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# Structure of the Organic Conductor $(BEDT\text{-}TTF)_2Br.C_2H_4(OH)_2$

By Natalya P. Karpova, Sergey V. Konovalikhin, Oleg A. Dyachenko,* Rimma N. Lyubovskaya and Elena I. Zhilyaeva

*Institute of Chemical Physics of the USSR Academy of Sciences, Chernogolovka, Moscow Region 142432, USSR*

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**Abstract.** Bis[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] bromide–ethylene glycol (1/1), $2C_{10}H_8S_8^{1/2+}.Br^-.C_2H_6O_2$, $M_r = 911.3$, monoclinic, $P12_1/n1$, $a = 14.950$ (2), $b = 33.692$ (4), $c = 6.621$ (1) Å, $\beta = 92.44$ (1)°, $V = 3331.8$ (8) Å$^3$, $Z = 4$, $D_x = 1.82$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1.541$ Å, $\mu = 107.1$ cm$^{-1}$, $R = 0.071$ for a total of 3115 independent reflections. The title compound is a new organic conductor [$\sigma(300) = 8\ \Omega^{-1}\,\text{cm}^{-1}$, with a metal–insulator transition at $T = 196$ K]. The structure is laminated. Cation and anion layers are parallel to the *ac* plane and alternate along the *b* axis. BEDT-TTF cations form stacks along the *a* axis. The anion layers consist of $Br^-$ ions and ethylene glycol molecules linked by hydrogen bonds, Br···H—O. In the cation layer, BEDT-TTF ions from neighbouring stacks are linked, in side-by-side bands, by short intermolecular contacts S···S 3.448 (4)–3.508 (4) Å. No short S···S contacts were found in the stacks.

**Introduction.** At present there are more than 40 organic superconductors known (Ishiguro, 1988). The cation-radical salts based on bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), which become superconducting at low temperature and at ambient pressure or under high pressure, constitute a considerable part of them and have a typical cation–anion ratio, *C*:*A* of 2:1. Scarce data on the structure and properties of the BEDT-TTF salts with monoatomic anions: $(BEDT\text{-}TTF)_3Br_2.(H_2O)_2$ (Urayama, Saito, Kawamoto & Tanaka, 1987), $(BEDT\text{-}TTF)_3Cl_2.(H_2O)_2$ (Mori & Inokuchi, 1987*a*,*b*; Rosseinsky, Kurmoo, Talham, Day, Chasseau & Watkin, 1988) and $\beta$-$(BEDT\text{-}TTF)_3Br_2$ (Parkin, Engler, Lee & Schumaker, 1985) testify to the fact that these compounds have a *C*:*A* ratio of 3:2 and a metal–insulator transition temperature ($T_{\rm MI}$) of 100–185 K. An exception is the salt $(BEDT\text{-}TTF)_3Cl_2.(H_2O)_2$ which is a superconductor at $T_c = 2$ K and pressure of $P_c = 16$ kbar (Mori & Inokuchi, 1987*a*,*b*). It has been shown (Shibaeva, Lobkovskaya, Rozenberg, Buravov, Ignatiev, Kushch, Laukhina, Makova, Yagubskii & Zvarykina, 1988) that changing the *C*:*A* ratio to 2:1 in the $(BEDT\text{-}TTF)_4Cl_2.4H_2O$ salt brings $T_{\rm MI}$ down to 20 K. In order to obtain compounds with monohaloid anions

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* Author for correspondence.

