

Financial support from the Consejo Nacional de Ciencia y Tecnología de México, CONACYT (Project No. PCCBBNA-021262), is acknowledged. We also thank Mr Abelardo Cuellar for technical assistance.

References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- AMIRTHALINGAM, V., GRANT, D. F. & SENOL, A. (1972). *Acta Cryst.* **B28**, 1340–1345.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOSEPH-NATHAN, P., ROMÁN, L. U., HERNÁNDEZ, J. D., TAIRA, Z. & WATSON, W. H. (1980). *Tetrahedron*, **36**, 731–734.
- SHELDRIK, G. M. (1981). *SHELXTL*, revision 3. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen.
- SORIANO-GARCÍA, M., WALLS, F. & TOSCANO, R. A. (1986). *Acta Cryst.* **C42**, 329–331.
- STORK, G. & CLARKE, F. H. JR (1961). *J. Am. Chem. Soc.* **83**, 3114–3125.
- SUTTON, L. E. (1965). In *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Spec. Publ. No. 18. London: The Chemical Society.
- WALLS, F., PADILLA, J., JOSEPH-NATHAN, P., GIRAL, F., ESCOBAR, M. & ROMO, J. (1966). *Tetrahedron*, **22**, 2387–2399.
- WALLS, F., PADILLA, J., JOSEPH-NATHAN, P., GIRAL, F. & ROMO, J. (1965). *Tetrahedron Lett.* **21**, 1577–1582.

Acta Cryst. (1986). **C42**, 1581–1584

Benzothiazine and Benzothiazepine Derivatives: Structures of *N*-*p*-Bromophenyl-6,7-dimethoxy-1,2-benzothiazin-3(4*H*)-one 1,1-Dioxide (BBTZ) and 4,5-Dihydro-8,9-dimethoxy-*N*-(5-methyl-2-pyridyl)-1,2-benzothiazepin-3-one 1,1-Dioxide (MPTE)

BY G. SALEM, S. E. FILIPPAKIS, A. HOUNTAS AND ARIS TERZIS*

X-ray Laboratory, Nuclear Research Center 'DEMOKRITOS', Aghia Paraskevi, 15310 Athens, Greece

(Received 2 January 1986; accepted 3 June 1986)

Abstract. BBTZ, C₁₆H₁₄BrNO₅S, $M_r = 412.3$, triclinic, $P\bar{1}$, $a = 8.067$ (3), $b = 11.449$ (3), $c = 9.280$ (2) Å, $\alpha = 83.40$ (2), $\beta = 106.39$ (2), $\gamma = 97.68$ (2)°, $V = 812.2$ (3) Å³, $D_m = 1.68$ (3) by flotation, $D_x = 1.685$ (2) g cm⁻³, $F(000) = 416$, $Z = 2$, m.p. 480–481 K, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 28.4$ cm⁻¹, $T = 300$ K, $R = 0.049$, 1755 reflections with $I \geq 2\sigma(I)$. MPTE, C₁₇H₁₈N₂O₅S, $M_r = 362.4$, orthorhombic, $Pbca$, $a = 11.090$ (6), $b = 14.099$ (6), $c = 21.574$ (7) Å, $V = 3373.3$ (6) Å³, $D_m = 1.42$ (3) by flotation, $D_x = 1.427$ (2) g cm⁻³, $F(000) = 1520$, $Z = 8$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 2.3$ cm⁻¹, $T = 300$ K, $R = 0.046$, 1517 reflections with $I \geq 2\sigma(I)$. The thiazine and thiazepine rings have a boat conformation. The methoxy groups are in the plane of the benzene rings and the non-bonding electrons of oxygen participate in the benzene ring resonance structure. The packing is such that it generates stacking of the aromatic rings at distances of 3.5 Å.

Introduction. 1,2-Benzothiazin-3(4*H*)-one 1,1-dioxide derivatives show considerable central nervous system (Sianesi, Redaelli, Magistretti & Massarani, 1973) and anti-inflammatory (Catsoulakos & Camoutsis, 1979)

activity. It has also been reported that the introduction of methoxy groups to the aromatic rings decreases their toxicity. Many similar heterocyclic compounds with sulfur and nitrogen have been synthesized with the intent of discovering new useful biologically active derivatives. In our attempt to establish structure–activity relationships we have solved the structures of a number of these derivatives. Here we report the structures of two such compounds, one with a six-membered (BBTZ) and one with a seven-membered (MPTE) heterocyclic ring.

