The tetrahedral coordination around the sulfur atom shows the expected distortion of sulfones in both molecules. The O—S—O angle of 119·3 and 118·4° for the thiazine and thiazepine derivatives respectively are larger, while the C—S—N angles of 100·4 and 106·1° are smaller than the tetrahedral value.

In the packing mode of both molecules we observe a stacking of the aromatic rings. In BBTZ the bromobenzene rings related by the centre of symmetry are 3·50 Å apart and in MPTE the pyridyl rings are 3·52 Å apart. A similar, 3·5 Å stacking distance is observed as well for the *o*-dimethoxybenzo groups of both molecules. This 3·5 Å interplanar distance compares well with that observed for aromatic acyl halides (Leser & Rabinovich, 1978).

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Structures of the Conducting Salts of Bis(pyrazino)tetrathiafulvalene (BPTTF): $(BPTTF)_2BF_4$ and $(BPTTF)_2PF_6$

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Abstract. BF_4^- salt (I): di($\Delta^{2,2'}$-bi-1,3-dithiolano[*e*]pyrazin)ium tetrafluoroborate, $(C_{10}H_4N_4S_4)_2BF_4$, $M_r = 703{\cdot}66$, orthorhombic, *Fddd*, $a = 11{\cdot}547\,(2)$, $b = 13{\cdot}127\,(3)$, $c = 34{\cdot}182\,(6)$ Å, $V = 5181\,(2)$ Å^3, $Z = 8$, $D_m = 1{\cdot}80$, $D_x = 1{\cdot}804$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}73$ cm^{-1}, $F(000) = 2824$, $T = 296\,(2)$ K. PF_6^- salt (II): di($\Delta^{2,2'}$-bi-1,3-dithiolano[*e*]pyrazin)ium hexafluorophosphate, $(C_{10}H_4N_4S_4)_2PF_6$, $M_r = 761{\cdot}81$, orthorhombic, *Fddd*, $a = 11{\cdot}642\,(2)$, $b = 13{\cdot}122\,(2)$, $c = 35{\cdot}339\,(5)$ Å, $V = 5398\,(1)$ Å^3, $Z = 8$, $D_m = 1{\cdot}86$, $D_x = 1{\cdot}874\,(1)$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}13$ cm^{-1}, $F(000) = 3048$, $T = 296\,(2)$ K. Final R values are 0·037 (I) and 0·058 (II) for 930 and 955 observed $[I \geq 2{\cdot}5\sigma(I)]$ reflections. The compounds are isostructural. There is only marginal stacking of BPTTF molecules but there are short intermolecular S···N contacts: 3·003 (I), 3·234 Å (II) and S···S contacts: 3·644 (I), 3·676 Å (II).

Introduction. Until recently, structural studies of most of the highly conducting molecular systems supported the view of these materials as quasi-one-dimensional systems containing clearly defined and largely isolated, parallel stacks of the constituent molecules (Hatfield, 1979). Organic metals known until recently were composed of planar donor and/or acceptor molecules with π-conjugated systems. They are stacked face-to-face to form segregated columns. The one-dimensional properties are considered to arise from the intermolecular π–π interaction along the columns (Shibaeva, 1982). Recent work has shown (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983; Beno, Blackman, Leung & Williams, 1983) that one of the principal requirements for retention of metal-like characteristics and eventual transition to a superconductive state at low temperature is higher-than-one dimensionality, *i.e.* intercolumn electronic interactions must be introduced.

In this paper we report on the structure of a type of organic metal where the planar molecules are only marginally stacked but are arranged side-by-side to form a two-dimensional system. The two-dimensionality of the structure originates from short intermolecular contacts between S and N atoms.