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Table 1. *Atomic coordinates* (× $10^4$) *and equivalent isotropic temperature factors* (Å$^2$) *with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Br | 2422 (1) | 2499 (1) | 2298 (2) | 5.60 |
| S(*A*1) | 813 (2) | 3617 (1) | 5210 (4) | 4.33 |
| S(*A*2) | 1129 (2) | 3345 (1) | 10244 (4) | 4.34 |
| S(*A*3) | 949 (2) | 4440 (1) | 6715 (4) | 3.94 |
| S(*A*4) | 1159 (1) | 4216 (1) | 10980 (3) | 3.47 |
| S(*A*5) | 1086 (2) | 5367 (1) | 8009 (4) | 3.88 |
| S(*A*6) | 1312 (2) | 5130 (1) | 12259 (4) | 3.85 |
| S(*A*7) | 1327 (2) | 6224 (1) | 8770 (4) | 4.32 |
| S(*A*8) | 1597 (2) | 5928 (1) | 13848 (4) | 4.68 |
| C(*A*1) | 1071 (6) | 4602 (2) | 9205 (14) | 3.11 |
| C(*A*2) | 1149 (6) | 4981 (2) | 9765 (15) | 3.42 |
| C(*A*3) | 1444 (13) | 3200 (4) | 6209 (22) | 7.95 |
| C(*A*4) | 1246 (13) | 3044 (3) | 8121 (19) | 7.96 |
| C(*A*5) | 924 (6) | 3938 (3) | 7258 (14) | 3.39 |
| C(*A*6) | 1025 (6) | 3830 (2) | 9212 (16) | 3.52 |
| C(*A*7) | 1304 (6) | 5748 (2) | 9777 (16) | 3.62 |
| C(*A*8) | 1403 (7) | 5632 (3) | 11738 (15) | 3.78 |
| C(*A*9) | 1386 (16) | 6518 (4) | 10971 (22) | 10.45 |
| C(*A*10) | 1659 (16) | 6413 (3) | 12853 (24) | 9.15 |
| S(*B*1) | 1162 (3) | 1423 (1) | 9300 (5) | 6.89 |
| S(*B*2) | 831 (2) | 1675 (1) | 4268 (4) | 4.53 |
| S(*B*3) | 1274 (2) | 602 (1) | 7794 (4) | 4.15 |
| S(*B*4) | 956 (2) | 816 (1) | 3537 (4) | 3.82 |
| S(*B*5) | 1361 (2) | −321 (1) | 6544 (4) | 4.07 |
| S(*B*6) | 1030 (2) | −106 (1) | 2286 (4) | 4.17 |
| S(*B*7) | 1524 (2) | −1178 (1) | 5823 (4) | 4.21 |
| S(*B*8) | 1109 (2) | −917 (1) | 731 (4) | 5.51 |
| C(*B*1) | 1124 (6) | 442 (2) | 5317 (15) | 3.39 |
| C(*B*2) | 1154 (7) | 54 (3) | 4760 (15) | 3.62 |
| C(*B*3) | 1295 (24) | 1863 (4) | 8260 (30) | 16.36 |
| C(*B*4) | 1186 (12) | 2003 (3) | 6310 (19) | 6.95 |
| C(*B*5) | 1095 (8) | 1104 (3) | 7247 (16) | 4.32 |
| C(*B*6) | 970 (6) | 1209 (2) | 5312 (16) | 3.79 |
| C(*B*7) | 1328 (6) | −709 (3) | 4751 (16) | 3.60 |
| C(*B*8) | 1187 (7) | −607 (3) | 2839 (16) | 4.03 |
| C(*B*9) | 1345 (8) | −1500 (3) | 3674 (18) | 4.84 |
| C(*B*10) | 1699 (8) | −1351 (3) | 1721 (20) | 5.35 |
| C(1) | 4338 (16) | 2346 (7) | 8266 (40) | 10.48 |
| C(2) | 4353 (19) | 2596 (8) | 6586 (39) | 11.47 |
| O(1′)* | 4369 (14) | 2433 (7) | 10123 (34) | 8.09 |
| O(1″)† | 3563 (24) | 2162 (8) | 8318 (46) | 11.24 |
| O(2′)‡ | 3573 (27) | 2820 (8) | 6399 (52) | 14.49 |
| O(2″)* | 4376 (18) | 2553 (11) | 4695 (56) | 13.25 |

* Population 0.50 (1).
† Population 0.49 (1).
‡ Population 0.54 (1).

