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N,*N*′-Dimethyl-1,4-dithiine-1,2:4,5-tetracarboximide and *N*,*N*′-dimethyl-1,4-diselenine-1,2:4,5-tetracarboximide

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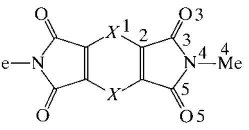
The title compounds of sulfur, $C_{10}H_6N_2O_4S_2$, (I), and selenium, $C_{10}H_6N_2O_4Se_2$, (II), are isomorphous. The crystallographically centrosymmetric molecules are planar. The bond distances and angles, except for those involving the S and Se atoms, are comparable. The molecules are disposed in layers parallel to the *bc* plane. The molecular axes differ by 75° for (I) and by 80° for (II) from one layer to the next.

Comment

Charge-transfer (CT) complexes and radical cation salts derived from 1,4-dithiine and its derivatives exhibit high electrical conductivities. It has been reported that *N*,*N*′-dimethyl-1,4-dithiine-1,2:4,5-tetracarboximide, (I), reacts with various anthracenes *via* charge-transfer complexes to give Diels–Alder adducts and that, in contrast, the reaction of (I) with acridine gives a stable 1:1 complex which does not give rise to any adducts (Hayakawa *et al.*, 1982). 1,4-Dithiines normally adopt a boat conformation in which the S atoms are tilted towards one another (Howell *et al.*, 1954). However, various molecular-orbital calculations have indicated that the energy barrier between the planar and boat conformers is very small (Galasso, 1981; Saebo *et al.*, 1984; Kao *et al.*, 1985). The observed structural trends for 1,4-dithiines suggest that the planar structure is stabilized by electron-withdrawing substitutents (Hayakawa *et al.*, 1982; Lozac'h, 1989). However, unlike other 1,4-dithiines, the 1:1 complex of (I) and acridine (Yamaguchi & Ueda, 1984) is almost planar. We now report the structural characterization of *N*,*N*′-dimethyl-1,4-dithiine-1,2:4,5-tetracarboximide, related to 1,4-dithiines, and *N*,*N*′-dimethyl-1,4-diselenine-1,2:4,5-tetracarboximide, (II), in which the S atoms are substituted by Se atoms.



(I) $X = \mathrm{S}$
(II) $X = \mathrm{Sc}$

Except for the *b* value, the other unit-cell dimensions are slightly larger for the Se derivative. In fact, the two compounds, which belong to the same space group, are isomorphous and the molecules are crystallographically centrosymmetric. Both molecules are planar. The diimide atoms (C3, C4, N4, C5, O3 and O5) almost lie in the plane of the six-membered ring. The largest deviations from the least-squares plane are 0.034 (6) and 0.023 (12) Å for the dithiine and diselenine compounds, respectively, and they are close to those reported for the 1:1 1,4-dithiine–acridine complex (Yamaguchi & Ueda, 1984). The bond distances and valence angles in (I), (II) and the 1:1 1,4-dithiine–acridine complex are comparable.

In both (I) and (II), the conjugated Csp^2-Csp^2 bond distances C2—C3 and C5—C6 are longer than the usual value of 1.462 Å (*International Tables for Crystallography*, 1995, Vol. C). A comparable situation has been reported in other structures involving the same tetracarboxylic *N*,*N*′-dimethyldiimide group. For example, in the 3,4,5,6-tetrahydrophthalimide (Kirfel, 1975), these distances are 1.489 (5) and 1.486 (5) Å, and in the maleimide (Boubekeur *et al.*, 1991), they are 1.510 (3) and 1.502 (3) Å. This observation may be attributed to the electronic repulsion between the lone pairs of the heteroatom and that of the O atom. These distances tend to increase with an increase in the van der Waals radius and tend towards the Csp^3-Csp^3 bond distance.

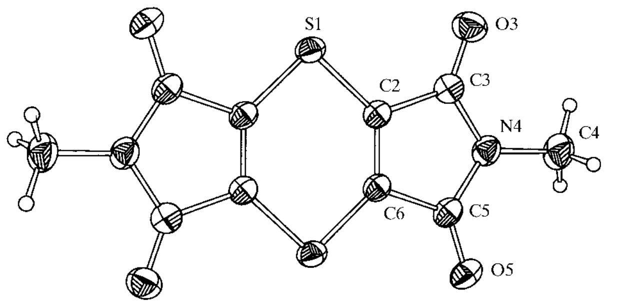


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) showing 40% probability displacement ellipsoids and the atomic numbering scheme.

