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X-Ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems. II. The Crystal Structure of Bis(4-dithieno[3,2;2′,3′-*f*]borepinyl) Ether, $(C_{10}H_6BS_2)_2O$

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The crystal and molecular structure of bis(4-dithieno[3,2;2′,3′-*f*]borepinyl) ether has been studied by the aid of three-dimensional X-ray diffraction data. The symmetry is monoclinic, space group $C2/c$. The unit cell contains 4 molecules $(C_{10}H_6BS_2)_2O$ and the cell dimensions are: $a = 23.101(9)$ $b = 6.819(2)$, $c = 11.991(4)$ Å and $\beta = 97.79(3)°$. The structure has been refined to an R-value of 0.059 for 1896 reflections. Each $C_{10}H_6BS_2$ part is approximately planar. The largest deviation from the best plane occurs for the boron atom and amounts to 0.09 Å. A twofold axis passes through the ether oxygen atom and the whole molecule has a propeller form. The two non-equivalent B – C distances have equal lengths, 1.533(3) Å.

The present investigation is part of a more general study on the aromaticity of a number of cycloheptadithiophene compounds and dithienoborepines by Gronowitz and coworkers.[1,2] The crystal structure of dithieno[2,1-*b*;4,5-*b*′]-tropylium perchlorate[3] has previously been discussed by Gronowitz *et al.*,[4] who pointed out that the tropylium cations in the compound are essentially planar, the largest deviations from the planes being about 0.05 Å. Besides the approximate planarity of the molecule, the crystal structure determination[3] gave as a result that the sulfur to tropylium carbon atom distances were slightly longer than the purely thiophenic sulfur-carbon distances.

X-RAY WORK

The compound bis(4-dithieno[3,2;2′,3′-*f*]-borepinyl) ether, $(C_{10}H_6BS_2)_2O$, was first synthesized by Gronowitz, Gassne and Yom-Tov.[1] Later on Jeffries[5] described another route to the synthesis of the compound. Single crystals for the present work were kindly supplied by Dr Jeffries. X-Ray powder diffraction photographs were recorded in a Guinier-Hägg focusing camera with Cu$K\alpha_1$ radiation and potassium chloride (a = 6.2909 Å) added as an internal standard. The following lattice parameters were obtained with the aid of least-squares calculations: a = 23.101(9) Å, b = 6.819(2) Å, c = 11.991(4) Å, β = 97.79(3)°, V = 1871 Å^3. The density 1.47 g cm^{-3} was obtained by flotation methods. Assuming 4 formula units $(C_{10}H_6BS_2)_2O$ per unit cell, the calculated density is 1.48 g cm^{-3}. The single crystal used for the structure determination had the form of a nearly rhombic prism with the basal lengths 0.21 mm and the height 0.074 mm. The acute angle of the rhomb was 75°. The monoclinic b axis extended along the short basal diagonal and the c axis approximately along the long one. The a axis was perpendicular to the basal plane. Intensity data (graphite-monochromatized Cu$K\alpha_1$ radiation) were collected for 1896 reflections with an Enraf-Nonius single crystal diffractometer using the $\omega - 2\theta$ scan technique with a scan interval $\Delta\omega = (0.90 + 0.50 \tan\theta)$. The background was measured by extending the scan interval by ¼ at each end. Out of the 1896 reflections 127 are not above the background by giving net counts less than 10 in a fast prescan of approximately 13 s. On data reduction another 320 reflections, although considered

