

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 BROOKS, P. R. & BISHOP, R. (1991). *J. Org. Chem.* In the press.
 CULLEN, E. R. & GUZIEC, F. S. (1986). *J. Org. Chem.* **51**, 1212–1216.
 GUZIEC, F. S., SANFILIPPO, L. J., MURPHY, C. J., MOUSTAKIS, C. A. & CULLEN, E. R. (1985). *Tetrahedron*, **41**, 4843–4852.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KONINGSVELD, H. VAN (1981). *Cryst. Struct. Commun.* **10**, 775–780.
 KONINGSVELD, H. VAN & PETERS, J. A. (1981). *Cryst. Struct. Commun.* **10**, 723–729.
 KONINGSVELD, H. VAN, PETERS, J. A. & JANSEN, J. C. (1984). *Acta Cryst.* **C40**, 158–160.
 KREBS, A., KALETTA, B., NICKEL, W.-U., RUGER, W. & TIKWE, L. (1986). *Tetrahedron*, **42**, 1693–1702.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

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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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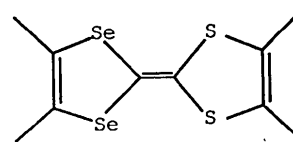
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Abstract. $2C_{10}H_{12}S_2Se_2^{1/2+} \cdot NO_3^-$, $M_r = 770.52$, triclinic, $P\bar{1}$, $a = 7.155$ (18), $b = 7.472$ (3), $c = 12.661$ (3) Å, $\alpha = 89.41$ (3), $\beta = 86.17$ (8), $\gamma = 70.90$ (5)°, $V = 638.1$ Å³, $Z = 1$, $D_x = 2.005$ 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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Table 1. Atomic coordinates and equivalent isotropic temperature factors (\AA^2)
$$B_{eq} = (4/3) \sum_j \beta_j \mathbf{a}_j \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
TS1*	0.2885 (1)	0.3579 (1)	0.61607 (7)	2.35 (2)
TS2*	0.1641 (1)	0.7535 (1)	0.51531 (7)	2.37 (2)
TS3*	0.3767 (2)	0.1604 (1)	0.37996 (8)	2.81 (2)
TS4*	0.2433 (2)	0.5541 (1)	0.27865 (8)	2.75 (2)
C1	0.2494 (9)	0.4980 (8)	0.4965 (5)	2.0 (1)
C2	0.2852 (9)	0.4146 (9)	0.3981 (5)	2.3 (1)
C3	0.2090 (9)	0.5685 (9)	0.7036 (5)	2.3 (1)
C4	0.1543 (9)	0.7403 (8)	0.6608 (5)	2.1 (1)
C5	0.381 (1)	0.1770 (9)	0.2338 (5)	2.5 (1)
C6	0.3219 (9)	0.3470 (8)	0.1916 (5)	2.2 (1)
C7	0.212 (1)	0.520 (1)	0.8193 (5)	3.2 (2)
C8	0.085 (1)	0.9256 (9)	0.7177 (5)	3.2 (2)
C9	0.452 (1)	-0.009 (1)	0.1749 (6)	4.3 (2)
C10	0.319 (1)	0.383 (1)	0.0756 (6)	3.9 (2)
N	0	0	0	6.6 (3)†
O1	-0.163 (4)	0.124 (3)	-0.013 (2)	6.0 (6)†
O2	0.074 (3)	-0.131 (3)	0.019 (2)	3.8 (4)†
O3	0.013 (4)	0.167 (3)	-0.063 (2)	6.0 (6)†
O4	-0.188 (3)	0.092 (2)	0.020 (1)	3.3 (4)†
O5	0.154 (3)	0.014 (3)	-0.022 (2)	5.4 (6)†
O6	0.058 (4)	-0.134 (3)	0.022 (2)	6.4 (6)†

* TS is a disordered atom with 50% contributions of S and Se atoms.

† Atom refined isotropically.