capable of forming of hydrogen bonds with solvent molecules, we have synthesized the (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ salt with a *C*:*A* ratio of 2:1. The chemical composition and structure of (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ were established by an X-ray study. The synthesis and physical properties have been described previously (Zhilyaeva, Lyubovskaya, Onischuk, Konovalikhin & Dyachenko, 1990). This compound is a metal at room temperature and an insulator at $T < 196$ K.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| S(*A*1)—C(*A*3) | 1.80 (1) | S(*B*1)—C(*B*3) | 1.65 (2) |
| S(*A*1)—C(*A*5) | 1.74 (1) | S(*B*1)—C(*B*5) | 1.73 (1) |
| S(*A*2)—C(*A*4) | 1.75 (1) | S(*B*2)—C(*B*4) | 1.81 (1) |
| S(*A*2)—C(*A*6) | 1.78 (1) | S(*B*2)—C(*B*6) | 1.72 (1) |
| S(*A*3)—C(*A*1) | 1.74 (1) | S(*B*3)—C(*B*1) | 1.73 (1) |
| S(*A*3)—C(*A*5) | 1.73 (1) | S(*B*3)—C(*B*5) | 1.75 (1) |
| S(*A*4)—C(*A*1) | 1.75 (1) | S(*B*4)—C(*B*1) | 1.74 (1) |
| S(*A*4)—C(*A*6) | 1.76 (1) | S(*B*4)—C(*B*6) | 1.77 (1) |
| S(*A*5)—C(*A*2) | 1.74 (1) | S(*B*5)—C(*B*2) | 1.75 (1) |
| S(*A*5)—C(*A*7) | 1.76 (1) | S(*B*5)—C(*B*7) | 1.77 (1) |
| S(*A*6)—C(*A*2) | 1.73 (1) | S(*B*6)—C(*B*2) | 1.73 (1) |
| S(*A*6)—C(*A*8) | 1.73 (1) | S(*B*6)—C(*B*8) | 1.74 (1) |
| S(*A*7)—C(*A*7) | 1.74 (1) | S(*B*7)—C(*B*7) | 1.75 (1) |
| S(*A*7)—C(*A*9) | 1.76 (1) | S(*B*7)—C(*B*9) | 1.80 (1) |
| S(*A*8)—C(*A*8) | 1.73 (1) | S(*B*8)—C(*B*8) | 1.74 (1) |
| S(*A*8)—C(*A*10) | 1.77 (1) | S(*B*8)—C(*B*10) | 1.82 (1) |
| C(*A*1)—C(*A*2) | 1.34 (1) | C(*B*1)—C(*B*2) | 1.36 (1) |
| C(*A*3)—C(*A*4) | 1.41 (2) | C(*B*3)—C(*B*4) | 1.38 (2) |
| C(*A*5)—C(*A*6) | 1.35 (1) | C(*B*5)—C(*B*6) | 1.33 (2) |
| C(*A*7)—C(*A*8) | 1.36 (1) | C(*B*7)—C(*B*8) | 1.32 (2) |
| C(*A*9)—C(*A*10) | 1.34 (2) | C(*B*9)—C(*B*10) | 1.50 (2) |
| C(1)—C(2) | 1.40 (4) | C(1)—O(1′) | 1.26 (4) |
| C(2)—O(2′) | 1.39 (5) | C(1)—O(1″) | 1.32 (4) |
| C(2)—O(2″) | 1.26 (5) | | |

