

Structure of 1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonane-9-selone

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Abstract. $C_9H_{14}S_2Se$, $M_r = 265.3$, orthorhombic, $Cmcm$, $a = 9.164$ (1), $b = 11.419$ (1), $c = 10.085$ (1) Å, $V = 1055$ (1) Å³, $Z = 4$, $D_x = 1.670$ g cm⁻³, $\lambda(Mo K\alpha) = 0.7107$ Å, $\mu = 38.16$ cm⁻¹, $F(000) = 536$, $T = 293$ (1) K, $R = 0.041$ for 552 observed reflections. The bicyclo[3.3.1]nonane molecule lies on a twofold axis and exists in the common double-chair conformation, having C_{2v} symmetry. The C=Se bond distance is 1.774 (6) Å.

Introduction. Hindered selenoketones (selones) were first prepared in 1975 (Back, Barton, Britten-Kelly & Guziec, 1975) and they have since found use as precursors to Δ^3 -1,3,4-selenadiazolines in the synthesis of hindered alkenes (Krebs, Kaletta, Nickel, Ruger & Tikwe, 1986; Cullen & Guziec, 1986). The chemistry of selones is governed by the poor $2p-4p$ π -bond overlap and hence selones are significantly less stable than thiones or ketones; fortunately, however, steric hindrance affords stability to these otherwise unstable compounds (Guziec, SanFilippo, Murphy, Moustakis & Cullen, 1985). Typically selones are deep-blue low-melting monomeric solids.

Our interest in 1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonaneselone (1) arose through attempts to prepare tetra-*tert*-butylethylene (Brooks & Bishop, 1991). Surprisingly, (1) is green in solution yet reversibly forms red-brown crystals. The X-ray crystal structure determination of (1) was undertaken in order to resolve this spectral anomaly and also as no other crystal structure of a selone has been reported.



(1)

Experimental. The selone (1) was prepared as reported elsewhere (Brooks & Bishop, 1991). Enraf-Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\alpha$ radiation; $\omega:2\theta$ scan technique. Cell parameters by least squares on 25 reflections ($2 \leq \theta \leq 13^\circ$) (de Boer & Duisenberg, 1984) on a crystal $0.36 \times 0.20 \times 0.25$ mm. Analytical absorption correction applied; max. and min. transmission factors 0.499 and 0.388 (Sheldrick, 1976). 784 reflections ($1.5 \leq \theta \leq 27.5^\circ$) measured in the range $0 \leq h \leq 11$, $0 \leq k \leq 14$, $-13 \leq l < 1$; some high-angle Friedel pairs were also included. No significant variation in the net intensities of three reference reflections (131, 242, 151) measured every 7200 s. 683 unique reflections, $R_{int} = 0.024$ and 552 satisfied $I \geq 2.5\sigma(I)$. Structure solved by direct methods (SHELXS86; Sheldrick, 1986), full-matrix least-squares refinement on 37 parameters based on F (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms located from difference map but only a common isotropic thermal parameter refined. At convergence $R = 0.041$, $wR = 0.044$, $w = [\sigma^2(F) + 0.003|F|^2]^{-1}$, $S = 1.04$, $(\Delta/\sigma)_{max} < 0.001$, $\Delta\rho_{max} = 0.54$, $\Delta\rho_{min} = -1.49$ e Å⁻³; no extinction correction applied. Scattering factors for neutral Se corrected for f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149) and for the remaining atoms as incorporated in SHELX76 (Sheldrick, 1976). All calculations on a SUN4/280 computer system. Atomic parameters are given in Table 1, selected interatomic parameters in Table 2* and the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54064 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

numbering scheme used is shown in Fig. 1 which was drawn with *ORTEP* (Johnson, 1976).

Discussion. The structure determination of (1) confirms the stoichiometry of the compound, Fig. 1, and proves the presence of the selone function. The molecule has C_{2v} symmetry in the crystal as is emphasized in Fig. 1(b). The C=Se atoms lie on a twofold axis along *b*. The C(2) and C(2') atoms lie on a mirror plane as do the S(1) atoms which lie on a mirror plane perpendicular to the first mirror plane. The crystal structure is molecular with the most significant intermolecular contacts in the crystal lattice occurring between the Se and H(3*b*) atoms (symmetry operation: $-0.5 + x, 0.5 + y, z$) of 3.28 (1) and 3.13 (1) Å between the S(1) and H(2'*b*)' atoms (symmetry operation: $-0.5 + x, -0.5 + y, 0.5 - z$).

There are two features of the structure of particular interest namely (i) the C=Se bond and (ii) the conformation of the bicyclic skeleton. In a recent survey of bond distances extracted from the Cambridge Crystallographic Data Centre (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) there was no listing of a distance for a C=Se bond. In (1) a distance of 1.774 (6) Å is found for the C=Se bond which may be compared to a bond distance of 1.97 Å for C—Se single bond (Allen *et al.*, 1987). This survey reported the average C—S and C=S distances to be 1.81 and 1.62 Å, respectively (Allen *et al.*, 1987), *i.e.* a difference of 0.19 Å. By extrapolation, and using 1.97 Å as the bond distance for a C—Se single bond, a distance of 1.78 Å would be the expected bond length for a C=Se double bond compared with the experimentally determined value of 1.774 (6) Å in (1).

