Table 4. *Selected torsion angles (°)*

C5—C6—C7—C8	−3.0 (6)	C5′—C6′—C7′—C8′	1.3 (6)
C15—C16—C17—C13	−3.9 (4)	C15′—C16′—C17′—C13′	7.1 (4)
C2—C3—C19—O4	51.3 (4)	C2′—C3′—C19′—O4′	114.6 (5)
C2—C3—C21—O6	−148.6 (3)	C2′—C3′—C21′—O6′	157.5 (3)

The disordered atoms in compound (2) were refined using the *SAME*, *SADI* and *SIMU* restraints in *SHELXL*93 (Sheldrick, 1993). Additional *FLAT* restraints were used for all disordered methyl esters. The refinement was very difficult and was carried out using many restraints to avoid divergency of the model. All non-H atoms were refined anisotropically. The disordered atoms were restrained to have their U^{ij} values equal to within an effective standard deviation of 0.01. The occupancy refinement shows a 0.590 (4)/0.410 (4) ratio for (2) and (2′), respectively. In conformation (2), the ester at C13 is disordered, together with the O2 ketone.

For all compounds, data collection: *NRCCAD DATCOL* (Le Page *et al.*, 1986); cell refinement: *NRCCAD TRUANG*; data reduction: *NRCVAX DATRD*2 (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX SOLVER*; program(s) used to refine structure: *SHELXL*93; molecular graphics: *ORTEP* in *Xtal_GX* (Johnson, 1995); software used to prepare material for publication: *SHELXL*93 *ACTA*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1350). Services for accessing these data are described at the back of the journal. A figure showing the two conformers of (2) observed as disorder in the crystal has also been deposited.

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Tetramethyltetrathiafulvalenium Bromide Benzonitrile Water Solvate

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Abstract

The title compound, $C_{10}H_{12}S_4^{\cdot+}.Br^-.0.5C_7H_5N.0.5H_2O$, is a cation–radical salt of tetramethyltetrathiafulvalene (TMTTF) and bromine with a ratio of TMTTF to Br of 1:1. The TMTTF cations have crystallographically imposed C_s symmetry with mirror planes at $y = 0$ and $y = \frac{1}{2}$ which lie along the central C═C bonds. The cations are stacked to form a column structure extending along the *c* axis and face each other to assume dimeric structures around the inversion centres, with short S⋯S contacts of 3.430 (2) and 3.508 (2) Å. The central double-bond lengths of 1.394 (9) and 1.413 (8) Å are longer than the reported value of the corresponding C—C distance of 1.35 Å in $TMTTF_2Br$. This is consistent with the findings that the greater the charge on the tetrathiafulvalene cation the longer the C═C bond distance.

Comment

TMTTF (tetramethyltetrathiafulvalene), when it is oxidized, gives cation–radical salts with proper anions such as BF_4^-, ClO_4^-, SCN^-, PF_6^- and Br^- (Delhaes *et al.*, 1979). They crystallize from an acetonitrile solution with a chemical stoichiometric TMTTF to anion ratio of 2:1. The crystal structure of the $TMTTF_2Br$ salt was reported by Galigne *et al.* (1978). In the present study, we obtained a different crystal form, (1), from a benzonitrile solution with a TMTTF to Br ratio of 1:1. The unit cell contains eight TMTTF cations and eight Br^- anions. Two TMTTF cations are independent. They have crystallographically imposed C_s symmetry with mirror planes at $y = 0$ and $y = \frac{1}{2}$ which lie along the central C═C bonds. The cations stack to form a column structure extending along the *c* axis. Pairs of non-independent cations related by the inversion centres at $(\frac{1}{2},0,0)$, $(0,\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$ face each other to assume dimeric structures with intermolecular S⋯S contacts [S1⋯S2($1-x$, y, $1-z$) 3.430 (2) and S3⋯S4($1-x$, y, $2-z$) 3.508 (2) Å], shorter than the sum of the van der Waals radii of 3.7 Å. The intermolec-

