

***N*-(Diphenylselenio)diphenylsulfimidium tetraphenylborate**Stephen M. Aucott, Sophie H. Dale, Mark R. J. Elsegood,
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The title compound, $C_{24}H_{20}NSe^+ \cdot C_{24}H_{20}B^-$, 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, Papa-georgiou & 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··· π interactions.

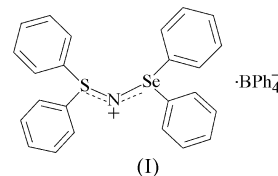
Comment

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 $[1,4-(PhNSePh_2)_2C_6H_4][BPh_4]_2$, 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 $(Me_3Si)_2N-Se-N(SiMe_3)_2$ (Björgvinsson *et al.*, 1990), respectively.

In the case of $[1,4-(PhNSePh_2)_2C_6H_4][BPh_4]_2$ (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).



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.

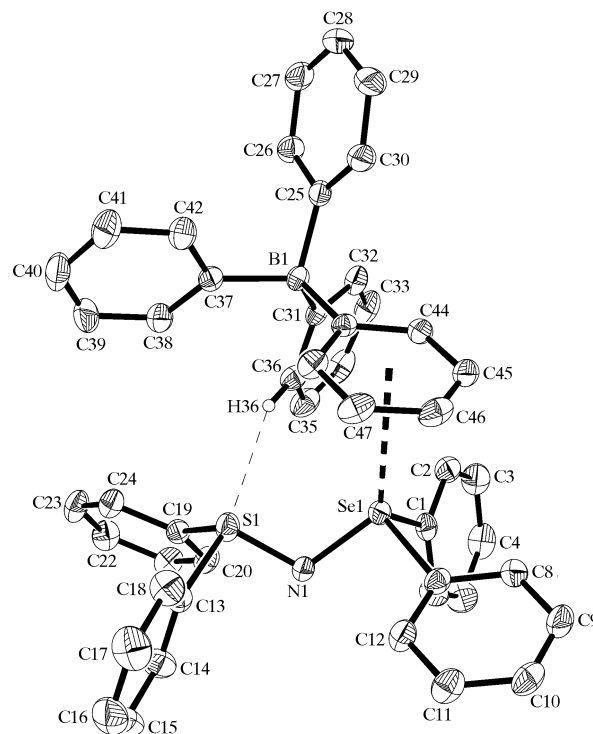


Figure 1
A view of (I), showing the atom-labelling scheme and the C–H···S and Se··· π cation–anion interactions. Displacement ellipsoids are drawn at the 50% probability level. The minor disorder component and H atoms (except H36) have been omitted for clarity. Non-bonded interactions are shown as dashed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

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···Br1ⁱ 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···π interaction with one phenyl ring of the BPh₄[−] 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···π 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 PPh₄⁺ cation (see, for example, Ansari *et al.*, 1989; Heuer *et al.*, 1988), compound (I) represents the first example of a compound containing close Se···π interactions with a BPh₄[−] anion.

Experimental

A precipitate of [Ph₂SNSePh₂][BPh₄] was prepared by the addition of Na[BPh₄] to a solution of [Ph₂SNSePh₂]Br (Aucott *et al.*, 2004) in methanol. Dissolution of the precipitate in CH₂Cl₂ 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 ⁺ ·C ₂₄ H ₂₀ B [−]	$D_x = 1.313 \text{ Mg m}^{-3}$
$M_r = 752.64$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 16 364 reflections
$a = 12.2627 (11) \text{ \AA}$	$\theta = 2.3\text{--}28.9^\circ$
$b = 27.860 (2) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$c = 12.2402 (11) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 114.438 (2)^\circ$	Block, colourless
$V = 3807.1 (6) \text{ \AA}^3$	$0.67 \times 0.26 \times 0.24 \text{ mm}$
$Z = 4$	

Data collection

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

Refinement

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

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 S1X and Se1X occupying identical positions to Se1 and S1, respectively. The anisotropic displacement parameters of the pairs S1/Se1X and Se1/S1X 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The data set was truncated at $2\theta = 55^\circ$, 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.

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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.

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