Theoretical studies of bicyclo[3.3.1]nonane derivatives have shown that three limiting conformations may be adopted. The most common of these, the double-chair conformation has been demonstrated in the X-ray structures of several examples (Bhattacharjee & Chacko, 1979). Examples of the less common chair-boat conformation also exist (Bhattacharjee & Chacko, 1979; van Koningsveld, 1981; van Koningsveld & Peters, 1981). Finally, the structure of 3 α ,7 α -bis(2-hydroxy-2-propyl)bicyclo[3.3.1]nonane was shown recently to adopt the rare double twist-boat conformation (van Koningsveld, Peters & Jansen, 1984). That the structure of (1) adopts the double-chair conformation is emphasized in Fig. 1. The S(1)⋯S(1)' separation of 3.286 (4) Å between the bridgehead hetero atoms, while less than the sum of the van der Waals radii for two S atoms of 3.6 Å (Bondi, 1964), is not indicative of a significant interaction between these atoms.

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Table 1. Fractional atomic coordinates and B_{eq} values (Å²)

	$B_{eq} = (8\pi^2/3) \text{ trace U.}$			B_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
Se	0.0	0.6311 (1)	0.25	3.24
S(1)	0.0	0.2331 (1)	0.4129 (1)	2.99
C(1)	0.0	0.4758 (5)	0.25	1.84
C(2)	0.1405 (4)	0.4048 (4)	0.25	2.02
C(2')	0.2793 (5)	0.4793 (5)	0.25	3.39
C(3)	0.1486 (3)	0.3318 (3)	0.3783 (3)	2.64

Table 2. Selected interatomic distances (Å) and bond angles (°)

Se(1)—C(1)	1.774 (6)	C(1)—C(2)	1.521 (5)
C(2)—C(2')	1.531 (6)	C(2)—C(3)	1.541 (4)
C(3)—S(1)	1.802 (4)		
Se(1)—C(1)—C(2)	122.2 (3)	C(1)—C(2)—C(2')	114.0 (4)
C(1)—C(2)—C(3)	109.2 (2)	C(2)—C(2)—C(3)	105.1 (2)
C(3)—C(2)—C(3) ⁱ	114.3 (4)	C(2)—C(3)—S(1)	117.7 (2)
C(3)—S(1)—C(3) ⁱⁱ	98.2 (2)		

Symmetry code: (i) $-x, y, 0.5 - z$; (ii) $-x, y, z$.

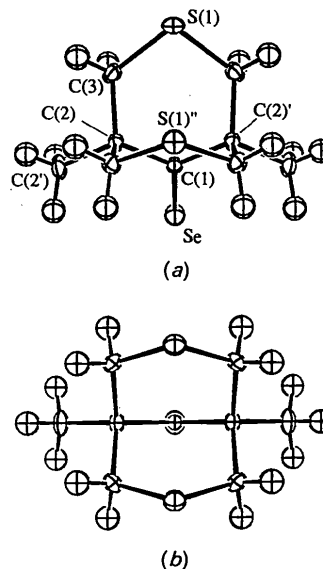


Fig. 1. (a) Crystallographic numbering scheme employed for $C_9H_{14}S_2Se$ (Johnson, 1976) with 25% probability levels and (b) molecular structure viewed along *b*.

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Structure of Di(3,3',4,4'-tetramethyl-2,5-dithia-2',5'-diselenafulvalen)ium Nitrate: (TMDTDSF)₂NO₃

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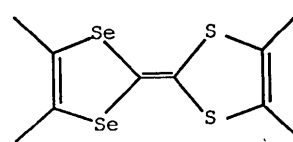
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Abstract. $2C_{10}H_{12}S_2Se_2^{1/2+} \cdot NO_3^-$, $M_r = 770.52$, triclinic, $P\bar{1}$, $a = 7.155$ (18), $b = 7.472$ (3), $c = 12.661$ (3) Å, $\alpha = 89.41$ (3), $\beta = 86.17$ (8), $\gamma = 70.90$ (5)°, $V = 638.1$ Å³, $Z = 1$, $D_x = 2.005$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 60.3$ cm⁻¹, $F(000) = 375$, $T = 293$ K, $R = 0.033$ based on 1233 observed reflections with $I \geq 3\sigma(I)$. In addition to the important disorder of the nitrate anion, the organic molecule also presents an orientational disorder which is reflected in the structure by a statistical distribution of the S and Se atoms. The bond distances [especially the C—S/Se ones: 1.81 (1)–1.86 (1) Å], the interplanar separations [3.556 (7) and 3.596 (7) Å] between successive organic molecules and the intrastack contacts increase while the interchain contacts decrease from (TMTTF)₂NO₃ to (TMTSF)₂NO₃ via the title compound (TMDTDSF)₂NO₃ which contains an organic donor constituted half from TMTTF and half from TMTSF.

Introduction. Recently a series of radical cation salts based on the hybrid molecule TMDTDSF have been studied in order to understand the instabilities occurring at low temperature in these derivatives (Auban, Jérôme, Lerstrup, Johannsen, Jorgensen, Bechgaard, 1989). However, few structural data are

available concerning such a series, so here we report the structure of the (TMDTDSF)₂NO₃ salt.



TMDTDSF

Experimental. The mixed molecule TMDTDSF was prepared using the procedure developed in the literature (Lerstrup, Johannsen & Jorgensen, 1988). Single crystals of (TMDTDSF)₂NO₃ were obtained by electro-oxidation on a platinum electrode of TMDTDSF (10^{-3} M) in tetrahydrofuran solution containing (Bu₄N)NO₃ (0.1 M) as supporting electrolyte. A black crystal with approximate dimensions 0.8 × 0.1 × 0.1 mm was selected for intensity data collection on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). θ - 2θ scans. Cell dimensions were obtained by least-squares refinement from the setting angles of 25 centred reflections ($\theta \leq 15^\circ$). Three standard reflections measured every hour: no fluctuation in intensities. 2434 reflections were recorded in the range $2 \leq 2\theta \leq 50^\circ$ with $0 \leq h \leq 8$, $-8 \leq k \leq 8$, $-15 \leq l \leq 15$.

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