Experimental. BBTZ crystals obtained by diffusing methanol into a chloroform solution. MPTE crystallized by evaporation of a 1:1 chloroform–methanol solution. Data collected on a Syntex P2₁ diffractometer, Zr-filtered Mo $K\alpha$ radiation, θ – 2θ scans, range $3 < 2\theta < 43^\circ$. Crystal sizes: BBTZ 0.42 × 0.18 × 0.22 mm; MPTE 0.48 × 0.26 × 0.15 mm. hkl ranges: for BBTZ $h0 \rightarrow 8$, $k-11 \rightarrow 11$, $l-9 \rightarrow 9$; for MPTE $h0 \rightarrow 11$, $k0 \rightarrow 15$, $l0 \rightarrow 23$. Lattice parameters from 15 automatically centred reflections, $20 < 2\theta < 22^\circ$. 1874 unique reflections, 1755 $I \geq 2\sigma(I)$ for BBTZ and 2209 unique reflections, 1517 $I \geq 2\sigma(I)$ for MPTE. Lorentz–polarization corrections performed but absorption correction applied only on BBTZ using ψ -scan method

* To whom correspondence should be addressed.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for BBTZ

$$B_{eq} = (B_{11} \times B_{22} \times B_{33})^{1/3}$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Br	-0.0731 (1)	0.1480 (1)	0.2782 (1)	6.31
S	0.5135 (2)	-0.2285 (1)	0.1888 (2)	4.04
O(1)	0.5646 (6)	-0.2095 (4)	0.0524 (6)	6.0
O(2)	0.5795 (5)	-0.1466 (4)	0.2996 (6)	4.4
O(3)	0.0382 (5)	-0.3406 (4)	0.0354 (5)	4.5
O(4)	0.6402 (5)	-0.7096 (3)	0.4382 (5)	4.4
O(5)	0.8286 (5)	-0.5401 (3)	0.5788 (4)	4.0
N	0.2961 (6)	-0.2377 (4)	0.1456 (6)	3.7
C(1)	0.1944 (8)	-0.3362 (5)	0.0751 (7)	3.8
C(2)	0.2923 (8)	-0.4346 (5)	0.0558 (7)	4.4
C(3)	0.4396 (7)	-0.4625 (5)	0.1907 (6)	3.7
C(4)	0.4693 (8)	-0.5778 (5)	0.2465 (7)	3.7
C(5)	0.6011 (7)	-0.6009 (5)	0.3745 (6)	3.4
C(6)	0.7068 (7)	-0.5067 (5)	0.4523 (6)	3.4
C(7)	0.6794 (8)	-0.3918 (5)	0.3944 (7)	3.8
C(8)	0.5480 (7)	-0.3713 (5)	0.2660 (6)	3.4
C(9)	0.2138 (7)	-0.1445 (5)	0.1790 (6)	3.5
C(10)	0.2386 (7)	-0.0306 (5)	0.1134 (6)	3.5
C(11)	0.1542 (8)	0.0571 (5)	0.1450 (7)	3.6
C(12)	0.0474 (8)	0.0301 (5)	0.2368 (6)	3.5
C(13)	0.0236 (8)	-0.0831 (6)	0.3034 (7)	4.6
C(14)	0.1058 (8)	-0.1699 (5)	0.2713 (7)	4.0
C(15)	0.5272 (9)	-0.8102 (6)	0.3722 (8)	5.0
C(16)	0.9394 (8)	-0.4488 (6)	0.6632 (7)	4.5

