

- KWIATKOWSKI, W. & KAROLAK-WOJCIECHOWSKA, J. (1990). *Acta Cryst.* **C46**, 913–915.
- KWIATKOWSKI, W., KAROLAK-WOJCIECHOWSKA, J., OBNISKA, J. & ZEJC, A. (1990). *Acta Cryst.* **C46**, 108–112.
- LANGE, J., RUMP, S., GALECKA, E., ILCZUK, I., LECHOWSKA-POSTEK, M., RABSZTYN, T., SZYMAŃSKA, T. & WALCZYNA, K. (1977). *Pharmazie*, **32**, 82–84.
- LANGE, J., RUMP, S., ILCZUK, I., ŁAPISZEWICZ, J., RABSZTYN, T. & WALCZYNA, K. (1977). *Pharmazie*, **32**, 579–581.
- ŁAPISZEWICZ, J., LANGE, J., RUMP, S. & WALCZYNA, T. (1978). *Eur. J. Med. Chem. Chim. Ther.* **13**, 465–468.
- ŁUCKA-SOBSTAŁ, B., ZEJC, A. & OBNISKA, J. (1977). *Arch. Immunol. Ther. Exp. Engl. Transl.* **25**, 285–289.
- SHELDRIK, G. M. (1985). *SHELX86. Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
- SHELDRIK, G. M. (1989). *SHELXTL-PC. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
- VICKOVIĆ, I. (1988). *J. Appl. Cryst.* **21**, 987–990.
- ZEJC, A. & OBNISKA, J. (1984). *Acta Pol. Pharmacol. Pharm.* **5**, 529–533.
- ZEJC, A., OBNISKA, J., CHOJNACKA-WÓJCIK, E., TATARCZYŃSKA, E. & WICZYŃSKA, B. (1987). *Pol. J. Pharmacol. Pharm.* **39**, 91–95.

Acta Cryst. (1991). **C47**, 1980–1982

Structure of Di(4,4',5,5'-tetramethyl-1,3-dithia-1',3'-diselenafulvalene) Tetrafluoroborate: (TMDTDSF)₂BF₄

BY ALLAL MHANNI, LAHCÈNE OUAHAB* AND DANIEL GRANDJEAN

Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA 254 CNRS, Université de Rennes I, 35042 Rennes CEDEX, France

AND JOSIANE AMOUROUX AND JEAN MARC FABRE

Laboratoire de Chimie Organique Structurale, USTL, Place E. Bataillon, 34060 Montpellier CEDEX, France

(Received 6 February 1991; accepted 21 February 1991)

Abstract. (C₁₀H₁₂S₂Se₂)₂BF₄, *M_r* = 795.31, triclinic, *P* $\bar{1}$, *a* = 7.208 (16), *b* = 7.571 (5), *c* = 13.068 (4) Å, α = 85.65 (4), β = 86.88 (7), γ = 70.46 (8)°, *V* = 669.9 Å³, *Z* = 1, *D_x* = 1.971 g cm⁻³, *F*(000) = 385, λ (Mo *K*α) = 0.71073 Å, μ = 57.59 cm⁻¹, *T* = 293 K, *R* = 0.044 based on 1206 observed reflections with *I* ≥ 3σ(*I*). The F atoms of the tetrahedral BF₄⁻ unit are disordered as already observed in such an anion. However, the B atom is located at the origin of the unit cell, in contrast with its distribution on both sides of the origin in (TMTCF)₂BF₄, *C* = S and Se. The heteroatoms (S and Se) also present a statistical disorder. The bond distances (specially C—S/Se: 1.80–1.85 Å), the interplanar separation (3.59 and 3.62 Å) between adjacent organic molecules and the intermolecular heteroatom contacts are midway between those observed in (TMTTF)₂BF₄ and (TMTSF)₂BF₄.

Experimental. The hybrid molecule TMDTDSF has been prepared using the procedure developed in the literature (Lerstrup, Johannsen & Jorgensen, 1988). Single crystals of (TMDTDSF)₂BF₄ are obtained by electro-oxidation on a platinum electrode of TMDTDSF (10⁻³*M*) in tetrahydrofuran solution