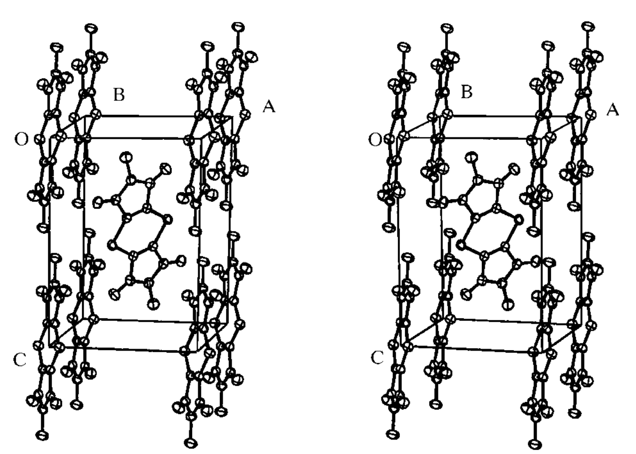


Figure 2
Stereoview showing the packing of the molecules of (I).

The molecules form layers parallel to the *bc* plane at intervals of *a*/2. Within each layer, the planes of the sulfur and selenium molecules are tilted by 40 (1) and 42 (1)° with respect to the *bc* plane. From one layer to the next the molecular axes differ by 75 (1) and 80 (1)° in (I) and (II), respectively.

The shortest intermolecular distances involve the diimide O5 atom. The contacts, which are shorter than the sum of the van der Waals radii, are $O5\cdots C5^{i}$ and $O5\cdots N4^{i}$ with values of 2.886 (3) and 2.969 (2) Å in (I), and 2.941 (4) and 2.990 (3) Å in (II) [symmetry code: (i) $-\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$].

Experimental

The title dithiine was synthesized according to the procedure of Draber (1967) from commercial *N*-methylmaleimide (Lancaster). Ring chlorination of *N*-methylmaleimide with $SOCl_2$ in the presence of pyridine gave *N*-methyldichloromaleimide which was further reacted with thiourea in ethanol. The green powder thus obtained (87% yield) was found pure from NMR spectra in DMSO-d_6 (H, 13 C). Small dark blue–green needles with a metallic sheen were grown by slow evaporation of a chloroform solution at room temperature. The title diselenine formed in 85% yield when selenourea (Aldrich) instead of thiourea was used in the above procedure. To our knowledge, this compound has not yet been reported. From the olive green powder, a crop of small dark blue–green needles was similarly obtained from a chloroform solution at room temperature. Both the S and Se derivatives are highly solvatochromic, with the solutions in halocarbons and aromatics appearing deep blue, and solutions in donor solvents ranging from yellow–green to orange–red.

Compound (I)

Crystal data

$C_{10}H_6N_2O_4S_2$
$M_r = 282.288$
Monoclinic, $P2_1/n$
$a = 8.905\ (3)$ Å
$b = 5.3010\ (10)$ Å
$c = 12.035\ (3)$ Å
$\beta = 95.40\ (3)°$
$V = 565.6\ (3)$ Å^3
$Z = 2$

$D_x = 1.658$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20–25°$
$\mu = 4.387$ mm^{-1}
$T = 293\ (2)$ K
Needle, dark blue–green
0.72 × 0.13 × 0.07 mm

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{\min} = 0.347$, $T_{\max} = 0.756$
3926 measured reflections
1071 independent reflections
954 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.017$
$\theta_{\max} = 69.81°$
$h = -10 \rightarrow 10$
$k = -6 \rightarrow 6$
$l = -14 \rightarrow 14$
5 standard reflections
frequency: 60 min
intensity variation: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.088$
$S = 1.140$
1071 reflections
84 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.0395P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.258$ e Å^{-3}
$\Delta\rho_{\min} = -0.237$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.0213 (19)

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

S1—C2	1.7447 (17)	C3—N4	1.386 (2)
S1—C6^{i}	1.7427 (18)	N4—C4	1.451 (2)
C2—C3	1.497 (2)	N4—C5	1.375 (2)
C2—C6	1.334 (2)	C5—O5	1.204 (2)
C3—O3	1.204 (2)	C5—C6	1.498 (2)
C6^{i}—S1—C2	96.0 (8)	C5—N4—C3	110.8 (2)
C6—C2—C3	108.7 (2)	C5—N4—C4	123.9 (2)
C3—C2—S1	120.2 (1)	O5—C5—N4	126.7 (2)
C6—C2—S1	131.2 (2)	O5—C5—C6	126.6 (2)
O3—C3—N4	126.5 (2)	N4—C5—C6	106.7 (2)
O3—C3—C2	127.6 (2)	C2—C6—C5	107.8 (2)
N4—C3—C2	105.9 (2)	C2—C6—S1^{i}	132.8 (2)
C3—N4—C4	125.0 (2)	C5—C6—S1^{i}	119.3 (2)