| | | | |
|---|---|---|---|
| C(*A*3)S(*A*1)C(*A*5) | 99.7 (6) | C(*A*6)S(*A*2)C(*A*4) | 104.0 (6) |
| C(*A*1)S(*A*3)C(*A*5) | 96.4 (6) | C(*A*1)S(*A*4)C(*A*6) | 95.6 (6) |
| C(*A*2)S(*A*5)C(*A*7) | 95.6 (6) | C(*A*2)S(*A*6)C(*A*8) | 95.8 (6) |
| C(*A*7)S(*A*7)C(*A*9) | 101.7 (6) | C(*A*8)S(*A*8)C(*A*10) | 104.0 (6) |
| S(*A*3)C(*A*1)C(*A*2) | 124.5 (8) | S(*A*4)C(*A*1)C(*A*2) | 121.4 (8) |
| S(*A*3)C(*A*1)S(*A*4) | 114.0 (5) | S(*A*5)C(*A*2)C(*A*1) | 121.8 (8) |
| S(*A*6)C(*A*2)C(*A*1) | 123.3 (8) | S(*A*5)C(*A*2)S(*A*6) | 114.9 (6) |
| S(*A*1)C(*A*3)C(*A*4) | 120 (1) | S(*A*2)C(*A*4)C(*A*3) | 122 (1) |
| S(*A*1)C(*A*5)S(*A*3) | 116.7 (5) | S(*A*2)C(*A*6)S(*A*4) | 114.4 (6) |
| S(*A*1)C(*A*5)C(*A*6) | 125.8 (8) | S(*A*2)C(*A*6)C(*A*5) | 128.9 (8) |
| S(*A*3)C(*A*5)C(*A*6) | 117.4 (8) | S(*A*4)C(*A*6)C(*A*5) | 116.5 (8) |
| S(*A*5)C(*A*7)S(*A*7) | 115.2 (5) | S(*A*6)C(*A*8)S(*A*8) | 114.5 (6) |
| S(*A*5)C(*A*7)C(*A*8) | 115.7 (8) | S(*A*6)C(*A*8)C(*A*7) | 117.8 (8) |
| S(*A*7)C(*A*7)C(*A*8) | 129.1 (8) | S(*A*8)C(*A*8)C(*A*7) | 127.7 (8) |
| S(*A*7)C(*A*9)C(*A*10) | 128 (1) | S(*A*8)C(*A*10)C(*A*9) | 125 (1) |
| C(*B*3)S(*B*1)C(*B*5) | 103.5 (8) | C(*B*6)S(*B*2)C(*B*4) | 103.3 (6) |
| C(*B*1)S(*B*3)C(*B*5) | 95.3 (5) | C(*B*6)S(*B*4)C(*B*1) | 95.4 (5) |
| C(*B*2)S(*B*5)C(*B*7) | 94.7 (5) | C(*B*2)S(*B*6)C(*B*8) | 95.5 (5) |
| C(*B*7)S(*B*7)C(*B*9) | 101.9 (5) | C(*B*8)S(*B*8)C(*B*10) | 100.3 (6) |
| S(*B*1)C(*B*3)C(*B*4) | 133 (2) | S(*B*2)C(*B*4)C(*B*3) | 121 (1) |
| S(*B*1)C(*B*5)S(*B*3) | 115.8 (6) | S(*B*1)C(*B*5)C(*B*6) | 126.2 (9) |
| S(*B*2)C(*B*6)S(*B*4) | 114.6 (6) | S(*B*2)C(*B*6)C(*B*5) | 129.4 (9) |
| S(*B*3)C(*B*1)S(*B*4) | 115.3 (6) | S(*B*3)C(*B*1)C(*B*2) | 123.4 (8) |
| S(*B*3)C(*B*5)C(*B*6) | 117.9 (8) | S(*B*4)C(*B*6)C(*B*5) | 116.0 (8) |
| S(*B*4)C(*B*1)C(*B*2) | 121.3 (8) | S(*B*5)C(*B*2)S(*B*6) | 115.1 (6) |
| S(*B*5)C(*B*2)C(*B*1) | 121.2 (8) | S(*B*6)C(*B*2)C(*B*1) | 123.7 (8) |
| S(*B*5)C(*B*7)S(*B*7) | 113.3 (6) | S(*B*5)C(*B*7)C(*B*8) | 116.8 (8) |
| S(*B*7)C(*B*7)C(*B*8) | 129.9 (8) | S(*B*6)C(*B*8)S(*B*8) | 114.2 (6) |
| S(*B*6)C(*B*8)C(*B*7) | 118.0 (8) | S(*B*8)C(*B*8)C(*B*7) | 127.8 (9) |
| S(*B*7)C(*B*9)C(*B*10) | 115.6 (8) | S(*B*8)C(*B*10)C(*B*9) | 113.3 (9) |
| C(2)C(1)O(1′) | 129 (2) | C(1)C(2)O(2′) | 111 (2) |
| C(2)C(1)O(1″) | 111 (2) | C(1)C(2)O(2″) | 137 (3) |

