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

# *N*-(Diphenylselenio)diphenylsulfimidium tetraphenylborate

**Stephen M. Aucott, Sophie H. Dale, Mark R. J. Elsegood, Liam M. Gilby, Kathryn E. Holmes and Paul F. Kelly***

Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England
Correspondence e-mail: p.f.kelly@lboro.ac.uk

Received 11 November 2004
Accepted 16 December 2004
Online 22 January 2005

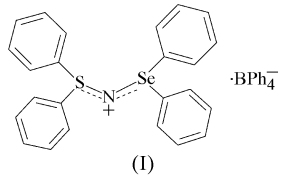
The title compound, $C_{24}H_{20}NSSe^{+}\cdot C_{24}H_{20}B^{-}$, exhibits disorder (S/Se scrambling) of the chalcogen sites within the S—N—Se triad. Similar disorder was observed in the bromide salt [Aucott, Bailey, Elsegood, Gilby, Holmes, Kelly, Papageorgiou & Pedrón-Haba (2004). *New J. Chem.* pp. 959–966]. The S—N and Se—N bond lengths are 1.6735 (15) and 1.8045 (14) Å, respectively. Whereas the chalcogens in the bromide salt are involved in S···Br and Se···Br interactions of very similar distances, the scrambled S and Se sites in the title compound are involved in distinct non-bonded interactions. The site predominantly occupied by sulfur is involved in C—H···S/Se interactions, while the site predominantly occupied by selenium is involved in Se/S···$\pi$ interactions.

## Comment

Until our recent investigations extending the chemistry of homochalcogen cationic sulfimide derivatives, such as $[Ph_2SNSPh_2]^{+}$, to mixed chalcogen species had not been reported. In synthesizing and fully characterizing $[Ph_2SNSePh_2]Br$ and $[1,4\text{-}(PhSNSePh_2)_2C_6H_4][BPh_4]_2$, we were able to obtain the first insight into the structure of *N*-seleniosulfimidium systems, which represent new additions to the general family of mixed S/Se—N compounds (Aucott *et al.*, 2004).

In the case of $[Ph_2SNSePh_2]Br$ (Aucott *et al.*, 2004), X-ray crystallography revealed Se—N and S—N bond lengths of 1.832 (3) and 1.678 (3) Å, respectively, with an S—N—Se angle of 107.61 (15)°, although disorder within the system means that there is some scrambling of the S and Se sites, the refined major occupancy of the disordered chalcogen sites being 83.2 (2)%. This suggests that the true Se—N distance in the system is actually longer than that quoted, which, intriguingly, places the bond within the range normally associated with Se—N single bonds. By way of illustration, an Se—N length of 1.844 (3) Å has been reported for $(Me_3SiNSN)_2Se$ (Konu *et al.*, 2002), while single-bond lengths of 1.827 (5) and 1.869 (2) Å have also been observed in OSN–Se–NSO (Haas *et al.*, 1991) and $(Me_3Si)_2N\text{–}Se\text{–}N(SiMe_3)_2$ (Björgvinsson *et al.*, 1990), respectively.

In the case of $[1,4\text{-}(PhSNSePh_2)_2C_6H_4][BPh_4]_2$ (Aucott *et al.*, 2004), X-ray crystallography revealed a structure with no disorder (but with an associated reduction in symmetry) and an Se—N bond length of 1.814 (2) Å. This again is long, more akin to an Se—N single bond, albeit shorter than in $[Ph_2SNSePh_2]Br$. In order to shed further light on these systems, we have now prepared and crystallized the title compound, (I) (Fig. 1).




(I)

Compound (I) crystallizes in a centrosymmetric space group with one complete formula unit in the asymmetric unit. The structure exhibits scrambling of the chalcogen sites, as was observed in the bromide salt [refined occupancies 85.21 (11):14.79 (11)%]. In (I), the Se—N and S—N bond lengths are 1.8045 (14) and 1.6735 (15) Å, respectively, with an S—N—Se angle of 109.71 (8)° (Table 1). The Se—N bond length is clearly shorter and the bond angle wider than was observed in the disordered bromide salt.