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Experimental. Title compounds were prepared by the electrocrystallization of BPTTF ($1{\cdot}55\times10^{-3}$ *M*) (Papavassiliou, Yiannopoulos & Zambouris, 1985) and Bu_4NX (5×10^{-3} *M*, $X = BF_4^-$, PF_6^-) in CH_2Cl_2 using platinum electrodes at 1 μA cm^{-2} and 295 K. They have a copper-black lustrous appearance and grow perpendicular to the electrode surface along their **c** direction. They are square bipyramidal and data crystals $0{\cdot}31\times0{\cdot}30\times0{\cdot}41$ (I), $0{\cdot}29\times0{\cdot}31\times0{\cdot}40$ mm (II) were cut perpendicular to **c** to a pyramidal shape. D_m by flotation in $CHCl_3/CHBr_3$. They decompose in air and the crystals used for data collection were mounted in sealed capillary tubes. Intensity data collected on a Syntex $P2_1$ computer-controlled diffractometer. Lattice parameters from 15 intermediate $\sin\theta$ reflections. Data in range $2\theta\le50°$ (I), $2\theta\le48{\cdot}5°$ (II) (range of *hkl*: $0\rightarrow13$, $-15\rightarrow15$, $0\rightarrow40$), $\omega/2\theta$ scan mode, scan speed 1–12° (2θ) min^{-1}, scan width 1·7° (2θ) plus $\alpha_1-\alpha_2$ divergence. Three reflections monitored periodically showed <3·0% intensity fluctuation, no absorption correction. Data collected/unique/$R_{\rm int}$, 2452/1156/0·010 (I), 2356/1105/0·011 (II). Data used with $F_o\ge 5{\cdot}0\sigma(F_o)$, 930 (I) and 955 (II). Structure solved with *MULTAN*84 (Main, Germain & Woolfson, 1984) and refined, based on *F*, with *SHELX*76 (Sheldrick, 1976) minimizing $\sum w(|F_o|-|F_c|)^2$, $w = 1{\cdot}0$, H (calculated) isotropic riding on carbons at 1·01 Å. $|\Delta/\sigma|_{\rm max} = 2{\cdot}08$ [*U*'s of F atoms, (II), disordered]. $(\Delta\rho)_{\rm max}/(\Delta\rho)_{\rm min}$ 0·6/–0·4 e Å^{-3} (I) and 0·9/–0·4 e Å^{-3} (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,* bond lengths and angles in Fig. 1 and an *ORTEP* (Johnson, 1976) stereoview of unit-cell packing in Fig. 2.

Discussion. The BF_4^- and PF_6^- salts are isostructural. Both anions are disordered. When B and P are placed at special positions refined anisotropically, U_{22} is very large. When we place B and P at half occupancy and allow *y* to refine it settles at the reported position and the *U*'s are normal. The fluorine atoms are disordered as well and while our model for BF_4^- is satisfactory the one for PF_6^- is not, as we can judge from the very large

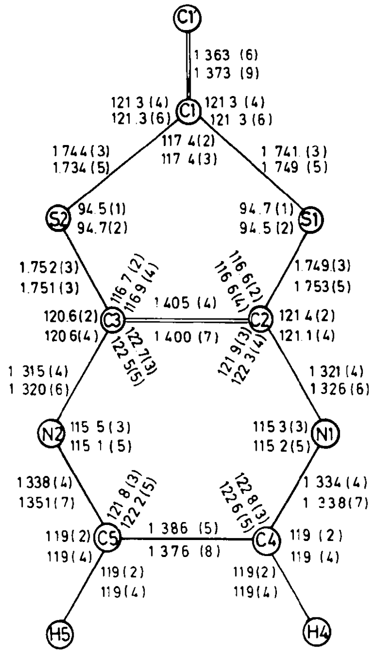

Fig. 1. Atom numbering and bond distances (Å) and angles (°) with e.s.d.'s in parentheses. Upper numbers refer to the BF_4^- salt and lower numbers to the PF_6^- salt.

Table 1. *Fractional coordinates* ($\times10^4$) *and equivalent isotropic temperature factors* (Å$^2\times10^3$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	BF_4^- salt				PF_6^- salt			
	x	*y*	*z*	$U_{\rm eq}/U_{\rm iso}$	*x*	*y*	*z*	$U_{\rm eq}/U_{\rm iso}$
S(1)	513 (1)	–40 (1)	664 (0)	39 (1)	523 (1)	–49 (1)	681 (0)	44 (1)
S(2)	2933 (1)	9 (1)	964 (0)	43 (1)	2918 (1)	–7 (1)	974 (0)	49 (1)
N(1)	1384 (3)	–61 (2)	–65 (1)	42 (1)	1392 (4)	–34 (4)	–24 (1)	51 (3)
N(2)	3668 (2)	–34 (2)	223 (1)	43 (1)	3657 (4)	–24 (4)	256 (1)	52 (3)
C(1)	1452 (3)	–21 (3)	1063 (1)	36 (1)	1457 (4)	–29 (4)	1068 (1)	39 (2)
C(2)	1617 (3)	–44 (3)	314 (1)	35 (2)	1626 (4)	–42 (4)	343 (1)	43 (3)
C(3)	2760 (3)	–31 (3)	455 (1)	37 (2)	2752 (4)	–28 (4)	48 (1)	44 (3)
C(4)	2307 (3)	–74 (3)	–300 (1)	47 (2)	2310 (5)	–29 (5)	–253 (2)	54 (3)
C(5)	3434 (3)	–55 (3)	–160 (1)	45 (2)	3418 (5)	–30 (4)	–118 (2)	55 (3)
H(4)	2178	–99	–592	53 (6)	2184	–33	–536	65 (12)
H(5)	4096	–57	–353	37 (5)	4079	–33	–303	50 (12)
B,P	6250	1460 (3)	1250	65 (5)	6250	1530 (4)	1250	60 (3)
F(1)	6852 (8)	2206 (6)	1052 (2)	170 (6)	7083 (10)	1530 (8)	93 (4)	134 (8)
F(2)	5508 (7)	966 (5)	966 (2)	112 (4)	6250	2700 (9)	1250	327 (15)
F(3)					7083 (10)	970 (9)	93 (4)	304 (14)
F(4)					6250	2140 (12)	1250	329 (16)