**Experimental.** (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ crystallizes as black plates with dimensions 0.50 × 0.70 × 0.06 mm. Refinement of cell parameters and measurement of intensities [$I \geq 2\sigma(I)$] of 3115 independent reflections were performed with Cu $K\alpha$ radiation and using the $\theta/2\theta$ method in the range $0.015 \leq \sin\theta/\lambda \leq 0.53$ Å$^{-1}$ on a RED-4 automated four-circle diffractometer. The structure was solved by direct methods and a series of subsequent *F* syntheses using the *RENTGEN*75 program package (Andrianov, Tarnopolskii & Safina, 1975). Refinement was carried out by the least-squares method using the full-matrix anisotropic approximation for all non-H atoms to $R = 0.117$. After absorption was taken into account using the *AREN*88 program (Andrianov, 1988) and further structural refinement performed, the *R* factor decreased to 0.071. H atoms were not localized. The populations of the disordered O-atom positions were calculated during refinement. Atomic coordinates and their equivalent isotropic temperature factors ($B_{eq}$) are given in Table 1,* bond lengths and angles are given in Table 2.

**Discussion.** The crystal structure of (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ (Fig. 1) consists of two crystallographically independent BEDT-TTF cation radicals (indicated as *A* and *B*), a Br$^-$ anion and a molecule of solvent, ethylene glycol C$_2$H$_4$(OH)$_2$ (*E*), forming alternating cation and anion layers along the *b* axis. It is noteworthy that the layer structure found in (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ is characteristic of most BEDT-TTF salts. The cation radicals

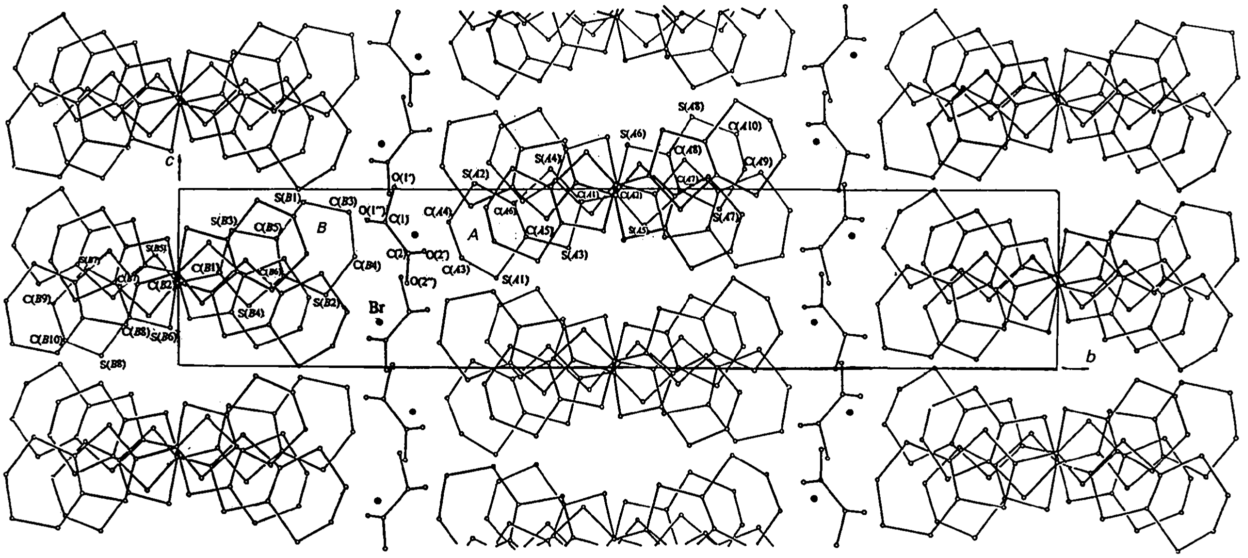

Fig. 1. Projection of the crystal structure of (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ on the *bc* plane.

