—C(7)—S(1)—C(5)	178.7 (4)
S(2)—C(5)—S(1)—C(7)	178.2 (2)	S(1)—C(7)—C(8)—C(9)	−178.4 (3)
S(1)—C(5)—N—C(6)	−0.5 (4)	C(3)—C(2)—O(1)—C(1)	−179.6 (3)
C(7)—C(6)—N—C(5)	0.8 (4)	C(3)—C(4)—S(3)—S(2)	75.7 (3)
C(11)—C(6)—C(7)—S(1)	178.6 (3)		

For the benzo H atoms H(81)-H(111), all atomic parameters were refined; the remaining H atoms were not refined. *SHELXS*86 (Sheldrick, 1985) was used for structure solution, *SHELX*76 (Sheldrick, 1976) for structure refinement, *PLATON* (Spek, 1982) for geometrical calculations and *ORTEP*II (Johnson, 1976) for preparation of the figure.

We are grateful to Professor Joachim Pickardt for the data collection and determining the cell dimensions. Support by Bayer AG and Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71624 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1057]

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Molecular Structure and Absolute Configuration of (*P*)-7-Phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole

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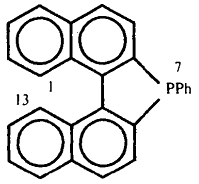
Abstract

An X-ray diffraction study of a crystal of the title compound, $C_{26}H_{17}P$, showed that the naphthyl rings bend away from each other and deviate significantly from planarity; the whole molecule has helical chirality. The crystal chosen for the crystallographic analysis had *P* absolute configuration, indicating that spontaneous resolution had occurred during crystallization.

Comment

Many effective and useful asymmetric catalyses using optically active transition-metal complexes have been developed (Nugent, RajanBabu & Burk, 1993). The 2,2′-binaphthyl group is considered to be a highly suitable moiety for endowing ligands with effective chirality (Kagan, 1985). In the course of our studies on the development of new chiral ligands for effective asymmetric catalysis using transition-metal complex catalysts, we have synthesized a monodentate phosphine ligand, (±)-7-phenyldinaphtho[2,1-*b*;1′,2′-*d*]phosphole (I), representing a new type of chiral phosphine based on the binaphthyl moiety, and have made a preliminary report of its preparation, properties and X-ray analysis (Tani, Tashiro & Yamagata, 1992). Recently, the preparation and properties of the same compound and the X-ray crystallographic analysis of the arsenic analogue were reported (Watson, Willis & Wild, 1993). Here we report the full details of the results of the crystallographic analysis of the title compound for comparison with that of the arsenic analogue.



(I)

The phosphine (I) was prepared from the reaction of dichlorophenylphosphine with a slight excess of (±)-2,2′-dilithio-1,1′-binaphthyl, analogously to the method reported in the literature (Watson, Willis & Wild, 1993), and was isolated in 60% yield after crystallization from ethanol as pale yellow crystals, m.p. 430.5–432 K. For the X-ray crystallographic study, a single crystal grown from methanol was used.

The molecular structure and a stereoscopic view are shown in Figs. 1 and 2, respectively. The molecular structure and the crystal dimensions are similar to those reported for the arsenic analogue (Watson, Willis & Wild, 1993). Although the five-membered phosphole ring and each benzene ring in the binaphthyl moieties are almost planar, the naphthyl rings are bent significantly away from each other, making the compound chiral. The maximum shifts from the calculated mean planes are 0.084 (4) Å for the phosphole five-membered ring and 0.075 (4) Å for the benzene rings. The crystal chosen for the X-ray analysis belonged to the enantiomeric space group $P2_1$ and the absolute configuration was determined to be *P*. This result indicates that spontaneous resolution had occurred during crystallization, although compound (I) racemized easily in solution