

polarization effects, but not for absorption. The scan speed was 3–12° min<sup>-1</sup> with width (1.2 + 0.14tanθ)°. The structures were solved by direct methods and refined by anisotropic full-matrix least squares. All the H atoms were found from Δρ maps and refined isotropically.

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980) for (2) and *SIR92* (Altomare *et al.*, 1994) for (4). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965), *PLUTO* (Motherwell & Clegg, 1976). Programs for checking the space group of (2): *TRACER* (Lawton & Jacobson, 1965), *NEWLAT* (Mugnoli, 1985), *LEPAGE* (Spek, 1988), *MISSYM* (Le Page, 1987) and the *SYMMOL* option of *PARST* (Nardelli, 1983a). Software used for geometrical calculations and to prepare material for publication: *PARST*, *PARSTCIF* (Nardelli, 1991). The calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffattometrica del CNR (Parma) and on a COMPAQ-486c portable computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
- Autodesk Inc. (1992). *HYPERCHEM*. Version 2.0. Autodesk Inc., 2320 Marinship Way, Sansalito, CA 94965, USA.
- Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffratometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo 220*. Internal Report 1–3/79. Centro di Studio per la Strutturistica Diffattometrica del CNR, Parma, Italy.
- Caubère, P. (1991). *Rev. Heteroatom. Chem.* **4**, 78–139.
- Caubère, C., Caubère, P., Ianelli, S., Nardelli, M. & Jamart-Grégoire, B. (1994). *Tetrahedron*, **54**, 11903–11920.
- Caubère, C., Caubère, P., Renard, P., Bizot-Espiart, J. G. & Jamart-Grégoire, B. (1993). *Tetrahedron Lett.* **34**, 6889–6892.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Dunitz, J. D. & Withe, D. N. J. (1973). *Acta Cryst.* **A29**, 148–150.
- Hendrickson, J. B. (1967). *J. Am. Chem. Soc.* **89**, 7036–7043.
- Hogle, G., Treglich, W. & Vorbroggen, H. (1972). *Synthesis*, pp. 619–621.
- Jamart-Grégoire, B., Brosse, N., Ianelli, S., Nardelli, M. & Caubère, P. (1993). *J. Org. Chem.* **58**, 4572–4578.
- Jamart-Grégoire, B., Léger, C. & Caubère, P. (1990). *Tetrahedron Lett.* **31**, 7599–7602.
- Jamart-Grégoire, B., Mercier-Girardot, S., Ianelli, S., Nardelli, M. & Caubère, P. (1995a). *Synlett*, **7**, 742–744.
- Jamart-Grégoire, B., Mercier-Girardot, S., Ianelli, S., Nardelli, M. & Caubère, P. (1995b). *Tetrahedron*, **51**, 1973–1984.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Lalloz, L. & Caubère, P. (1975). *J. Chem. Soc. Chem. Commun.* p. 745.
- Lawton, S. L. & Jacobson, R. A. (1965). *The Reduced Cell and its Crystallographic Applications*. Ames Laboratory. Available from the Clearinghouse for Federal Scientific and Technical Information, National Institute of Standards and Technology, US Department of Commerce, Springfield, Virginia, USA.
- Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* **A30**, 580–589.
- Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
- Minato, M., Yamamoto, K. & Tsuji, J. (1990). *J. Org. Chem.* **55**, 766–768.
- Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
- Mugnoli, A. (1985). *J. Appl. Cryst.* **18**, 183–184.
- Nardelli, M. (1983a). *Comput. Chem.* **7**, 95–98.
- Nardelli, M. (1983b). *Acta Cryst.* **C39**, 1141–1142.
- Nardelli, M. (1991). *PARSTCIF. Program for Creating a CIF from the Output of PARST*. University of Parma, Italy.
- Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Serena Software (1989). *PCMODEL*. Version 4.0. Serena Software, Bloomington, IN 47402–3076, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.
- Trueblood, K. N. (1984). *THMV. Program for Thermal Motion Analysis*. University of California, Los Angeles, USA.
- Acta Cryst.* (1996). **C52**, 1248–1250

## 2,3,6,7-Tetrakis(methylthio)benzo[b]thiophene

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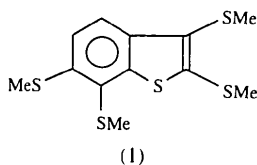
## Abstract

Crystals of the title compound, C<sub>12</sub>H<sub>14</sub>S<sub>5</sub>, are composed of independent molecules separated by normal van der Waals distances. The benzothiophene moiety is essentially planar and substituted by four methylthio groups, two of which, those at positions 2 and 6, lie almost in the plane, with the remaining two, those at positions 3 and 7, lying almost perpendicular to the plane. The mean values of the important bond distances are S—C<sub>sp<sup>3</sup></sub>, 1.805 (17) and S—C<sub>sp<sup>2</sup></sub>, 1.767 (19) Å.