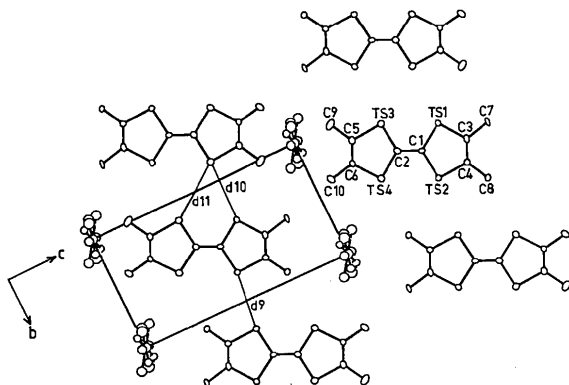


Fig. 1. Projection of the structure showing atom numbering and interstack interactions corresponding to those given in Table 3.

Lorentz-polarization corrections. Empirical absorption correction was applied using the *DIFABS* procedure (Walker & Stuart, 1983). The min. and max. correction factors were 0.79 and 1.27. The structure was solved by direct methods and successive Fourier difference syntheses. 1233 independent reflections with $I \geq 3\sigma(I)$, after averaging of the symmetry-related reflections ($R_{int} = 0.019$), were used for the refinements. H atoms placed at computed positions [$d(C-H) = 1.0 \text{ \AA}$; $B_{eq} = 5 \text{ \AA}^2$]. Full-matrix least-squares anisotropic (β_{ij}) refinement on F , atoms of the NO_3^- unit refined isotropically and isotropic H atoms not refined; secondary-extinction value, $g = 1.150 \times 10^{-8}$. The convergence was obtained by the introduction of a disordered atom TS (see Table 1) with 50% contributions of S and Se atoms. $R =$

Table 2. Comparison of the bond distances (\AA) and bond angles ($^\circ$) of TMDTDSF with those observed in $(TMTTF)_2NO_3$ and $(TMTSF)_2NO_3$

	$(TMTTF)_2NO_3^a$	$(TMDTDSF)_2NO_3^b$	$(TMTSF)_2NO_3^c$
TS1—C1	1.755	1.816 (6)	1.864 (12)
TS1—C3	1.748	1.842 (6)	1.906 (13)
TS2—C1	1.727	1.817 (6)	1.889 (13)
TS2—C4	1.754	1.842 (6)	1.880 (13)
TS3—C2	1.723	1.806 (6)	1.887 (13)
TS3—C5	1.731	1.852 (7)	1.888 (13)
TS4—C2	1.714	1.814 (7)	1.862 (13)
TS4—C6	1.747	1.819 (6)	1.907 (13)
C1—C2	1.375	1.369 (9)	1.336 (17)
C3—C4	1.345	1.334 (9)	1.304 (17)
C3—C7	1.507	1.505 (9)	1.530 (19)
C4—C8	1.506	1.485 (9)	1.469 (20)
C5—C6	1.358	1.320 (9)	1.289 (16)
C5—C9	1.505	1.50 (1)	1.473 (20)
C6—C10	1.527	1.491 (9)	1.531 (18)
C1—TS1—C3	96.7	93.2 (3)	93.7 (5)
C1—TS2—C4	96.9	93.9 (3)	94.2 (5)
C2—TS3—C5	96.0	93.0 (3)	93.2 (6)
C2—TS4—C6	95.0	93.6 (2)	93.5 (5)
TS1—C1—TS2	113.4	116.1 (3)	113.9 (7)
TS1—C1—C2	122.6	121.5 (5)	124.3 (11)
TS1—C3—C4	116.3	119.2 (4)	119.2 (11)
TS2—C4—C3	116.7	117.5 (4)	119.0 (11)
TS2—C1—C2	124.0	122.3 (5)	121.9 (10)
TS3—C2—C1	122.4	122.1 (4)	121.4 (10)
TS3—C5—C6	115.9	118.2 (4)	119.8 (11)
TS4—C2—C1	121.7	121.6 (5)	124.1 (11)
TS4—C6—C5	117.2	118.9 (5)	119.0 (10)

References: (a) Liautard *et al.* (1982); the e.s.d.'s are 0.010 for the S—C and 0.014 \AA for the C—C bond lengths and 0.5° for the bond angles. (b) This work. (c) Soling *et al.* (1982).