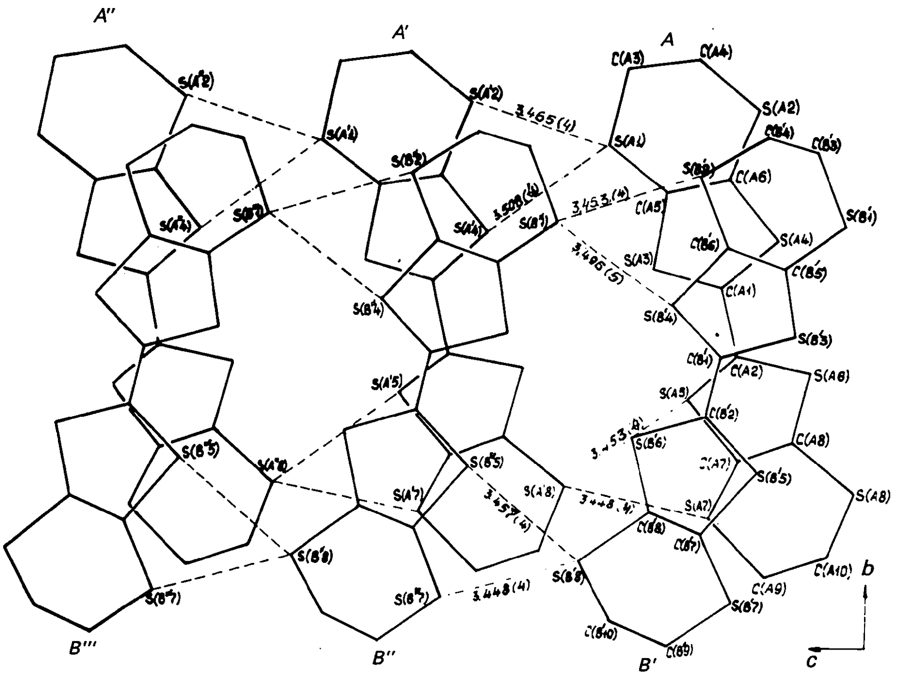

Fig. 2. Atomic symbols in the molecules and short S···S intermolecular contacts (Å) in the cation layer. Symmetry matrices: (*a*) *x*, *y*, *z* + 1 for molecule *A*′; (*b*) *x*, *y*, *z* + 2 for molecule *A*″; (*c*) 0.5 − *x*, 0.5 + *y*, 1.5 − *z* for molecule *B*′; (*d*) 0.5 − *x*, 0.5 + *y*, 0.5 − *z* for molecule *B*″; (*e*) 0.5 − *x*, 0.5 + *y*, −0.5 − *z* for molecule *B*‴.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54139 (51 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

form face-to-face stacks in the direction of the *a* axis. Both types of molecules occur in the stacks. *B* molecules are shifted with respect to the *A* molecules by the length of the central C═C bond and rotated by an angle of $\theta = 32.2°$* (Fig. 2). The angle between the planes of molecules *A* and *B* is 5.7°. In the stacks the molecules alternate in the following way: *A*···*A*···*B*···*B*···*A*···*A*···*B*···*B*···. Molecules of one particular type are stacked parallel to each other, shifted by the length of the central C═C bond. All the intrastack intermolecular S···S distances are larger than the sum of van der Waals radii (3.68 Å) of S atoms (Zefirov & Zorki, 1974). The minimum distances in the stacks are S(*A*)···S(*A*) 3.797 (3), S(*B*)···S(*B*) 3.814 (6), S(*A*)···S(*B*) 3.889 (5) Å.

Both *A* and *B* molecules from the neighbouring stacks in the crystal are linked in side-by-side type bands parallel to the *bc* plane (Fig. 2). The angles between the average planes of the BEDT-TTF molecules and the *bc* plane are 10.8 and 12.1° for molecules *A* and *B*, respectively. The short S···S intermolecular contacts are given in Fig. 2. It follows from this figure that each molecule in the band is connected to the two neighbouring ones by eight short S···S contacts in the range 3.448 (4)–3.508 (4) Å for molecule *A* and 3.448 (4)–3.496 (5) Å for molecule *B*. Analogous contacts in the salts (BEDT-TTF)$_3$Br$_2$.(H$_2$O)$_3$ (Urayama *et al.*, 1987) and (BEDT-TTF)$_4$Cl$_2$.4H$_2$O (Shibaeva *et al.*, 1988) are in the range 3.376–3.655 and 3.453–3.549 Å, respectively.