containing (Bu₄N)BF₄ (0.1*M*) as supporting electrolyte. A black crystal with approximate dimensions 0.4 × 0.1 × 0.1 mm was selected for data collection on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo *K*α radiation (λ = 0.71073 Å). ω –2θ scan. Cell dimensions were obtained by least-squares refinement from 25 centered reflections ($\theta \leq 50^\circ$). Three standard reflections measured every hour: no fluctuations in intensities. 2566 reflections were recorded in the range $2 \leq 2\theta \leq 50^\circ$ with $0 \leq h \leq 8$, $-8 \leq k \leq 8$, $-15 \leq l \leq 15$. Lorentz–polarization correction. Absorption correction was performed by using the *DIFABS* procedure (Walker & Stuart, 1983). Min. and max. correction factors were 0.803 and 1.520. The structure was solved by direct methods and a successive Fourier difference synthesis. 1206 unique reflections with *I* ≥ 3σ(*I*), after averaging of the symmetry related reflections (*R*_{int} = 0.030), were used for the refinements. H atoms from computed positions (C—H = 1 Å, *B*_{eq} = 4 Å²). Full-matrix least squares (on *F*) anisotropic (β_{ij}) refinement. Atoms of the disordered BF₄ unit were refined isotropically with an occupancy of 0.5 for the F atoms: H atoms were not refined. Secondary-extinction refinement, *g* = -5.2618×10^{-8} . The convergence was obtained by the introduction of a disordered atom TS (see Table

* Author to whom correspondence should be addressed.

Table 1. Atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
TS1	0.1654 (2)	0.7473 (2)	0.5106 (1)	2.63 (3)
TS2	0.2957 (2)	0.3463 (2)	0.61273 (9)	2.71 (3)
TS3	0.3709 (2)	0.1726 (2)	0.3850 (1)	2.81 (3)
TS4	0.2305 (2)	0.5740 (2)	0.2831 (1)	2.60 (3)
C1	0.164 (1)	0.718 (1)	0.6505 (7)	2.5 (2)
C2	0.223 (1)	0.545 (1)	0.6968 (6)	2.0 (2)
C3	0.248 (1)	0.496 (1)	0.4959 (7)	2.4 (2)
C4	0.230 (1)	0.490 (2)	0.8088 (8)	4.0 (3)
C5	0.095 (1)	0.896 (1)	0.7031 (7)	3.0 (2)
C6	0.309 (1)	0.375 (1)	0.1991 (7)	2.6 (2)
C7	0.370 (1)	0.199 (1)	0.2442 (7)	2.4 (2)
C8	0.283 (1)	0.422 (1)	0.4012 (7)	2.1 (2)
C9	0.440 (1)	0.027 (1)	0.1887 (8)	4.2 (3)
C10	0.295 (1)	0.425 (1)	0.0867 (7)	3.5 (2)
B	0	0	0	12. (1)
F1	0.025 (2)	0.139 (2)	0.047 (1)	7.9 (4)*
F2	-0.194 (2)	0.111 (2)	0.029 (1)	8.7 (5)*
F3	-0.043 (3)	0.113 (3)	-0.098 (2)	11.9 (6)*
F4	-0.118 (5)	-0.100 (4)	0.020 (3)	20. (1)*

Starred atoms were refined isotropically.

Table 2. Bond distances (\AA) and bond angles ($^\circ$) in $(\text{TMDTDSF})_2\text{BF}_4$

TS1—C3	1.816 (8)	C1—C5	1.48 (1)
TS1—C1	1.825 (9)	C2—C4	1.49 (1)
TS2—C3	1.808 (8)	C6—C7	1.35 (1)
TS2—C2	1.849 (8)	C6—C10	1.49 (1)
TS3—C8	1.803 (8)	C7—C9	1.46 (1)
TS3—C7	1.835 (9)	B—F1	1.33 (2)
TS4—C8	1.832 (8)	B—F2	1.42 (2)
TS4—C6	1.846 (9)	B—F3	1.47 (2)
C3—C8	1.37 (1)	B—F4	1.32 (4)
C1—C2	1.34 (1)		
C3—TS1—C1	92.9 (4)	TS2—C2—C4	114.4 (6)
C3—TS2—C2	93.7 (4)	C1—C2—C4	128.8 (9)
C8—TS3—C7	94.3 (4)	TS4—C6—C7	117.9 (7)
C8—TS4—C6	93.5 (3)	TS4—C6—C10	116.0 (6)
TS1—C3—TS2	116.5 (5)	C7—C6—C10	126.2 (9)
TS1—C3—C8	122.2 (6)	TS3—C7—C6	118.3 (7)
TS2—C3—C8	121.2 (6)	TS3—C7—C9	117.1 (6)
TS3—C8—TS4	116.1 (5)	C6—C7—C9	124.6 (9)
TS3—C8—C3	122.9 (6)	F1—B—F2	104. (1)
TS4—C8—C3	121.0 (6)	F1—B—F3	92. (1)
TS1—C1—C2	120.0 (6)	F1—B—F4	132. (2)
TS1—C1—C5	114.4 (6)	F2—B—F3	96. (1)
C2—C1—C5	125.6 (8)	F2—B—F4	113. (1)
TS2—C2—C1	116.7 (6)	F3—B—F4	112. (2)