Table 1. Positional and thermal parameters of the atoms of $(C_{10}H_6BS_2)_2O$. Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are based on the expression: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.18309(3)	−0.09547(11)	0.46017(6)	0.00243(2)	0.02534(17)	0.00780(5)	0.00237(4)	−0.00081(2)	0.00196(7)
C(2)	0.11630(14)	−0.2021(4)	0.4491(2)	0.00339(7)	0.0217(6)	0.0083(2)	0.0008(2)	0.00083(10)	0.0027(3)
C(3)	0.07545(11)	−0.0953(3)	0.3851(2)	0.00205(5)	0.0211(5)	0.0080(2)	−0.0004(1)	0.00094(8)	0.0003(3)
B(4)	0.05760(9)	0.2241(3)	0.2685(2)	0.00109(3)	0.0174(5)	0.0059(2)	0.0002(1)	0.00043(6)	−0.0020(2)
C(5)	0.04330(9)	0.5311(3)	0.1384(2)	0.00165(4)	0.0240(5)	0.0064(1)	0.0013(1)	0.00052(6)	0.0013(2)
C(6)	0.07122(12)	0.6832(4)	0.0985(2)	0.00236(5)	0.0278(6)	0.0077(2)	0.0022(2)	0.00135(8)	0.0047(3)
S(7)	0.14310(3)	0.68680(10)	0.15009(6)	0.00211(1)	0.02303(16)	0.00936(6)	−0.0050(4)	0.00176(2)	0.00368(7)
C(8)	0.18938(9)	0.4068(4)	0.2923(2)	0.00127(4)	0.0282(6)	0.0083(2)	−0.0013(1)	0.00044(7)	−0.0003(3)
C(9)	0.19737(8)	0.2463(4)	0.3558(2)	0.00103(3)	0.0303(6)	0.0076(2)	0.0004(1)	−0.00000(6)	−0.0009(3)
C(2′)	0.15639(9)	0.0990(3)	0.3768(2)	0.00148(4)	0.0209(5)	0.0056(1)	0.0011(1)	−0.00002(6)	−0.0005(2)
C(3′)	0.09703(8)	0.0807(3)	0.3421(2)	0.00139(4)	0.0174(4)	0.0056(1)	0.0003(1)	0.00066(6)	−0.0009(2)
C(5′)	0.07987(8)	0.4066(3)	0.2130(2)	0.00131(3)	0.0182(4)	0.0052(1)	0.0006(1)	0.00044(5)	−0.0007(2)
C(6′)	0.13698(8)	0.4759(3)	0.2273(2)	0.00155(4)	0.0196(5)	0.0061(1)	−0.0004(1)	0.00083(6)	0.0000(2)
O	0(0)	0.1770(3)	¼(0)	0.00110(4)	0.0210(5)	0.0132(3)	0(0)	0.00020(8)	0(0)

	x	y	z	B(Å^2)
H(2)	0.1115(14)	−0.332(5)	0.477(3)	3.6(7)
H(3)	0.0349(12)	−0.130(3)	0.371(2)	1.8(5)
H(5)	0.0018(11)	0.505(4)	0.123(2)	1.4(4)
H(6)	0.0556(16)	0.786(5)	0.050(3)	4.6(8)
H(8)	0.2235(11)	0.492(4)	0.292(2)	2.1(5)
H(9)	0.2367(11)	0.221(4)	0.390(2)	2.0(5)

above the background during the prescan, were found to be weaker than $3\sigma(I)$, where I is the intensity and $\sigma(I)$ its standard deviation. The intensities were corrected for Lorentz, polarization and absorption effects. The linear absorption coefficient used for the crystal was 44.6 cm^{-1}. Systematically absent reflections were hkl with $h+k=2n+1$ and $h0l$ with $l=2n+1$, indicating either the space group Cc (No. 9) or $C2/c$ (No. 15). As a reasonable structure was obtained assuming space group $C2/c$, the space group Cc was not further considered.