The anion layer consists of Br$^-$ ions and ethylene glycol molecules (Fig. 1). Both O atoms of the molecule (*E*) are disordered over two positions. It was confirmed experimentally that two O atoms occupy four approximately equally populated positions O(1′), O(1″) and O(2′), O(2″) (Fig. 1, Table 1). All the evidence indicates that the disorder of the O atoms in molecule *E* arises from the fact that there are two ethylene glycol molecules: *E′* [torsion angle O(1′)C(1)C(2)O(2′) = 67.7 (4)°] and *E″* [torsion angle O(1″)C(1)C(2)O(2″) = 67.1 (4)°]. Equal population of the positions of the O atoms indicates that *E′*:*E″* = 1:1. Under the conditions of uniform distribution, this ratio can be ensured either by molecules *E′* and *E″* alternating along the main crystal axes (Fig. 3*a*), or by alternating the chains involving only molecules *E′* or *E″* (Fig. 3*b*) along the *a* and *b* axes.

The distances between the Br$^-$ ions and the O atoms in (*E*) are 3.27–3.40 Å which is comparable with the sum of the Pauling's van der Waals radii for Br and O atoms (3.35 Å). Such distances of Br$^-$····O 3.36 and 3.26 Å in the structure of (BEDT-TTF)$_3$Br$_2$.(H$_2$O)$_2$ are considered to be the parameters of the Br$^-$···H—O hydrogen bond (Urayama *et al.*, 1987). The formation of hydrogen bonds in (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ between Br$^-$ anions and *E* molecules may be realized by two schemes (Fig. 3). As shown in the first scheme (Fig. 3*a*), the realization of the *tGg′* conformation in molecules *E′* and *E″* with an intramolecular hydrogen bond, which is most favourable energetically for (*E*) (Strelkova & Ginzburg, 1986), leads to the formation of associates of molecules *E′* and *E″* linked to each other by Br$^-$ anions *via* intermolecular hydrogen bonds. The parameters of the O—H···Br hydrogen bonds [O(1′)···Br 3.31 (2) and O(2″)···Br 3.27 (2) Å, C(1)O(1′)···Br 116 (1) and C(2)O(2″)···Br 118 (2)°] coincide with those found earlier for (BEDT-TTF)$_3$Br$_2$.2H$_2$O (Urayama *et al.*, 1987). It should be noted that the scheme shown in Fig. 3(*a*) suggests the presence of Br$^-$ anions both taking part and not taking part in hydrogen-bond formation.

The second scheme (Fig. 3*b*) represents molecules *E′* and *E″* in the *tGt′* conformation. As has already been shown (Radom, Lathan, Hehre & Pople, 1973), this conformation is energetically less favourable than the *tGg′* conformation by 23.4 kJ mol$^{-1}$. However, it is this conformation of (*E*) with its O—H···Br$^-$ hydrogen bonds that ensures linking of the *E′* and *E″* molecules and all the Br$^-$ anions into infinite chains along the *c* axis. Taking into consideration that the O—H···Br$^-$ bond energy is 12.5–21 kJ mol$^{-1}$ (Yufit, Struchkov & Barykina, 1987), we may assume that the energy gain due to the formation of two hydrogen bonds by one *E* molecule should be 25–42 kJ mol$^{-1}$ and compensate for the energy losses arising from rupture of the O—H···O intramolecular hydrogen bond. The geometric parameters of the O···Br contacts [O(1″)···Br 3.40 (2) Å, C(1)O(1″)···Br 110 (2)° and O(2′)···Br 3.33 (2) Å, C(2)O(2′)···Br 108 (2)°] are indicative of the formation of less-stable hydrogen bonds than those shown in Fig. 3(*a*). In spite of this, this scheme of hydrogen-bond formation in (BEDT-

