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Two Organic Diselenides: Dimesityl Diselenide and Bis(2,4,6-triisopropylphenyl) Diselenide

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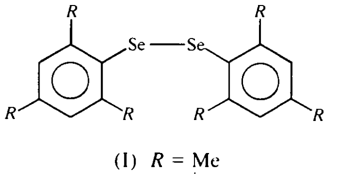
Abstract

The organic diselenides dimesityl diselenide [$C_{18}H_{22}Se_2$, (I)] and bis(2,4,6-triisopropylphenyl) diselenide [$C_{30}H_{46}Se_2$, (II)] display normal diselenide geometries: Se—Se bond lengths are 2.3341 (6) in (I) and 2.3389 (6) Å in (II), and the absolute C—Se—Se—C torsion angles are 83.96 (12) in (I) and 73.38 (16)° in (II).

Comment

We are interested in the structural chemistry of organic disulfides and diselenides. The use of bulky organic groups might be expected to change the C—*E*—*E*—C (*E* = chalcogenide) torsion angle from the usual region of *circa* 90° as in 2,2′-dipyridyl diselenide [84.3 (2)°; Kienitz *et al.*, 1996] to larger (*trans*) values; this was indeed achieved for bis[tris(trimethylsilyl)methyl]-disulfane, which displays crystallographic inversion of symmetry and thus a C—S—S—C torsion angle of 180° (Ostrowski *et al.*, 1993). Here we present the structures of two diselenides: dimesityl diselenide, (I), and bis(2,4,6-triisopropylphenyl) diselenide, (II).



(I) R = Me
(II) R = ^{i}Pr

Both compounds (Figs 1 and 2) crystallize without imposed symmetry, although (II) displays non-crystallographic twofold symmetry to a good approximation. The absolute torsion angles about the Se—Se bonds lie in the normal region [(I) 83.96 (12); (II) 73.38 (16)°] and the organic groups are thus not bulky enough to promote a *trans* geometry. The bond lengths and angles involving the Se atoms are normal (Tables 1 and 2).

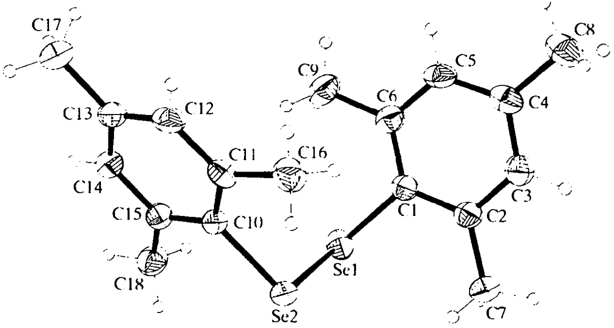


Fig. 1. Structure of dimesityl diselenide in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

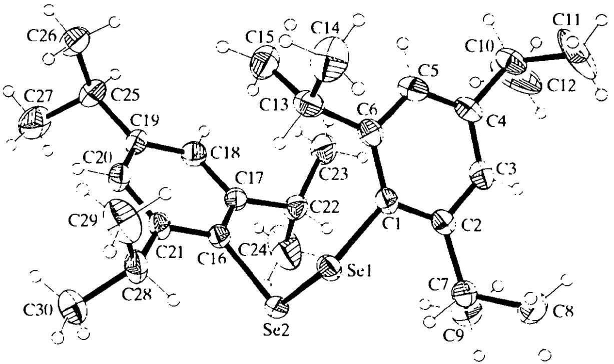


Fig. 2. Structure of bis(2,4,6-triisopropylphenyl) diselenide in the crystal. Ellipsoids represent 40% probability levels. H-atom radii are arbitrary.

The diselenide (II) is also known to form a 2:1 adduct with molecular iodine (du Mont *et al.*, 1990), involving weak Se···I contacts of 3.483 (1) Å; in this adduct, which has Se—Se 2.353 (2) Å and C—Se—Se—C 73.0°, the dimensions of (II) are closely similar to those reported here.