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors for MPTE

$$B_{eq} = (B_{11} \times B_{22} \times B_{33})^{1/3}$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
S	0.1850 (1)	0.0342 (1)	0.3831 (1)	3.19
O(1)	0.1274 (3)	-0.0381 (2)	0.4186 (1)	4.5
O(2)	0.1379 (2)	0.1281 (2)	0.3861 (1)	4.2
O(3)	0.1820 (3)	-0.1088 (2)	0.2336 (1)	4.6
O(4)	0.6930 (2)	0.0816 (2)	0.4535 (1)	4.0
O(5)	0.5304 (2)	0.1967 (2)	0.4957 (1)	4.3
N(1)	0.1746 (3)	0.0028 (2)	0.3086 (1)	2.9
N(2)	0.2413 (3)	0.1101 (2)	0.2327 (1)	3.2
C(1)	0.2057 (3)	-0.0881 (3)	0.2867 (2)	3.3
C(2)	0.2746 (4)	-0.1508 (2)	0.3302 (2)	3.4
C(3)	0.4042 (4)	-0.1142 (3)	0.3397 (2)	3.8
C(4)	0.4239 (3)	-0.0276 (3)	0.3803 (2)	2.9
C(5)	0.5437 (4)	-0.0122 (2)	0.3980 (2)	3.0
C(6)	0.5782 (4)	0.0626 (3)	0.4352 (2)	3.3
C(7)	0.4904 (4)	0.1269 (3)	0.4572 (2)	3.2
C(8)	0.3734 (4)	0.1155 (3)	0.4384 (2)	3.1
C(9)	0.3399 (3)	0.0384 (3)	0.4001 (2)	2.7
C(10)	0.1475 (3)	0.0761 (2)	0.2637 (2)	2.6
C(11)	0.0322 (3)	0.1077 (2)	0.2561 (2)	3.2
C(12)	0.0130 (3)	0.1822 (3)	0.2160 (2)	3.9
C(13)	0.1076 (4)	0.2216 (2)	0.1842 (2)	3.4
C(14)	0.2190 (3)	0.1808 (3)	0.1937 (2)	3.5
C(15)	0.0931 (4)	0.3049 (3)	0.1417 (2)	5.4
C(16)	0.7854 (4)	0.0184 (3)	0.4330 (2)	4.4
C(17)	0.4404 (4)	0.2610 (3)	0.5188 (2)	5.2

with the *TAPER* program of the *XTL* package (Syntex, 1973). Structures solved by *MULTAN* (Germain, Main & Woolfson, 1971), zerovalent scattering factors (*International Tables for X-ray Crystallography*, 1974). Full-matrix least-squares refinement in blocks, minimizing $\sum w(|F_o| - |F_c|)^2$. All H atoms located in difference maps were refined, assigned B equal to B_{eq} of carrier atoms (not refined). BBTZ: $w = 1/\sigma^2 + 0.01|F_o|$ from counting statistics, refinement converged at $R = 0.049$, $wR = 0.062$, $S = 2.51$, $\Delta/\sigma < 0.5$, no peak greater than 0.4 e \AA^{-3} (except around Br) in final difference map. MPTE: $w = 1/\sigma^2 + 0.018|F_o|$, final $R = 0.045$, $wR = 0.046$, $S = 1.31$, $\Delta/\sigma < 0.4$, no peaks greater than 0.5 e \AA^{-3} in final difference map. Calculations carried out on a NOVA 1200 computer.

Discussion. Positional parameters for the non-hydrogen atoms are listed in Table 1 for BBTZ and Table 2 for MPTE.* Bond distances and angles are given in Fig. 1 for BBTZ and Fig. 2 for MPTE and structural and conformational features in Fig. 3. The thiazine (BBTZ) and the thiazepine (MPTE) rings have the boat conformation. Atoms C(2) and S are $0.487(5)$ and $0.668(2) \text{ \AA}$ respectively above the plane defined by C(1), C(3), C(8), N (BBTZ) and $0.842(6)$ and $0.732(3) \text{ \AA}$ respectively above the 'plane' defined by C(1), C(3), C(4), C(9), N (MPTE).