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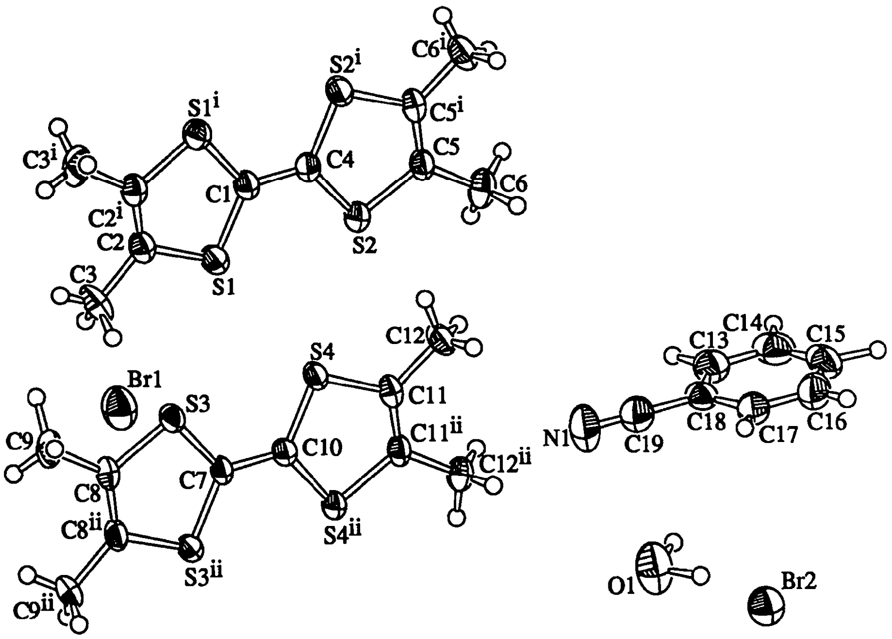
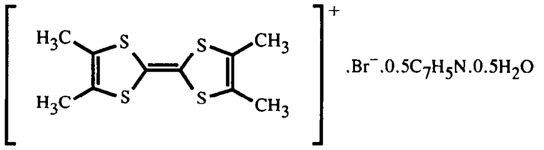


Fig. 1. The molecular structure of (1) along with the atomic labels. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, 2-y, z$; (ii) $x, -y, -z$.]

ular S···S distances between the dimeric structures are 3.979 (2) and 4.057 (2) Å for S1···S4($1-x, 1-y, 1-z$) and S2···S3($1-x, 1-y, 1-z$), respectively.



$[C_{10}H_{12}S_4]^{+}.Br^{-}.0.5C_7H_5N.0.5H_2O$

(1)

The best-fit planes defined by atoms S1, S2, C1 and C4 (plane I), S1, C2 and C3 (plane II), and S2, C5 and C6 (plane III) have dihedral angles I/II 2.1 (2) and I/III 4.0 (2)°. The planes defined by atoms S3, S4, C7 and C10 (plane IV), S3, C8 and C9 (plane V), and S4, C11 and C12 (plane VI) have dihedral angles IV/V 1.4 (2) and IV/VI 3.1 (2)°.

The central double-bond lengths [C1=C4 1.394 (9) and C7=C10 1.413 (8) Å] are longer than the corresponding C—C distance of 1.35 Å in $TMTTF_2Br$. Taking the chemical stoichiometric ratios into account, the charge on the TMTTF cations in the present structure should be larger than that of the cation in $TMTTF_2Br$. This is consistent with the findings in the tetrathiafulvalene (TTF) analogue salts in which the larger charged TTF shows the longer C=C bond distance (Katayama *et al.*, 1985).

The unit cell also contains four benzonitrile and four water molecules as solvates. Both molecules lie on the crystallographic mirror plane along with the Br^{-} ions. These three components form a flat-sheet structure along the *c* axis. Two almost linear hydrogen bonds link the water molecules with the adjacent Br^{-} ions.

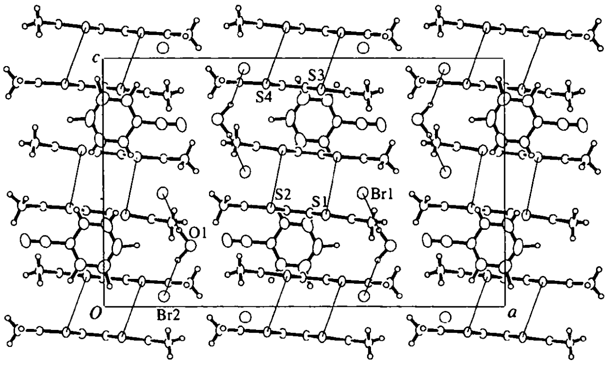


Fig. 2. The crystal structure projected along the *b* axis. Displacement ellipsoids are drawn at the 40% probability level. Atomic labels for atoms S1 and S2 indicate ($x, -1-y, z$) positions, and those for atoms S3 and S4 indicate ($x, -y, z$) positions. The short intermolecular S···S contacts and intermolecular hydrogen bonds are indicated by thin solid lines.

Experimental

The title compound was prepared according to literature methods (Galigne *et al.*, 1978). TMTTF was oxygenated with hydrobromic acid in the presence of hydrogen peroxide in benzonitrile solution, although the literature used acetonitrile as the solvent.

