Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Sodium thiophenolate *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

**Erik Heigel,* Hans Bock, Volker Krenzel and Mark Sievert**

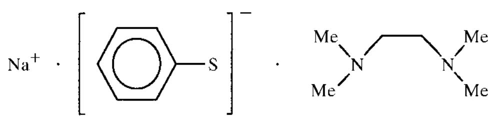
Chemische Institute der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany
Correspondence e-mail: erik.heigel@gmx.de

Received 7 August 2000
Accepted 7 November 2000

The title compound, $Na^+\cdot C_6H_5S^-\cdot C_6H_{16}N_2$, forms lipophilically wrapped infinite sodium chains along the *a* axis. Each sodium cation is coordinated by three thiophenolate S atoms and two N centres of one tetramethylethylenediamine molecule.

## Comment

Strong phenyl–phenyl interactions stabilize the dimer of tris(phenylthio)methane, even in the gas phase (Bock *et al.*, 2001). An attempt to add a negative charge by reduction with sodium metal failed due to the decomposition of tris(phenylthio)methane to thiophenolate, which crystallizes in the presence of a sodium metal mirror and tetramethylethylenediamine to give another lipophilically wrapped polyion aggregate, (I) (Bock, Hauck *et al.*, 1995; Bock, Schödel *et al.*, 1995; Bock *et al.*, 1998, 2000; Bock & Heigel, 2000*a*,*b*).



(I)

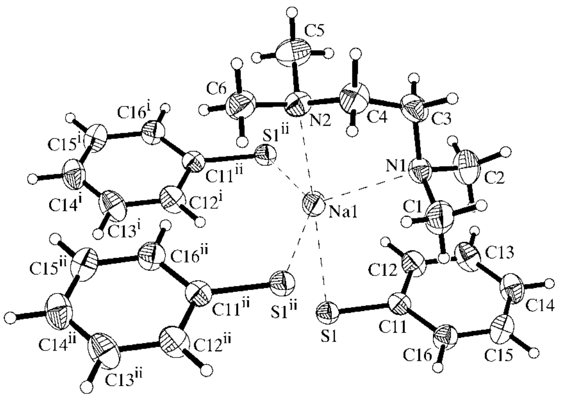
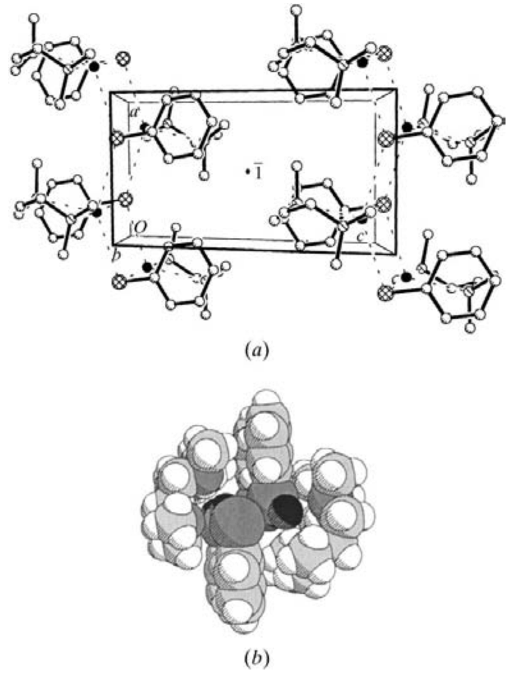


**Figure 1**
The coordination sphere of sodium in (I) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii. The symmetry codes are as in Table 1.

The sodium cations form distorted trigonal bipyramids with sulfur centres from the thiophenolates and N centres from tetramethylethylenediamine. The axial positions are occupied by S1 and N2, and the equatorial positions by S1*A*, S1*B* and N1 [Fig. 1; symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$]. These interatomic contacts agree with the sum of the van der Waals radii. Nevertheless, the interaction of the sodium cation with S1*A* and S1*B* decreases, but the geometry of a trigonal bipyramid is well defined (Fig. 1). The sodium cations are connected by Na···S···Na bridges to form infinite chains along the *a* axis with alternate Na···Na distances of 4.132 (1) and 4.361 (1) Å (Fig. 2*a*). The C—S bond of the thiophenolate has a distance of 1.754 Å, which is in the mean band of 1.77 (3) calculated for the C—S distances in 472 crystal structures incorporating thiophenolate registered in the Cambridge Structural Database. The C—S bond of thiophenolates shows a broad variety in length obviously independent of the cation. Therefore, bis(tetra-*n*-butylammonium)tetrakis(benzenethiolatoiron) containing only iron cations exhibits C—S distances with maximum differences of 0.04 Å in every published crystal structure (Guodong *et al.*, 1987; Gloux *et al.*, 1987; Excoffon *et al.*, 1991). The lipophilic wrapping by phenyl rings and methyl groups (Fig. 2*b*) is responsible for the kinetic stability of the polyion aggregate in analogy to the hexameric sodium tetraphenylimidodiphosphate (Bock, Schödel *et al.*, 1995).