0.033, $wR = 0.051$, $w = 4F_o^2 / [\sigma^2(F_o^2) + (0.06F_o^2)^2]$, $S = 1.358$, $(\Delta/\sigma)_{max} = 0.16$, $\Delta\rho_{max} = 0.488 \text{ e \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the calculations were performed on a MicroVAX 3100 using the *SDP* programs (B. A. Frenz & Associates Inc., 1985). Final atomic positional and thermal parameters are given in Table 1.* The atomic numbering is shown in Fig. 1.

Discussion. The title compound is isomorphous to those of the $(TMTTF)_2X$ ($X = Br^-, NO_3^-, BF_4^-, ClO_4^-, PF_6^-, \dots$) (Brun, Liautard, Peytavin, Maurin, Toreilles, Fabre, Giral & Galigné, 1977) and $(TMTSF)_2X$ series (Bechgaard, Jacobsen, Mortensen, Pedersen & Thorup, 1980). The organic donor TMDTDSF can be described as a connection of half a TMTTF and half a TMTSF molecule (see scheme). The unit-cell parameters of $(TMDTDSF)_2NO_3$ (Table 3) are greater than those of $(TMTTF)_2NO_3$ (Liautard, Peytavin, Brun &

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54056 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Comparison of the crystal data and the shortest intermolecular interactions (Å) of (TMDTDSF)₂NO₃ with those observed in (TMTTF)₂NO₃ and (TMTSF)₂NO₃

	(TMTTF) ₂ NO ₃ ^a TS = S	(TMDTDSF) ₂ NO ₃ ^b TS = S/Se	(TMTSF) ₂ NO ₃ ^c TS = Se
Crystal data			
<i>a</i> (Å)	7.061 (4)	7.155 (18)	7.127 (7)
<i>b</i> (Å)	7.395 (2)	7.472 (3)	7.567 (2)
<i>c</i> (Å)	12.547 (4)	12.661 (3)	12.822 (2)
α (°)	89.50 (3)	89.41 (3)	89.14 (2)
β (°)	93.91 (4)	86.17 (8)	86.61 (3)
γ (°)	108.97 (3)	70.90 (5)	70.56 (4)
<i>V</i> (Å ³)	618.2	638.1	659.1
Interplanar distances			
<i>d</i> 1	3.57	3.596 (7)	3.61
<i>d</i> 2	3.50	3.556 (7)	3.60
Intrastack contacts			
<i>d</i> 3: TS1—TS4 ⁱ	3.88 (2)	3.935 (2)	3.965
<i>d</i> 4: TS2—TS3 ⁱ	3.83 (2)	3.867 (2)	3.899
<i>d</i> 5: TS1—TS2 ⁱ	3.94 (2)	3.978 (2)	4.041
<i>d</i> 6: TS2—TS3 ⁱⁱ	3.78 (1)	3.853 (2)	3.913
<i>d</i> 7: TS1—TS4 ⁱⁱ	3.73 (1)	3.794 (2)	3.850
<i>d</i> 8: TS1—TS2 ⁱⁱ	4.00	4.057 (2)	4.120
Interstack contacts			
<i>d</i> 9: TS2—TS2 ⁱⁱⁱ	3.78	3.697 (2)	3.676
<i>d</i> 10: TS1—TS3 ^{iv}	3.94	3.832 (2)	3.822
<i>d</i> 11: TS3—TS3 ^v	4.05	3.987 (2)	4.023

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 2-y, 1-z$; (iv) $1-x, -y, 1-z$.

References: (a) Liautard *et al.* (1982). (b) This work. (c) Soling *et al.* (1982); the e.s.d.'s of intermolecular Se...Se distances are 0.002–0.003 Å.