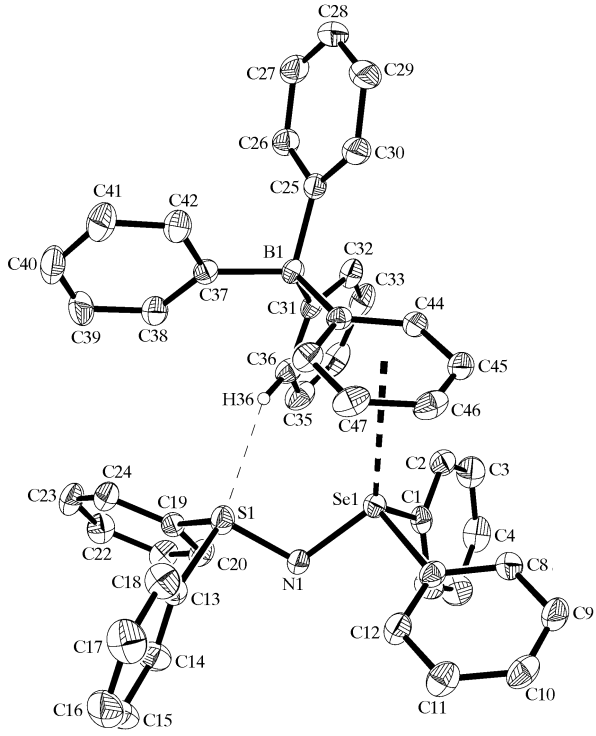



**Figure 1**
A view of (I), showing the atom-labelling scheme and the C—H···S and Se···$\pi$ cation–anion interactions. Displacement ellipsoids are drawn at the 50% probability level. The minor disorder component and H atoms (except H36) have been omitted for clarity. Non-bonded interactions are shown as dashed lines.

  DOI: 10.1107/S0108270104033505 

There are non-bonded interactions between the cations and anions in both the bromide salt and in (I). In the bromide salt, cation–anion interactions take the form of non-bonded contacts between the $Br^-$ anion and the chalcogen atoms. There are three interactions: S1···Br1 of 3.4550 (8) Å, Se1···Br1 of 3.3208 (5) Å and Se1···Br1$^{i}$ of 3.3993 (5) Å [symmetry code: (i) $1-x$, $1-y$, $-z$]. In the following discussion of the intermolecular interactions in (I), only those of the major disorder component will be highlighted (the same interactions apply to the minor disorder component, with Se and S atoms interchanged).

Atom S1 is involved in a C—H···S interaction (C36—H36···S1), with C···S 3.8276 (19) Å, H···S 2.92 Å and C—H···S 161°. Atom Se1 participates in an Se···$\pi$ interaction with one phenyl ring of the $BPh_4^-$ anion, with atom Se1 lying 3.1503 (9) Å from the least-squares plane of the aromatic ring containing atoms C43–C48 (Fig. 1). The Se···C distances between atom Se1 and the C atoms of the phenyl ring range from 3.3327 (18) (C46) to 3.6239 (16) Å (C43), averaging 3.462 (11) Å.

A search of the Cambridge Structural Database (Version 5.25, November 2003 update; Allen, 2002; Fletcher *et al.*, 1996) for Se···$\pi$ interactions (with search conditions for an Se atom having contacts in the range 3–4 Å with all six C atoms of a phenyl ring) identified 33 structures containing such interactions. The Se···C contact distances (within the search limits) are in the range 3.335–3.999 Å, averaging 3.75 (13) Å, indicating the Se···C distances observed in (I) to be relatively short. It is interesting to note that, although six of the structures contain the $PPh_4^+$ cation (see, for example, Ansari *et al.*, 1989; Heuer *et al.*, 1988), compound (I) represents the first example of a compound containing close Se···$\pi$ interactions with a $BPh_4^-$ anion.