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* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43142 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

U's of the F atoms in PF_6^- and the small residual positive electron density at positions close to the F atoms. B—F and P—F bonds were restricted during the refinement at 1·38 and 1·52 Å respectively. Bond distances and angles of the BPTTF radical ions in the two structures are in very good agreement; most of them within one e.s.d and only five bonds within two e.s.d.'s.

These structures are of a type of organic metal where planar molecules are not stacked face-to-face but are arranged side-by-side to form a two-dimensional system as has been observed in the perchlorate salt of bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF) (Kobayashi, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1983). Unlike other organic metals with column structures, like those of the salts of tetramethyltetraselenafulvalene (TMTSF) (Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981), the present structures exhibit only slight intermolecular overlapping. However, they may be considered pseudo-two-dimensional since there are intermolecular S···S distances [3·644 Å for (I) and 3·676 Å for (II)] parallel to **b** and S···N distances [3·003 Å for (I) and 3·234 Å for (II)] perpendicular to **b** which are short compared with the respective van der Waals distances (3·70 Å for S···S and 3·35 Å for S···N). The S···S interaction would seem to be very weak and the S···N interaction rather strong judging from the comparison of the S···S and S···N distances with their respective van der Waals distances. However, one would have to know the hybridization of the S and N atoms in order to discuss orbital overlap, because of the directionality of the orbitals involved.

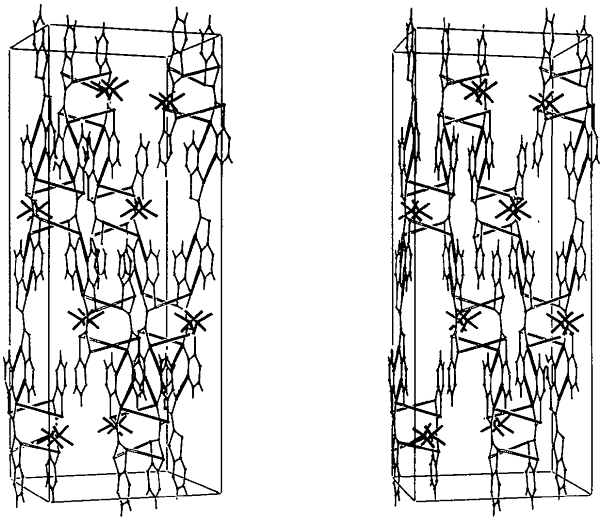

Fig. 2. Stereofigure of $(BPTTF)_2BF_4$ looking down the a axis.

Perhaps we should speak of these salts as 'pseudo-three-dimensional' because the packing of the BPTTF molecules and the space-group symmetry introduce a third 'dimensionality', namely the chains of BPTTF molecules that are formed because of the S···N contacts in the ac planes run along the *two different ac* diagonals in alternate ac planes every $\frac{1}{4}b$ (Fig. 2). The S···N contacts therefore introduce conductivity in the ac plane. Perpendicular to these planes, along **b**, we have the S···S contacts and the π–π overlap of the C(1)—C(1′) double bonds at 3·28 Å. Both the S···S and π–π overlap form dimers along **b** (Fig. 2) which are joined only through the S···N contacts. So conductivity in the third dimension, b, must pass through S···N contacts as well. Preliminary results of conductivity measurements on the BF_4^- salt showed that these salts are indeed 'pseudo-three-dimensional' (σ_{RT} varies between 10^{-2} and $10^{-4}\,\Omega^{-1}\,cm^{-1}$ in the three directions).

A comparison of unit-cell parameters and other important distances of the two salts reveals some interesting aspects. While PF_6^- is larger than BF_4^- the b dimension of the former salt's unit cell is slightly *shorter* than that of the latter salt. However, the S···S contacts (Fig. 2) which run almost parallel to **b** are larger in the PF_6^- salt by 0·032 Å.