Crystal data

$C_{10}H_{12}S_4^+.Br^-.$-
$0.5C_7H_5N.0.5H_2O$
M_r = 400.92
Monoclinic
*C*2/*m*
a = 23.424 (4) Å
b = 9.689 (4) Å
c = 14.470 (3) Å
β = 90.53 (2)°
V = 3284 (1) Å^3
Z = 8
D_x = 1.622 Mg m^{-3}
D_m = 1.617 Mg m^{-3}
D_m measured by flotation in KI aqueous solution

Mo *K*α radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 13.1–15.0°
μ = 3.001 mm^{-1}
T = 293 K
Plate
0.50 × 0.48 × 0.03 mm
Black

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min}$ = 0.325, $T_{\max}$ = 0.914
5174 measured reflections
5060 independent reflections

2552 reflections with $I > 1\sigma(I)$
$R_{\rm int}$ = 0.028
$\theta_{\max}$ = 30.00°
$h = 0 \rightarrow 32$
$k = 0 \rightarrow 13$
$l = -20 \rightarrow 20$
3 standard reflections every 200 reflections intensity decay: −2.38%

Refinement

Refinement on *F*
R = 0.0530
wR = 0.0597
S = 1.320
2552 reflections
199 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00063|F_o|^2]$

$(\Delta/\sigma)_{\max}$ = 0.0004
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Br1	0.64624 (4)	1/2	0.45850 (7)	0.0667 (3)
Br2	0.14852 (4)	0	0.04282 (6)	0.0599 (3)
S1	0.55375 (5)	0.8505 (1)	0.37034 (9)	0.0407 (4)
S2	0.41656 (5)	0.8508 (1)	0.39712 (9)	0.0400 (4)
S3	0.54319 (5)	0.1495 (1)	0.87496 (9)	0.0374 (3)
S4	0.40603 (5)	0.1503 (1)	0.89619 (9)	0.0344 (3)
O1	0.2157 (3)	0	0.2463 (4)	0.081 (2)
N1	0.1933 (3)	0	0.7319 (6)	0.078 (3)
C1	0.5147 (3)	1	0.3774 (5)	0.036 (2)
C2	0.6194 (2)	0.9319 (5)	0.3543 (3)	0.038 (1)
C3	0.6693 (2)	0.8355 (7)	0.3418 (4)	0.058 (2)
C4	0.4556 (3)	1	0.3876 (5)	0.035 (2)
C5	0.3504 (2)	0.9302 (5)	0.4049 (3)	0.037 (1)
C6	0.2990 (2)	0.8390 (6)	0.4083 (4)	0.051 (2)
C7	0.5046 (3)	0	0.8812 (5)	0.033 (2)
C8	0.6096 (2)	0.0703 (5)	0.8618 (3)	0.035 (1)
C9	0.6598 (2)	0.1635 (6)	0.8533 (4)	0.048 (2)
C10	0.4445 (3)	0	0.8899 (5)	0.033 (2)
C11	0.3397 (2)	0.0691 (5)	0.9022 (3)	0.034 (1)
C12	0.2874 (2)	0.1576 (5)	0.9048 (4)	0.045 (1)
C13	0.0589 (4)	0	0.8296 (6)	0.056 (3)
C14	−0.0007 (4)	0	0.8375 (7)	0.064 (3)
C15	−0.0328 (4)	0	0.7579 (9)	0.071 (3)
C16	−0.0080 (4)	0	0.6707 (7)	0.065 (3)
C17	0.0496 (3)	0	0.6637 (6)	0.049 (2)
C18	0.0831 (3)	0	0.7439 (6)	0.044 (2)
C19	0.1443 (4)	0	0.7358 (6)	0.057 (3)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.716 (4)	S4—C11	1.744 (4)
S1—C2	1.746 (5)	C1—C4	1.394 (9)
S2—C4	1.717 (4)	C2—C2$^{\rm i}$	1.321 (10)
S2—C5	1.736 (4)	C5—C5$^{\rm i}$	1.352 (10)
S3—C7	1.711 (3)	C7—C10	1.413 (8)
S3—C8	1.746 (4)	C8—C8$^{\rm ii}$	1.362 (10)
S4—C10	1.715 (4)	C11—C11$^{\rm ii}$	1.339 (10)
C1—S1—C2	95.6 (2)	S2—C4—C1	122.6 (2)
C4—S2—C5	96.2 (2)	S2—C5—C5$^{\rm i}$	116.3 (2)
C7—S3—C8	96.1 (2)	S3—C7—S3$^{\rm ii}$	115.7 (4)
C10—S4—C11	95.1 (2)	S3—C7—C10	122.1 (2)
S1—C1—S1$^{\rm i}$	115.1 (4)	S3—C8—C8$^{\rm ii}$	116.1 (2)
S1—C1—C4	122.4 (2)	S4—C10—S4$^{\rm ii}$	116.2 (4)
S1—C2—C2$^{\rm i}$	116.8 (2)	S4—C10—C7	121.9 (2)
S2—C4—S2$^{\rm i}$	114.7 (4)	S4—C11—C11$^{\rm ii}$	116.8 (2)