## Comment

The one-step thioalkylation of heteroaromatic compounds is a desirable process as it can lead to the for-

mation of heteroaromatic thiols by reduction of the S atom. Our experiments involving benzo[*b*]thiophene and excess methyl disulfide yielded the title compound, (1), as a yellow solid. An X-ray identification of (1) was needed as the 2,3,4,5-tetrakis(methylthio) and 2,3,6,7-tetrakis(methylthio) compounds would give similar  $^1\text{H}$  and  $^{13}\text{C}$  spectra. The present report describes the crystal structure of compound (1).



An ORTEPII diagram (Johnson, 1976) of (1) is presented in Fig. 1, along with the atomic numbering scheme. The molecular dimensions in the benzothiofene moiety involving C atoms are normal with mean bond distances  $\text{C}-\text{C}_{\text{aromatic}}$  1.38 (3),  $\text{C}_{\text{sp}^2}-\text{C}_{\text{sp}^2}$  1.440 (12) and  $\text{C}=\text{C}$  1.353 (12) Å, while the  $\text{S}-\text{C}_{\text{sp}^2}$  distances of 1.757 (9) and 1.733 (8) Å are significantly longer than those reported for 2,3-bis(ethylsulfonyl)-benzo[*b*]thiophene [mean 1.725 (1) Å] (Parvez, Mesher & Clark, 1996). The remaining  $\text{S}-\text{C}$  distances, with mean values for  $\text{S}-\text{C}_{\text{sp}^2}$  and  $\text{S}-\text{C}_{\text{sp}^3}$  of 1.767 (19) and 1.805 (17) Å, respectively, are normal (Allen *et al.* 1992). The benzothiofene moiety is essentially planar within experimental error, with a maximum deviation of 0.019 (12) Å for the C7a atom. There are four methylthio groups attached to the benzothiofene moiety, two of which, those at positions 2 and 6, are almost coplanar with it; the dihedral angles between the benzothiofene plane and these groups are 7.9 (8) and 6.5 (9)°, respectively. The methylthio groups at positions 3 and 7 are almost perpendicular to the benzothiofene

plane, with dihedral angles of 96.7 (8) and 80.7 (8)°, respectively.

The crystal structure of (1) is composed of discrete molecules separated by normal van der Waals distances.

## Experimental

The title compound was prepared as previously described by Clark, Mesher & Primak (1996). Crystals were obtained as yellow plates by evaporation from a solution of hexanes/THF (95:5).

### Crystal data

$\text{C}_{12}\text{H}_{14}\text{S}_5$   
 $M_r = 318.54$   
 Monoclinic  
 $P2_1/n$   
 $a = 13.131 (3) \text{ \AA}$   
 $b = 7.541 (1) \text{ \AA}$   
 $c = 14.758 (3) \text{ \AA}$   
 $\beta = 96.03 (2)^\circ$   
 $V = 1453.3 (4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.456 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 10-15^\circ$   
 $\mu = 0.772 \text{ mm}^{-1}$   
 $T = 170 \text{ K}$   
 Plate  
 $0.34 \times 0.30 \times 0.10 \text{ mm}$   
 Yellow

### Data collection

Rigaku AFC-6S diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 $\psi$  scan (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.62$ ,  $T_{\max} = 1.00$   
 2910 measured reflections  
 2785 independent reflections  
 1365 observed reflections  
 $[I > 3\sigma(I)]$

$R_{\text{int}} = 0.0272$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = 0 \rightarrow 15$   
 $k = 0 \rightarrow 8$   
 $l = -17 \rightarrow 17$   
 3 standard reflections monitored every 200 reflections  
 intensity decay: 4.4%

### Refinement

Refinement on  $F$   
 $R = 0.0638$   
 $wR = 0.0641$   
 $S = 2.838$   
 1365 reflections  
 154 parameters  
 H atoms riding with C—H  
 0.95 Å  
 $w = 1/[\sigma^2(F_o) + 0.015(F_\sigma^2)]$

$(\Delta/\sigma)_{\text{max}} = 0.0248$   
 $\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
S1	0.0698 (2)	-0.1934 (3)	0.4565 (2)	0.0362 (7)
S2	0.1843 (2)	-0.1592 (4)	0.6494 (2)	0.0575 (9)
S3	0.3154 (2)	0.1576 (3)	0.5569 (2)	0.0443 (8)
S4	0.0433 (2)	0.0689 (3)	0.1068 (2)	0.0355 (7)
S5	-0.0426 (2)	-0.1995 (3)	0.2434 (2)	0.0350 (7)
C2	0.1606 (6)	-0.0929 (11)	0.5363 (5)	0.030 (3)
C3	0.2111 (6)	0.0395 (11)	0.4982 (6)	0.030 (3)