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

Compound (II)

Crystal data

$C_{10}H_6N_2O_4Se_2$
$M_r = 376.088$
Monoclinic, $P2_1/n$
$a = 9.173\ (2)$ Å
$b = 5.3020\ (10)$ Å
$c = 12.239\ (4)$ Å
$\beta = 93.69\ (2)°$
$V = 594.0\ (3)$ Å^3
$Z = 2$

$D_x = 2.103$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20–25°$
$\mu = 7.900$ mm^{-1}
$T = 293\ (2)$ K
Plate, dark blue–green
0.50 × 0.10 × 0.04 mm

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{\min} = 0.263$, $T_{\max} = 0.736$
4037 measured reflections
1129 independent reflections
896 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\max} = 69.81°$
$h = -11 \rightarrow 11$
$k = -6 \rightarrow 6$
$l = -14 \rightarrow 14$
5 standard reflections
frequency: 60 min
intensity decay: none

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

Se1—C2	1.882 (3)	C2—C6	1.322 (4)
Se1—C6^{i}	1.885 (3)	C5—C6	1.506 (4)
O3—C3	1.205 (4)	C3—N4	1.374 (4)
O5—C5	1.200 (4)	C5—N4	1.369 (4)
C2—C3	1.503 (4)	N4—C4	1.454 (4)
C6^{i}—Se1—C2	93.5 (1)	O5—C5—C6	126.3 (3)
C6—C2—C3	108.7 (3)	N4—C5—C6	106.2 (3)
C3—C2—Se1	118.9 (2)	O3—C3—N4	127.3 (3)
C6—C2—Se1	132.4 (2)	O3—C3—C2	127.0 (3)
C2—C6—C5	107.9 (3)	N4—C3—C2	105.7 (2)
C2—C6—Se1^{i}	134.0 (2)	C5—N4—C3	111.4 (2)
C5—C6—Se1^{i}	118.1 (2)	C5—N4—C4	123.0 (3)
O5—C5—N4	127.4 (3)	C3—N4—C4	125.1 (3)

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

Acta Cryst. (2000). C**56**, 190–192 François Brisse *et al.* • $C_{10}H_6N_2O_4Se_2$ and $C_{10}H_6N_2O_4S_2$ **191**

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\max} = 0.466$ e Å^{-3}
$wR(F^2) = 0.073$	$\Delta\rho_{\min} = -0.465$ e Å^{-3}
$S = 1.181$	Extinction correction: *SHELXL*96 (Sheldrick, 1996)
1129 reflections	Extinction coefficient: 0.0032 (4)
84 parameters	
H-atom parameters constrained	

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973); program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990); program(s) used to refine structure: *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96 (Sheldrick, 1996); molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1563). Services for accessing these data are described at the back of the journal.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM*/360. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.

Boubekeur, K., Grandjean, D., Florac, C. & Robert, A. (1991). *Acta Cryst.* C**47**, 1107–1108.

Draber, W. (1967). *Chem. Ber.* **100**, 1559–1570.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Galasso, V. (1981). *J. Mol. Struct.* **85**, 159–162.

Hayakawa, K., Mibu, N., Osawa, E. & Kanematsu, K. (1982). *J. Am. Chem. Soc.* **104**, 7136–7142.

Howell, P. A., Curtis, R. M. & Lipscomb, W. N. (1954). *Acta Cryst.* **7**, 498–503.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kao, J., Eyermann, C., Southwick, E. & Leister, D. (1985). *J. Am. Chem. Soc.* **107**, 5323–5332.

Kirfel, A. (1975). *Acta Cryst.* B**31**, 2494–2495.

Lozac'h, N. (1989). *Sulfur Rep.* **9**, 153–206.

Saebo, S., Radom, L. & Ritchi, G. L. D. (1984). *J. Mol. Struct.* **108**, 59–63.

Sheldrick, G. M. (1990). *SHELXS*96. University of Göttingen, Germany.

Sheldrick, G. M. (1996). *SHELXL*96. University of Göttingen, Germany.

Yamaguchi, Y. & Ueda, I. (1984). *Acta Cryst.* C**40**, 113–115.