Symmetry codes: (i) $x, 2-y, z$; (ii) $x, -y, z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H18···Br1$^{\rm i}$	1.14	2.36	3.488 (6)	167
O1—H19···Br2	1.14	2.24	3.326 (7)	159

Symmetry code: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

The standard reflections showed an intensity decay of 2.4% and a polynomial correction was applied. All the H atoms were obtained from difference Fourier syntheses and were fixed during the final refinement with isotropic displacement parameters of 1.2$B_{\rm eq}$ in the benzonitrile molecule, and 1.5$B_{\rm eq}$ in the water molecule and the methyl groups in the TMTTF molecules.

Data collection: *AFC/MSC Diffractometer Control Software* (Rigaku Corporation, 1988). Cell refinement: *AFC/MSC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS* (Molecular Structure Corporation, 1994). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH* (Molecular Structure Corporation, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1035). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 264–266

(2*R*,3*R*)-2,3-Dibenzyloxy-1,4-bis(diphenylphosphino)butane

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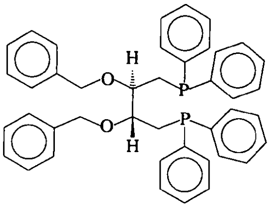
Abstract

The crystal structure of the title compound, $C_{42}H_{40}O_2P_2$, an open-chain diphosphine, is reported. The absolute structure determined by the Flack method [Flack (1983). *Acta Cryst.* A**39**, 876–881] confirms that the stereochemistry at the chiral centers is (2*R*,3*R*). The dihedral angles between the two rings bonded to each phosphine group are 70.94 (10) and 70.20 (10)°, and the angle between the rings of the benzyloxy groups is 59.31 (13)°.

Comment

Catalytic enantioselective synthesis is an area of great interest, where much study has been devoted to the development of new and efficient catalysts (Ojima, 1993; Blystone, 1989; Noyori, 1989; Ojima *et al.*, 1989). The synthesis of chiral diphosphines is an important area of study, due to their vast application as bidentate ligands in homogeneous enantioselective catalysis. Ligands such as DIOP [(2*R*,3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] (Kagan & Dang, 1972), along with others containing a backbone with two chiral C atoms, have demonstrated very efficient chiral induction in catalytic processes by creating a chiral environment around the metal center which allows for the discrimination of the enantiotopic faces of prochiral substrates during the catalytic cycle. Our interest in the development of new enantioselective catalysts led us to synthesize diphosphino DIOP-bz [(2*R*,3*R*)-2,3-dibenzyloxy-1,4-bis(diphenylphosphino)butane], (I), a chiral open-chain analog of DIOP.



(I)

The Rh^I complexes of DIOP-bz will be used to study the enantioselective reduction of prochiral functionalized olefins by hydrogenation with molecular hydrogen as well as transfer hydrogenation. A detailed structural knowledge of these types of ligands is required in order to rationalize the efficiency of their transition metal complexes in inducing chirality on the reaction products.

The average P—C_{aryl} and P—C_{alkyl} distances of 1.834 (2) and 1.846 (2) Å, respectively, are not significantly different from values observed in DIOP and other related ligands (Ball *et al.*, 1981; Ball & Trotter, 1981). The mean C_{sp3}—C_{sp3} and C—O bond lengths are 1.524 (3) and 1.425 (5) Å, respectively; the internal angles of the molecule are unexceptional.

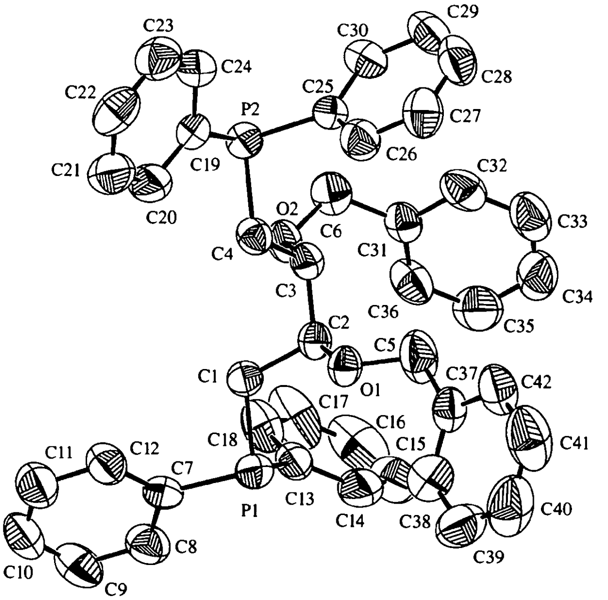


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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