## Experimental

A precipitate of $[Ph_2SNSePh_2][BPh_4]$ was prepared by the addition of $Na[BPh_4]$ to a solution of $[Ph_2SNSePh_2]Br$ (Aucott *et al.*, 2004) in methanol. Dissolution of the precipitate in $CH_2Cl_2$ and crystallization by slow vapour diffusion of diethyl ether into this solution produced X-ray quality colourless crystals of (I).

*Crystal data*

$C_{24}H_{20}NSSe^+\cdot C_{24}H_{20}B^-$
$M_r$ = 752.64
Monoclinic, $P2_1/c$
$a$ = 12.2627 (11) Å
$b$ = 27.860 (2) Å
$c$ = 12.2402 (11) Å
$\beta$ = 114.438 (2)°
$V$ = 3807.1 (6) Å$^3$
$Z$ = 4
$D_x$ = 1.313 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 16 364 reflections
$\theta$ = 2.3–28.9°
$\mu$ = 1.08 mm$^{-1}$
$T$ = 150 (2) K
Block, colourless
0.67 × 0.26 × 0.24 mm

*Data collection*

Bruker SMART 1000 CCD area-detector diffractometer
Thin-slice $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min}$ = 0.532, $T_{max}$ = 0.782
32 563 measured reflections
9135 independent reflections
7611 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.078
$\theta_{max}$ = 28.9°
$h = -16 \rightarrow 15$
$k = -37 \rightarrow 37$
$l = -16 \rightarrow 16$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.116
$S$ = 1.02
9135 reflections
470 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.077P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.93 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.94 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Se1—N1 | 1.8045 (14) | S1—N1 | 1.6735 (15) |
| Se1—C1 | 1.9066 (18) | S1—C13 | 1.8088 (18) |
| Se1—C7 | 1.9231 (18) | S1—C19 | 1.8249 (17) |
| S1—N1—Se1 | 109.71 (8) | | |

Compound (I) exhibits disorder with respect to the positions of the S and Se atoms, and this scrambling was successfully modelled with minor disorder atoms S1*X* and Se1*X* occupying identical positions to Se1 and S1, respectively. The anisotropic displacement parameters of the pairs S1/Se1*X* and Se1/S1*X* were constrained to be identical. This disorder modelling resulted in a reduction of 0.018 in the value of $R_1$ and in final refined occupancies of 85.21 (11):14.79 (11)%. H atoms were placed in geometrically calculated positions (C—H = 0.95 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The data set was truncated at $2\theta$ = 55°, as only statistically insignificant data were present above this limit.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

The authors acknowledge the EPSRC for PDRA support (LMG and SMA) and use of the EPSRC Chemical Database Service at Daresbury Laboratory (Fletcher *et al.*, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1600). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Ansari, M. A., Chau, C.-N., Mahler, C. H. & Ibers, J. A. (1989). *Inorg. Chem.* **28**, 650–654.
Aucott, S. M., Bailey, M. R., Elsegood, M. R. J., Gilby, L. M., Holmes, K. E., Kelly, P. F., Papageorgiou, M. J. & Pedrón-Haba, S. (2004). *New J. Chem.* pp. 959–966.
Björgvinsson, M., Roesky, H. W., Pauer, F., Stalke, D. & Sheldrick, G. M. (1990). *Inorg. Chem.* **29**, 5140–5143.
Bruker (2001). *SMART* (Version 5.611) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Haas, A., Kasprowski, J., Angermund, K., Betz, P., Kruger, C., Tsay, Y.-H. & Werner, S. (1991). *Chem. Ber.* **124**, 1895–1906.
Heuer, W. B., True, A. E., Swepston, P. N. & Hoffman, B. M. (1988). *Inorg. Chem.* **27**, 1474–1482.
Konu, J., Maaninen, A., Paananen, K., Ingman, P., Laitinen, R. S., Chivers, T. & Valkonen, J. (2002). *Inorg. Chem.* **41**, 1430–1435.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2003). *SADABS*. Version 2.08. University of Göttingen, Germany.