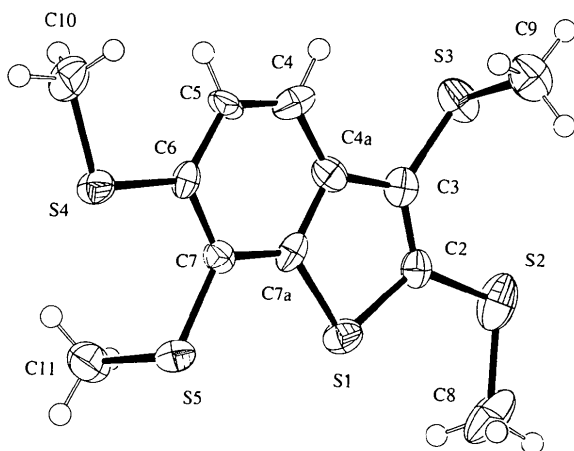


Fig. 1. An ORTEPII view (Johnson, 1976) of the title compound with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

C4a	0.1799 (6)	0.0688 (12)	0.4029 (6)	0.031 (3)
C4	0.2133 (7)	0.1846 (12)	0.3415 (6)	0.036 (3)
C5	0.1756 (6)	0.1858 (12)	0.2550 (6)	0.035 (3)
C6	0.0992 (6)	0.0701 (11)	0.2208 (5)	0.026 (2)
C7	0.0606 (6)	-0.0530 (11)	0.2801 (6)	0.029 (2)
C7a	0.1028 (7)	-0.0513 (12)	0.3721 (6)	0.031 (3)
C8	0.0810 (9)	-0.3182 (15)	0.6577 (7)	0.067 (4)
C9	0.2527 (7)	0.3571 (13)	0.5882 (7)	0.049 (3)
C10	0.1200 (8)	0.2245 (13)	0.0537 (6)	0.050 (3)
C11	0.0254 (8)	-0.3734 (13)	0.1896 (7)	0.049 (3)

Table 2. Selected geometric parameters (Å, °)

S1—C2	1.757 (9)	S4—C6	1.763 (8)
S1—C7a	1.733 (8)	S4—C10	1.781 (10)
S2—C2	1.739 (8)	S5—C7	1.787 (9)
S2—C8	1.824 (12)	S5—C11	1.816 (10)
S3—C3	1.780 (9)	C2—C3	1.353 (12)
S3—C9	1.798 (9)	C3—C4a	1.440 (12)
C2—S1—C7a	90.7 (4)	C2—C3—C4a	114.7 (8)
C2—S2—C8	101.2 (5)	C3—C4a—C4	132.0 (9)
C3—S3—C9	101.2 (4)	C3—C4a—C7a	109.9 (8)
C6—S4—C10	102.6 (4)	S4—C6—C5	124.4 (7)
C7—S5—C11	100.8 (4)	S4—C6—C7	116.7 (7)
S1—C2—S2	124.0 (5)	S5—C7—C6	122.0 (6)
S1—C2—C3	111.5 (6)	S5—C7—C7a	120.4 (7)
S2—C2—C3	124.4 (7)	S1—C7a—C4a	113.2 (6)
S3—C3—C2	123.5 (7)	S1—C7a—C7	125.7 (7)
S3—C3—C4a	121.6 (7)		

The space group was uniquely determined to be  $P2_1/n$  from the systematic absences:  $h0l$ ,  $h + l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ .

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFD Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a stereoview of the unit-cell packing, have been deposited with the IUCr (Reference: FG1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 685–844. Dordrecht: Kluwer Academic Publishers.
- Clark, P. D., Mesher, S. T. E. & Primak, A. (1996). *Phosphorus Sulfur Silicon*. In the press.
- Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCI/AFD Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

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## S-[(Dicyclohexylamino)(phenyl)(1-pyrrolidinyl)phosphinimino]cyclotrithiazene

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## Abstract

In the title compound, (C<sub>6</sub>H<sub>5</sub>)(NC<sub>4</sub>H<sub>8</sub>)[N(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]PN-(S<sub>3</sub>N<sub>3</sub>), the cyclotrithiazene ring adopts a distorted-chair conformation. The tricoordinated S atom has a maximum deviation of 0.658 (6) Å from the mean plane of the other five atoms of the S<sub>3</sub>N<sub>3</sub> ring.

## Comment

Very few crystal structure data on monosubstituted cyclotrithiazene derivatives are available (Chivers, Oakley, Cordes & Pennington, 1981; Elias, Sudheendra Rao & Varghese, 1990; Holt & Holt, 1974; Holt, Holt & Watson, 1977). Phosphiniminocyclotrithiazenes, which are examples of 8π-electron systems, provide an opportunity to study experimentally the effects of varying the substituents attached to phosphorus on the bonding pattern and the conformation of the heterocycle. A detailed and systematic investigation has been undertaken and the present work on the title compound, (I), forms a part of this study.