The positions of the sulfur atoms were derived from the three-dimensional Patterson function and the positions of all other atoms from successive difference Fourier maps. The positions of all atoms were refined using a full-matrix least-squares computer program. At this refinement all non-zero 1769 reflections were used, but reflections outside the limits $0.5 \leq |F_o|/|F_c| \leq 2.0$ were given zero weight. The number of zero-weighted reflections was 97, and all but one had initial I values less than $3\sigma(I)$. The weight factor used was $w_i = (\sigma^2(F_o) + 0.002 \cdot F_o^2 + 0.067)^{-1}$. Anisotropic temperature factors were used for the non-hydrogen and isotropic ones for the hydrogen atoms. The final R_1 values, $\sum|\Delta F|/\sum|F_o|$, were 0.0592 for all 1896 reflections and 0.0469 for 1672 reflections. The weighted factor $R_2 = (\sum w_i(\Delta F)^2/\sum w_i(F_o)^2)^{1/2}$ was 0.0592 for the 1672 reflections. The value of S (goodness of fit) was 1.00. The final weighting scheme gave the following $\overline{w_i\Delta^2}$ values for the ten $|F_o|$ intervals: 0.34 for the $|F_o|$ interval 0.0 – 1.8 and 0.91 to 1.17 for the rest of the intervals. The isotropic formal equivalents of the anisotropic temperature factors for the non-hydrogen atoms varied between 2.88 and 5.07 Å^2. Final positional and thermal parameters of the atoms are given in Table 1. Lists of observed and calculated structure factors are available on request from the Division of Inorganic Chemistry 2, Lund.

DISCUSSION OF THE STRUCTURE

Intramolecular distances and angles. Pertinent distances and angles for the present compound are given in Fig. 1. *E.s.d.*'s for distances between non-hydrogen atoms vary between 0.002 and 0.004 Å, and corresponding values for angles between 0.1 and 0.2°. *E.s.d.*'s for

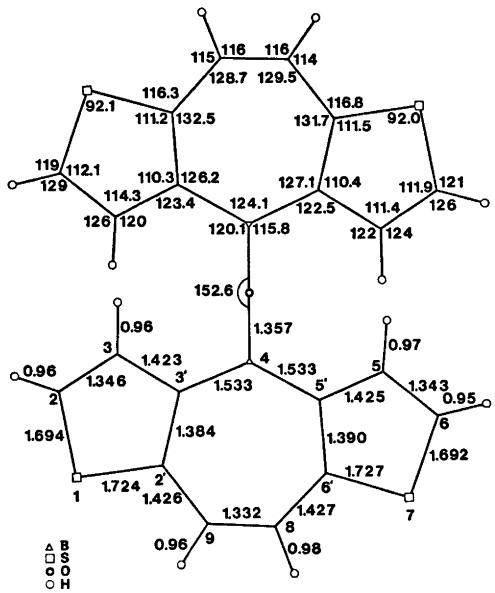

Fig. 1. Pertinent distances and angles in one $(C_{10}H_6BS_2)_2O$ molecule. Each $C_{10}H_6BS_2$ part is projected on its best plane. The carbon atoms are numbered but not marked.

carbon-hydrogen distances vary between 0.03 and 0.04 Å, and are about 2° for the S – C – H and C – C – H angles.

A twofold axis passes through the ether oxygen atom, and the whole molecule has a propeller form (Fig. 2). The two dithienoborepinyl parts form an acute angle of 63.2(7)°. As seen from Fig. 1, each $C_{10}H_6BS_2$ part of the molecule has an approximative symmetry plane passing through the boron atom B(4) and the midpoint of the line C(8) – C(9). The borepinyl ring is, however, not quite symmetrical; the corresponding angles within the ring differ at levels $(3.0 \pm 0.3)\sigma$. The difference between the external angles O – B(4) – C(3′) and O – B(4) – C(5′) is strongly significant, $\Delta/\sigma(\Delta)$ being 16. The two thiophene groups of the asymmetric part of the unit cell do not differ significantly with respect to the distances and angles. Each of the sulfur-borepinyl carbon distances [S(1) – C(2′); S(7) – C(6′)] is significantly longer than the purely thiophenic sulfur-carbon distances [S(1) – C(2); S(7) – C(6)], $\Delta/\sigma(\Delta)$ being 8 and 10 in the two cases. The same tendency was found for the sulfur-carbon distances in dithienotropylium perchlorate,[3]