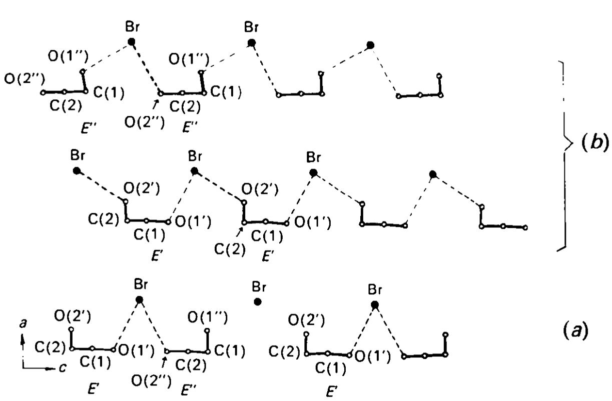

Fig. 3. Probable hydrogen-bonding systems between the Br$^-$ ions and ethylene glycol in conformations *tGg′* (*a*) and *tGt′* (*b*).

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* $\theta$ is the angle between C(*A*1)═C(*A*2) and C(*B*1)═C(*B*2).

TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ may also be possible, since it involves all the Br anions, just like the salts (BEDT-TTF)$_3$Br$_2$(H$_2$O)$_2$ (Urayama *et al.*, 1987) and (BEDT-TTF)$_3$Cl$_2$.(H$_2$O)$_2$ (Mori & Inokuchi, 1987*a*,*b*; Rosseinsky *et al.*, 1988). Unfortunately, determination of O-atom positions is not sufficiently accurate to allow us to draw definite conclusions about the system of anion hydrogen bonds in the crystal.

The molecular structures of cation radicals *A* and *B* (Table 2) are analogous to the structure of BEDT-TTF with a formal charge of $+\frac{1}{2}$ in the (BEDT-TTF)$_4$Cd$_2$I$_6$ (Gritsenko, Konovalikhin, Dyachenko, Lyubovskaya & Zhilyaeva, 1990), (BEDT-TTF)$_4$(Hg$_2$Cl$_6$).C$_6$H$_5$Cl (Dyachenko, Gritsenko, Mkoyan, Shilov & Atovmyan, 1991), (BEDT-TTF)$_4$-(Hg$_2$Br$_6$).C$_6$H$_5$Cl and (BEDT-TTF)$_4$(Hg$_2$Br$_6$) salts investigated by us.

The BEDT-TTF molecules in (BEDT-TTF)$_2$Br.C$_2$H$_4$(OH)$_2$ are not planar, only the TTF fragments are planar. In molecule *A*, the rest of the atoms are displaced out of the TTF fragment plane by 0.01–0.62 Å, and in molecule *B* by 0.01–0.55 Å. Ethylene carbons are disordered in accordance with their high $B_{\rm eq}$ values (Table 1).

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# 9-Oxobicyclo[3.3.1]nonane-1-carboxylic Acid: Structure and Hydrogen-Bonding Pattern

BY HUGH W. THOMPSON, ROGER A. LALANCETTE* AND PEGGY A. VANDERHOFF

*Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ* 07102, *USA*

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**Abstract.** (I) $C_{10}H_{14}O_3$, $M_r = 182.220$, orthorhombic, *Ibam*, $a = 12.795$ (2), $b = 13.178$ (2), $c = 11.092$ (2) Å, $V$(246 K) = 1870.2 (5), $V$(295 K) = 1891.8 (4) Å$^3$, $Z = 8$, $D_m$(295 K) = 1.26 (1), $D_x$(295 K) = 1.280 g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1.5418 Å, $\mu$ = 7.80 cm$^{-1}$, $F$(000) = 784, $T$ = 246 (1) K, $R$ = 0.047 for 418 observed reflections. Compound (I) adopts a conformation having two flattened chair cyclohexanone rings, with the plane of the carboxyl group orthogonal to that of the ketone. Pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups, leaving the ketone carbonyls uninvolved. The two conformationally enantiomeric arrangements of the carboxyl group are disordered in the crystal.

**Introduction.** Simple crystalline keto carboxylic acids have four known hydrogen-bonding states which dictate or affect the intermolecular association. By far the most common has carboxyl groups paired by mutual hydrogen bonding in which the ketone is not involved (Leiserowitz, 1976; Lalancette, Vanderhoff

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* To whom correspondence should be addressed.

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