Maurin, 1982) and smaller than those of (TMTSF)₂NO₃ (Soling, Rindorf & Thorup, 1982). The bond distances, bond angles, interplanar separations, and intra- and interstack TS...TS contacts of (TMDTDSF)₂NO₃ are displayed in Figs. 1 and 2 and compared in Tables 2 and 3 to those observed in (TMTTF)₂NO₃ and (TMTSF)₂NO₃. From these comparisons, it appears that the TS—C bond distances, the C—TS—C bond angles and the inter-

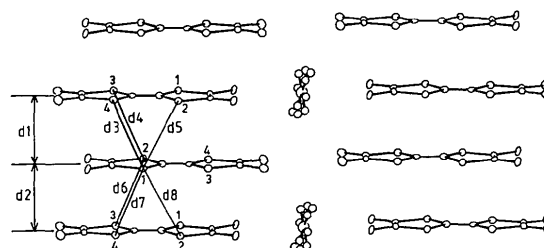


Fig. 2. Side view of stacks showing shorter S/Se...S/Se contacts corresponding to those given in Table 3.

molecular interactions are nearly midway between those observed in the TMTTF salt and those observed in the TMTSF salt. It is noted that the intrastack interactions increase while the interstack ones decrease from the TMTTF to the TMTSF salts.

The important disorder observed for the NO₃⁻ anion is the same as that described in detail in (TMTTF)₂NO₃ (Liautard *et al.*, 1982), *i.e.* the central N atom is surrounded by 12 statistically disordered O atoms in such a way that they form a planar disc. A dihedral angle of 103° is observed between the planar NO₃ and TMDTDSF counterparts.

References

- AUBAN, P., JÉRÔME, D., LERSTRUP, K., JOHANNSEN, I., JORGENSEN, M. & BECHGAARD, K. (1989). *J. Phys. (Paris)*, **50**, 2727–2739.
- B. A. FRENZ & ASSOCIATES INC. (1985). *SDP Structure Determination Package*. College Station, Texas, USA.
- BECHGAARD, K., JACOBSEN, J., MORTENSEN, K., PEDERSEN, H. J. & THORUP, N. (1980). *Solid State Commun.* **33**, 1119–1125.
- BRUN, G., LIAUTARD, B., PEYTAVIN, S., MAURIN, M., TOREILLES, E., FABRE, J. M., GIRAL, L. & GALIGNÉ, J. L. (1977). *J. Phys. (Paris) Colloq.* **38**, 266–269.
- LERSTRUP, K., JOHANNSEN, I. & JORGENSEN, M. (1988). *Synth. Met.* **27**, B9–B13.
- LIAUTARD, B., PEYTAVIN, S., BRUN, G. & MAURIN, M. (1982). *Acta Cryst.* **B38**, 2746–2749.
- SOLING, H., RINDORF, G. & THORUP, N. (1982). *Cryst. Struct. Commun.* **11**, 1975–1980.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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2,2-Dimethyl-1,2,3,4-tetrahydrobenzimidazo[3,2-a]pyrimid-4-one

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Abstract. C₁₂H₁₃N₃O, *M*_r = 215.25, triclinic, *P* $\bar{1}$, *a* = 6.678 (3), *b* = 9.635 (3), *c* = 9.947 (5) Å, α = 114.79 (3), β = 106.01 (4), γ = 90.39 (4)°, *V* = 553.0 Å³, *Z* = 2, *D*_x = 1.29 Mg m⁻³, λ (Cu K α) = 1.5418 Å, μ = 0.655 mm⁻¹, *F*(000) = 228, *T* =

298 K, *R* = 0.036, *wR* = 0.036 for 1302 significant reflections out of a total 1383 [*I* > 2.5 σ (*I*)]. The molecular structure comprises a planar benzimidazole fused to a reduced pyrimidine ring, which contains an N atom bonded to an exocyclic H atom.