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and packing diagrams for both molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43141 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

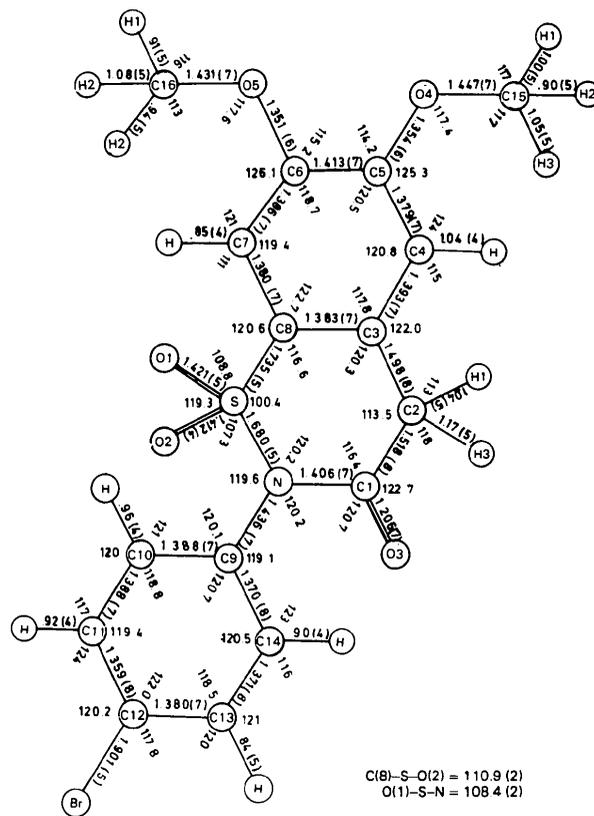


Fig. 1. Bond distances (\AA) and angles ($^\circ$) for BBTZ with e.s.d.'s in parentheses.

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).

References

- CATSOUKAKOS, P. & CAMOUTSI, C. (1979). *J. Heterocycl. Chem.* **16**, 1503–1524.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 LESER, J. & RABINOVICH, R. (1978). *Acta Cryst.* **B34**, 2272–2280.
 MARTINIS, C. & MACKAY, M. F. (1980). *Acta Cryst.* **B36**, 1606–1610.
 PANAGIOTOPOULOS, N. G. & FILIPPAKIS, S. E. (1980). *Cryst. Struct. Commun.* **9**, 321–324.
 ROHRER, D. & DUAX, W. (1978). *Acta Cryst.* **B34**, 3475–3477.
 SIANESI, E., REDAELLI, R., MAGISTRETTI, M. J. & MASSARANI, E. (1973). *J. Med. Chem.* **16**, 1133–1137.
 Syntex (1973). *XTL Structure Determination System*. Syntex Analytical Instruments, Cupertino, California.

Acta Cryst. (1986). **C42**, 1584–1587

Structures of the Conducting Salts of Bis(pyrazino)tetrathiafulvalene (BPTTF): (BPTTF)₂BF₄ and (BPTTF)₂PF₆

BY A. TERZIS* AND A. HOUNTAS

X-ray Laboratory, Nuclear Research Center 'DEMOKRITOS', Aghia Paraskevi, 15310 Athens, Greece

AND G. C. PAPAVALASSIOU

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou, Athens 501/1, Greece

(Received 7 January 1986; accepted 3 June 1986)

Abstract. BF₄⁻ salt (I): di($\Delta^{2,2'}$ -bi-1,3-dithiolano[e]-pyrazin)ium tetrafluoroborate, (C₁₀H₄N₄S₄)₂BF₄, *M_r* = 703.66, orthorhombic, *Fddd*, *a* = 11.547 (2), *b* = 13.127 (3), *c* = 34.182 (6) Å, *V* = 5181 (2) Å³, *Z* = 8, *D_m* = 1.80, *D_x* = 1.804 g cm⁻³, Mo *K*α, *λ* = 0.71069 Å, *μ* = 6.73 cm⁻¹, *F*(000) = 2824, *T* = 296 (2) K. PF₆⁻ salt (II): di($\Delta^{2,2'}$ -bi-1,3-dithiolano[e]-pyrazin)ium hexafluorophosphate, (C₁₀H₄N₄S₄)₂PF₆, *M_r* = 761.81, orthorhombic, *Fddd*, *a* = 11.642 (2), *b* = 13.122 (2), *c* = 35.339 (5) Å, *V* = 5398 (1) Å³, *Z* = 8, *D_m* = 1.86, *D_x* = 1.874 (1) g cm⁻³, Mo *K*α, *λ* = 0.71069 Å, *μ* = 7.13 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* ≥ 2.5σ(*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.

* To whom correspondence should be addressed.