The difference in size of the anions is reflected primarily in the c dimension (and volume of unit cells) but also in the a dimension. As a result the S···N contacts which run along the ac diagonals are considerably shorter in the BF_4^- salt. This effect is rather pronounced if we compare it with the plot of unit-cell volume *vs* interstack Se···Se distance (Whangbo, Williams, Beno & Dorfman, 1983) for a series of TMTSF salts with anions ranging in size from BF_4^- to PF_6^- to AsF_6^- where for 4·3% volume increase the Se···Se distance increased from 3·81 to 3·93 Å. In our case we have a 6% volume increase between the BF_4^- and PF_6^- salts and a S···N distance increase from 3·000 to 3·234 Å. This suggests that while the S···N distance is sensitive to the size of the anion the S···S is not, and by choosing a smaller anion one may strengthen the S···N but not the S···S contacts.

The charge and spin on the BPTTF radical ions are completely delocalized since the ions lie on a twofold crystallographic axis perpendicular to the C(1)—C(1′) bond. There are some weak C—H···F hydrogen bonds (we observe H···F distances of 2·43 to 2·58 Å) but because of the anion disorder we will not discuss them here.

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Structure of *rel*-(3*R*,3a*S*,7a*S*)-Hexahydro-4,4-dimethoxy-3-(methylthio)-3-pentyl-2(3*H*)-benzo[*b*]furanone

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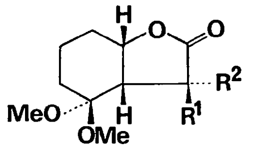
Abstract. $C_{16}H_{28}O_4S$, $M_r = 316{\cdot}5$, triclinic, $P\bar{1}$, $a = 15{\cdot}964\,(2)$, $b = 13{\cdot}261\,(2)$, $c = 9{\cdot}019\,(1)$ Å, $\alpha = 110{\cdot}82\,(1)$, $\beta = 89{\cdot}57\,(1)$, $\gamma = 103{\cdot}48\,(1)°$, $V = 1729{\cdot}5$ Å^3, $Z = 4$, $D_m = 1{\cdot}26\,(2)$ by flotation, $D_x = 1{\cdot}215$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}59$ cm^{-1}, $F(000) = 688$, room temperature, $R = 0{\cdot}066$ for 3048 reflections [$F > 2\sigma(F)$]. The structure contains two crystallographically independent molecules with similar geometry. The six-membered ring (chair conformation) is linked *cis* to the furanone. The stereochemistry of the introduced methylthio substituent is established as *endo*, bond lengths S—C(methyl) 1·797 (7) and 1·796 (5) Å, S—C(ring) 1·850 (5) and 1·842 (4) Å.



(1) $R^1 = C_5H_{11}$, $R^2 = H$ (2) $R^1 = C_5H_{11}$, $R^2 = SCH_3$
(3) $R^1 = SCH_3$, $R^2 = C_5H_{11}$ (4) $R^1 = SC_6H_5$, $R^2 = C_5H_{11}$

Introduction. During the course of model studies directed towards the synthesis of paniculides B and C (Baker, Gibson, Swain & Tapolczay, 1985), the title compound (2) was prepared by the treatment of bicyclic lactone (1) with lithium diisopropylamide followed by dimethyl disulfide. The stereochemistry of the introduced methylthio ether moiety could not be unequivocally elucidated from the ^{1}H NMR. As a *cis* relationship between the methylthio substituent and the adjacent methine is crucial for the generation of an endocyclic double bond (Grieco & Reap, 1974, and references therein), an X-ray structure analysis of the title compound (2) was undertaken.

Experimental. Enraf–Nonius CAD-4 diffractometer, ω–2θ scan, graphite-monochromated Mo $K\alpha$ radiation ($1{\cdot}5 \le \theta \le 22°$). Cell constants obtained by least squares from 25 accurately centred reflections; crystal dimensions 0·40 × 0·25 × 0·20 mm; 4233 unique reflections ($-16 \le h \le 16$, $-13 \le k \le 12$, $0 \le l \le 9$); three check reflections ($\bar{6}2\bar{1}$, $1\bar{3}\bar{3}$, $6\bar{2}1$) showed decay (18%) during the experiment and a (linear) correction was applied to the data. Lorentz–polarization correction but no absorption correction. 3048 reflections with $F > 2\sigma(F)$ were used in the refinement. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An E map based on 418 reflections with $|E| \ge 1{\cdot}66$ having the highest combined figure of merit (2·80) showed all the non-H atoms. Full-matrix least-squares refinement using *SHELX*76 (Sheldrick, 1976) minimizing $\sum w(\Delta F)^2$, $w = 1/[\sigma^2(F) + 0{\cdot}0004F^2]$, anisotropic (S, O, C) atoms. A difference electron density synthesis showed many of the H atoms and these were introduced into the model in geometrically calculated positions [d(C—H) 1·08 Å] with two common refined isotropic temperature factors (one for the

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