(*a*)

(*b*)

**Figure 2**
(*a*) The unit cell viewed along the *b* axis showing two infinite chains of (I) along the *a* axis and (*b*) a space-filled drawing of one chain (profile) illustrating the lipophilic wrapping of the polyionic chain inside (sodium: black; sulfur, nitrogen: dark grey; carbon: grey; hydrogen: white).

## Experimental

From gentle heating of sodium (0.1 g, 4.3 mmol) at $10^{-3}$ Pa, a mirror was generated on the wall of a dried Schlenk trap. Addition of tris(phenylthio)methane (100 mg, 0.2 mmol) in aprotic tetramethylethylenediamine (10 ml) produced a yellow solution, which after standing for 1 d at room temperature, was covered with a layer of aprotic hexane (10 ml). After one week, yellow crystals were collected from the trap wall near the phase border line.

*Crystal data*

$Na^+ \cdot C_6H_5S^- \cdot C_6H_{16}N_2$
$M_r = 248.36$
Triclinic, $P\overline{1}$
$a = 5.9440$ (10) Å
$b = 11.200$ (2) Å
$c = 11.899$ (2) Å
$\alpha = 62.58$ (1)°
$\beta = 87.14$ (2)°
$\gamma = 81.32$ (2)°
$V = 694.9$ (2) Å$^3$

$Z = 2$
$D_x = 1.187$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 81 reflections
$\theta = 8.5$–18°
$\mu = 0.241$ mm$^{-1}$
$T = 180$ (2) K
Block, yellow
0.60 × 0.42 × 0.25 mm

*Data collection*

Siemens *P*4 four-circle diffractometer
$\theta$–$2\theta$ scans
3921 measured reflections
3066 independent reflections
2636 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$

$\theta_{\rm max} = 28°$
$h = -1 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
4 standard reflections every 100 reflections intensity decay: <5%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.052$
3066 reflections
149 parameters
H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.1435P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.34$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.21$ e Å$^{-3}$

All H atoms were located from the difference map and placed in idealized positions using a riding model with distances $C—H_{\rm phenyl} = 0.95$, $C—H_{\rm methylene} = 0.99$ and $C—H_{\rm methyl} = 0.98$ Å. The torsion of the methyl H atoms and the isotropic displacement parameters of all H atoms (groupwise for methyl and methylene H atoms) were refined.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1991); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—Na1 | 2.8219 (8) | Na1—S1$^{\rm i}$ | 3.0310 (8) |
| Na1—N2 | 2.5375 (14) | Na1—S1$^{\rm ii}$ | 3.1966 (8) |
| Na1—N1 | 2.5482 (13) | Na1—Na1$^{\rm i}$ | 4.1323 (12) |
| | | | |
| N2—Na1—N1 | 73.60 (4) | S1—Na1—S1$^{\rm i}$ | 90.249 (18) |
| N2—Na1—S1 | 174.95 (4) | N2—Na1—S1$^{\rm ii}$ | 87.62 (3) |
| N1—Na1—S1 | 106.93 (3) | N1—Na1—S1$^{\rm ii}$ | 93.31 (3) |
| N2—Na1—S1$^{\rm i}$ | 93.77 (3) | S1—Na1—S1$^{\rm ii}$ | 87.338 (19) |
| N1—Na1—S1$^{\rm i}$ | 120.38 (3) | S1$^{\rm i}$—Na1—S1$^{\rm ii}$ | 145.28 (2) |

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$.

The present project has been supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the Fonds der Chemischen Industrie and the A. Messer Foundation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1063). Services for accessing these data are described at the back of the journal.

## References

Bock, H., Beck, R., Havlas, Z. & Schödel, H. (1998). *Eur. J. Inorg. Chem.* pp. 2075–2077.
Bock, H., Hauck, T., Näther, C., Rösch, N., Staufer, M. & Häberlein, O. D. (1995). *Angew. Chem.* **107**, 1439–1441; *Angew. Chem. Int. Ed. Engl.* **34**, 1353–1355.
Bock, H., Havlas, Z., Krenzel, V. & Sievert, M. (2001). *Angew. Chem.* In the press.
Bock, H. & Heigel, E. (2000*a*). *Z. Naturforsch. Teil B*, **55**, 785–795.
Bock, H. & Heigel, E. (2000*b*). *Z. Naturforsch. Teil B*, **55**, 1053–1066.
Bock, H., Heigel, E. & Nagel, N. (2000). *Z. Naturforsch Teil B*, **55**, 773–784.
Bock, H., Schödel, H., Havlas, Z. & Herrmann, E. (1995). *Angew. Chem.* **107**, 1441–1443; *Angew. Chem. Int. Ed. Engl.* **34**, 1355–1357.
Excoffon, P., Laugier, J. & Lamotte, B. (1991). *Inorg. Chem.* **30**, 3075–3081.
Gloux, J., Gloux, P., Hendriks, H. & Rius, G. (1987). *J. Am. Chem. Soc.* **119**, 3220–3224.
Lin, G., Zhang, H., Hu, S. Z. & Mak, T. C. W. (1987). *Acta Cryst.* C**43**, 352–353.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XSCANS*. Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.