1) with 50% contributions from S and Se atoms. $R = 0.044$, $wR = 0.065$, $w = 4F_o^2/[\sigma^2(F_o^2) + (0.07F_o^2)^2]$, $S = 1.481$, $(\Delta/\sigma)_{\max} = 0.08$, $\Delta\rho_{\max} = 0.69 \text{ e \AA}^{-3}$. 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. The bond distances and bond angles are presented in Table 2.

Related literature. Physical studies of $(\text{TMDTDSF})_2X$ ($X = \text{PF}_6^-$, NO_3^- , BF_4^- , ReO_4^- , ...) have been reported (Auban, Jérôme, Lerstrup,

* 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 54024 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

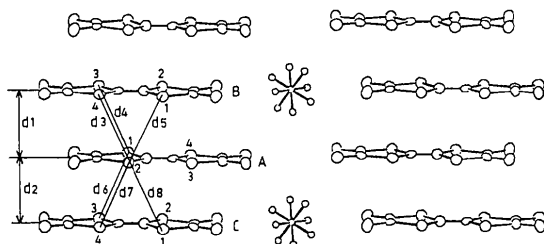


Fig. 1. Projection of the structure showing atomic numbering and interchain interactions (\AA): $d1 = 3.62$; $d2 = 3.59$; $d3 = 3.987$ (2); $d4 = 3.922$ (2); $d5 = 3.980$ (2); $d6 = 3.893$ (2); $d7 = 3.825$ (2); $d8 = 4.059$ (2). $A(x, y, z)$; $B(1-x, 1-y, 1-z)$; $C(-x, 1-y, 1-z)$.

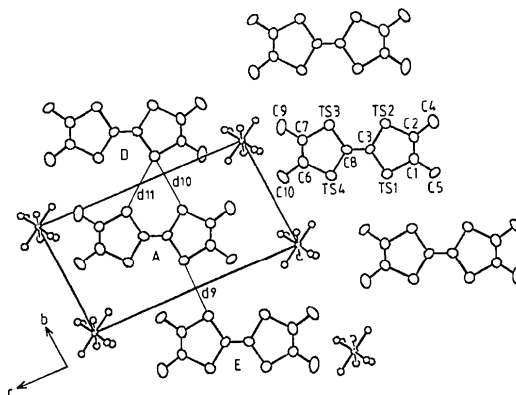


Fig. 2. Side view of stacks showing shorter intrastack (S/Se...S/Se) contacts (\AA): $d9 = 3.770$ (2); $d10 = 3.858$ (2); $d11 = 3.937$ (2). $A(x, y, z)$; $D(1-x, -y, 1-z)$; $E(-x, 2-y, 1-z)$.

Johannsen, Jorgensen & Bechgaard, 1989). These compounds are isomorphous with $(\text{TMTTF})_2X$ (Brun, Liautard, Peytavin, Maurin, Toreilles, Fabre, Giral & Galigné, 1977) and $(\text{TMTSF})_2X$ (Bechgaard, Jacobsen, Mortensen, Pedersen & Thorup, 1980). The interplanar separations and the intra- and interstack TS...TS contacts are displayed in Figs. 1 and 2. The TS—C bond distances and the C—TS—C bond angles and the intermolecular interactions compare well with those observed in the corresponding nitrate salt (Triki, Ouahab, Grandjean, Amouroux & Fabre, 1991). They are nearly midway between those observed in $(\text{TMTTF})_2\text{BF}_4$ (TS = 100%S) (Galigné, Liautard, Peytavin, Brun, Maurin, Fabre, Torreilles & Giral, 1979) and $(\text{TMTSF})_2\text{BF}_4$ (TS = 100%Se) (Kobayashi, Kobayashi, Saito & Inokuchi, 1982). We note that the B atom is located at the origin

of the unit cell, in contrast with its distribution on both sides of the origin in $(TMTTF)_2BF_4$ and $(TMTSF)_2BF_4$.