A search of the Cambridge Structural Database (October 1997 version; Allen & Kennard, 1993) revealed 16 diaryl diselenides, with Se—Se bond lengths ranging from 2.287 to 2.380 Å (mean 2.335 Å). Absolute torsion angles C—Se—Se—C lie in the range 70–100°, with the extremely bulky di(2,6-dimesitylphenyl) diselenide providing the exception at 128.3° (Ellison *et al.*, 1995).

The interplanar angles between the aromatic rings are 30.39 (11) for (I) and 39.10 (13)° for (II). In (II) the

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isopropyl groups are all arranged with one terminal C atom on each side of the ring.

Experimental

The diselenides were obtained by treatment of the appropriate magnesium Grignard reagents with grey selenium in tetrahydrofuran and subsequent aerial oxidation. Removal of the solvent and treatment of the solid residue by Soxhlet extraction from petroleum ether led to a red solution of the crude products. The solvent was evaporated again under reduced pressure, and the pure diselenides were obtained as large orange crystals on recrystallization from petroleum ether (40/60) at 255 K.

Compound (I)

Crystal data

$C_{18}H_{22}Se_2$
$M_r = 396.28$
Monoclinic
$P2_1/c$
$a = 6.2064\,(15)$ Å
$b = 18.379\,(4)$ Å
$c = 14.943\,(4)$ Å
$\beta = 96.18\,(2)°$
$V = 1694.5\,(7)$ Å^3
$Z = 4$
$D_x = 1.553$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–11.5°$
$\mu = 4.353$ mm^{-1}
$T = 178\,(2)$ K
Tablet
0.7 × 0.4 × 0.15 mm
Yellow

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.261$, $T_{\max} = 0.647$
4395 measured reflections
2993 independent reflections
2546 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\max} = 25.05°$
$h = -7 \rightarrow 2$
$k = -3 \rightarrow 21$
$l = -17 \rightarrow 17$
3 standard reflections every 147 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.084$
$S = 1.042$
2993 reflections
187 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.593P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.128$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Se1—C1	1.930 (3)	Se2—C10	1.931 (3)
Se1—Se2	2.3341 (6)		
C1—Se1—Se2	100.28 (8)	C10—Se2—Se1	100.71 (8)
C1—Se1—Se2—C10	83.96 (12)	Se2—Se1—C1—C2	82.2 (2)
Se2—Se1—C1—C6	−97.7 (2)		

Compound (II)

Crystal data

$C_{30}H_{46}Se_2$
$M_r = 564.59$
Orthorhombic
Pbca
$a = 15.177\,(3)$ Å
$b = 22.357\,(4)$ Å
$c = 17.653\,(4)$ Å
$V = 5990\,(2)$ Å^3
$Z = 8$
$D_x = 1.252$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–11.5°$
$\mu = 2.483$ mm^{-1}
$T = 178\,(2)$ K
Prism
0.70 × 0.30 × 0.25 mm
Yellow

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\min} = 0.472$, $T_{\max} = 0.538$
6715 measured reflections
5266 independent reflections
2921 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.023$
$\theta_{\max} = 25.06°$
$h = 0 \rightarrow 18$
$k = -26 \rightarrow 0$
$l = -20 \rightarrow 4$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.103$
$S = 0.952$
5266 reflections
301 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Se1—C1	1.933 (4)	Se1—Se2	2.3389 (6)
Se2—C16	1.938 (4)		
C1—Se1—Se2	99.82 (11)	C16—Se2—Se1	101.17 (11)
C1—Se1—Se2—C16	−73.38 (16)	Se2—Se1—C1—C2	−75.1 (3)
Se2—Se1—C1—C6	105.4 (3)		

H atoms were included using rigid methyl groups (starting positions taken from difference syntheses and then allowed to rotate but not tip) or a riding model starting from calculated positions. The rotation of the methyl group at C9 in (II) converged slowly, which may indicate the presence of slight rotational disorder.