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.
 GALIGNÉ, J. L., LIAUTARD, B., PEYTAVIN, S., BRUN, G., MAURIN, M., FABRE, M., TORREILLES, E. & GIRAL, L. (1979). *Acta Cryst.* **B35**, 1129–1135.
 KOBAYASHI, H., KOBAYASHI, A., SAITO, G. & INOKUCHI, H. (1982). *Chem. Soc. Jpn, Chem. Lett.* pp. 245–248.
 LERSTRUP, K., JOHANNSEN, I. & JORGENSEN, M. (1988). *Synth. Met.* **27**, B9–B13.
 TRIKI, S., OUAHAB, L., GRANDJEAN, D., AMOUROUX, J. & FABRE, J. M. (1991). *Acta Cryst.* **C47**, 1941–1943.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1991). **C47**, 1982–1983

3',3',4',4'-Tetrafluoro-4-iodo-1-phenyl-2,3-cyclobutenonaphthalene

BY M. G. BARLOW, R. G. PRITCHARD, S. TAJAMMAL AND A. E. TIPPING

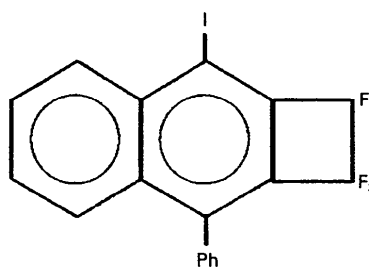
Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(Received 6 December 1990; accepted 13 February 1991)

Abstract. $C_{18}H_9F_4I$, $M_r = 428.2$, orthorhombic, *Pbca*, $a = 20.039$ (7), $b = 18.800$ (9), $c = 8.167$ (3) Å, $V = 3077$ Å³, $Z = 8$, $D_x = 1.848$ Mg m⁻³, $F(000) = 1648$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.09$ mm⁻¹, $T = 293$ K, $R = 0.034$ for 1555 unique reflexions [$F \geq 3\sigma(F)$]. The title compound is a by-product (up to 11.5%) in the synthesis of 3,3-difluoro-3-iodo-1-phenylpropyne, $\text{Ph}-\text{C}\equiv\text{C}-\text{CF}_2\text{I}$. It would have been formed by dimerization of the latter *via* elimination of iodine to give 1,6-diphenyltetrafluoro-hexa-1,5-diyne, $\text{Ph}-\text{C}\equiv\text{C}-\text{CF}_2-\text{CF}_2-\text{C}\equiv\text{C}-\text{Ph}$, followed by a double cyclization, induced by electrophilic attack by iodine on a carbon adjacent to a phenyl ring. The planar naphthalene moiety retains a bond shortening pattern typical of its class and is inclined at $54(1)^\circ$ to the phenyl ring. This ring is directed away from a C—I bond, which at 2.094 (6) Å falls within the expected range.

Experimental. Sample preparation involved treating a solution of 3-bromo-3,3-difluoro-1-phenylpropyne (0.088 mol in 100 ml acetone) with an excess of sodium iodide (0.367 mol in 200 ml acetone) followed by refluxing in a nitrogen atmosphere for 35 h. The resulting solution was partitioned between *n*-hexane and water prior to drying the organic layer over MgSO_4 . The solvent was then removed using a rotary evaporator and the crude product separated into its three components using dry-column flash chromatography (70/55 mm sinter packed with Kieselgel silica eluted with petroleum ether, b.p.

313–333 K). The products in order of elution were (i) 3,3-difluoro-3-iodo-1-phenylpropyne (R_F 0.57; 60%), identified by spectral (¹H, ¹³C and ¹⁹F NMR and mass) data and elemental analysis, (ii) (*E*)-1-bromo-1,2-diiido-2-phenylethene (R_F 0.42; ca 1%), formed by addition of iodine across the triple bond of 1-bromo-2-phenylethyne impurity in the reactant and identified by single-crystal X-ray crystallography (Barlow, Tajammal & Tipping, 1991), and (iii) the title compound (R_F 0.33; 11.5%).



Crystal dimensions $0.10 \times 0.15 \times 0.25$ mm, Rigaku AFC6S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, unit-cell dimensions from setting angles of 25 accurately centered reflexions ($12.2 \leq 2\theta \leq 18.7^\circ$), ω - 2θ scan mode, ω -scan width ($1.15 + 0.30 \tan \theta$)^o and scan speed of 8° min^{-1} with up to two additional scans of weak reflexions [$I < 10\sigma(I)$], $0 \leq h \leq 23$, $0 \leq k \leq 22$, $-9 \leq l \leq 0$, $0 \leq \theta \leq 25^\circ$, 3108 unique reflexions measured, 1555 observed [$I \geq$