For both compounds, data collection: *P*3 *Software* (Nicolet, 1987*a*); cell refinement: *P*3 *Software*; data reduction: *XDISK* (Nicolet, 1987*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1242). Services for accessing these data are described at the back of the journal.

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Salts of the Bis(catecholato)borate Anion with Organic Cations

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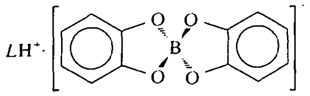
Abstract

In a series of six salts with organic nitrogen and phosphorus cations [2-methylpyridinium bis(pyrocatecholato-*O*,*O*′)borate, $C_6H_8N^+\cdot C_{12}H_8BO_4^-$, (1); 4-methylpyridinium bis(pyrocatecholato-*O*,*O*′)borate, $C_6H_8N^+\cdot C_{12}H_8BO_4^-$, (2) and (3) (two polymorphs); 1,10-phenanthrolinium bis(pyrocatecholato-*O*,*O*′)borate, $C_{12}H_9N_2^+\cdot C_{12}H_8BO_4^-$, (4), and its dichloromethane solvate, $C_{12}H_9N_2^+\cdot C_{12}H_8BO_4^-\cdot CH_2Cl_2$, (5); and trimethylphosphonium bis(pyrocatecholato-*O*,*O*′)borate, $C_3H_{10}P^+\cdot C_{12}H_8BO_4^-$, (6)], the bis(catecholato)borate anion has approximate D_{2d} ($\bar{4}2m$) symmetry, with the central spiro-B atom distorted from regular tetrahedral coordination geometry by reduction of the two intra-ring O—B—O bond angles. The two chelate rings show small deviations from planarity by folding about the O···O axis. Ion pairs are formed by N—H···O hydrogen bonding in all five salts with nitrogen-based cations, but there is no hydrogen bonding in the phosphonium salt; the hydrogen bonding leads to slight elongation of the B—O bond involved.

Comment

We report the structures of a series of salts of the bis(catecholato)borate [bis(benzene-1,2-diolato)borate] anion with organic nitrogen and phosphorus cations. These have been obtained as side products in the study of the reactions of diboron compounds with organic bases to produce Lewis acid–base adducts. The formation of the bis(catecholato)borate anion seems to be favoured under a wide variety of conditions. Traces of moisture are probably responsible for the reactions leading to these products.



(1) L = 2-MeC$_5$H$_4$N
(2),(3) L = 4-MeC$_5$H$_4$N
(4),(5) L = 1,10-phenanthroline
(6) L = Me$_3$P

The specific compounds reported here contain the cations 2-methylpyridinium, (1), 4-methylpyridinium, (2) and (3), 1,10-phenanthrolinium, (4) and (5), and trimethylphosphonium, (6).

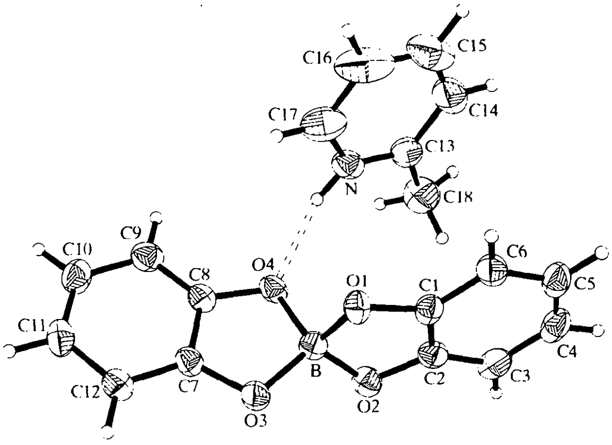


Fig. 1. The molecular structure of (1), with atom labels and 50% probability ellipsoids for non-H atoms.