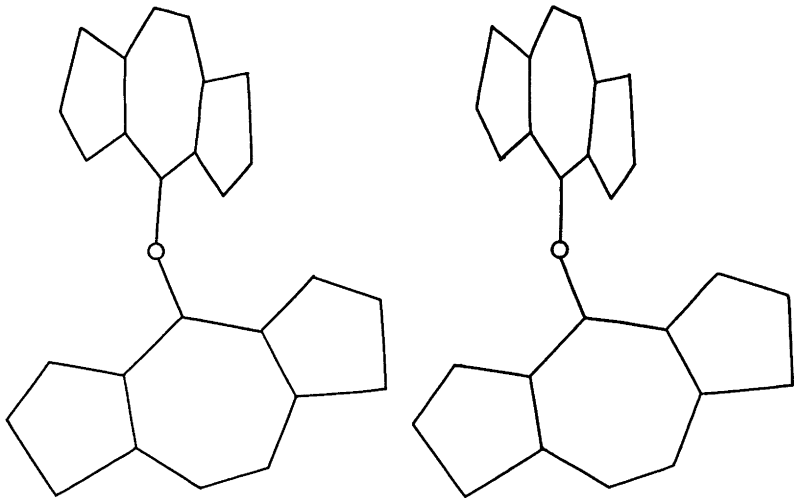

Fig. 2. A stereoscopic view of one $(C_{10}H_6BS_2)_2O$ molecule. Only non-hydrogen atoms are shown. The crystallographic y axis points towards the reader. The ether oxygen atom is marked by a small ring.

and the corresponding sulfur-carbon distances compare quite well in the two compounds. Similar disparities of C–S bonds in thiophene derivatives have been discussed by, *e.g.*, Goldberg and Shmueli,[6] who suggest that the longer sulfur-carbon bond is the one connecting sulfur to the carbon atom more actively engaged in the π delocalization (*e.g.* the borepinyl carbon atoms in the present compound). The fused double bonds C(2′)–C(3′) and C(5′)–C(6′) (Fig. 1) in the thiophene groups of the present borepinyl compound are significantly longer than the thiophenic ones, $\Delta/\sigma(\Delta)$ being 8 and 9, respectively.

The same situation was indicated in the crystal structure of dithienotropylium perchlorate.[3] The differences in the C–S and C–C distances may tend to support the view that the borepinyl ring, and probably also the tropylium ring, have aromatic properties.

The boron atoms are three-coordinated to two carbon atoms and one oxygen atom in a planar arrangement. The B–C distances are 1.533(3) Å. These distances are slightly longer, or perhaps equal to, the bond length 1.519(5) Å obtained for the B–C distances in the borin (C_5H_5B) skeleton.[7] It may also be mentioned that similar short B–C distances, 1.528(5) Å, have also been found in 7-hydroxy-6-methyl-7,6-borazarothieno(3,2-*c*) pyridine.[8] The short B–C distances now obtained seem reasonable since the boron atom takes part in a borepinyl ring. Another consequence of this participation is that the C(3′)–B(4)–C(5′) angle is larger than 120°. The boron-ether oxygen distance, 1.357(2), is shorter than the B–O distance of 1.395(7) Å found by Huttner, Krieg and Gartzke[7] in bis(1-methoxyborinato)cobolt(0). It is also shorter than the mean value of the B–O distances, 1.372 Å, obtained for the crystal structure of B_2O_3 *I*, where boron is three-coordinated,[9] although individual bond lengths in this compound are as short as 1.34(2) Å. Thus the boron and oxygen atoms in the present compound are partially double bonded. However, the B–O distance, 1.357Å, compares well to the B–OH distance of 1.352(5) Å found in the borazaro compound,[8] discussed above. As mentioned previously, the boron atom has a planar coordination in the present structure. The angles around boron deviate significantly from 120°. The same situation is encountered in other compounds with three-coordinated boron, *e.g.* $Na_2B_4O_7$.[10] The B–O–B angle of 152.6(3)° (Fig. 1) is essentially larger than is usually found for boron-oxygen compounds. According to Krogh-Moe,[11] values of 123–138° are normal for intergroup B–O–B

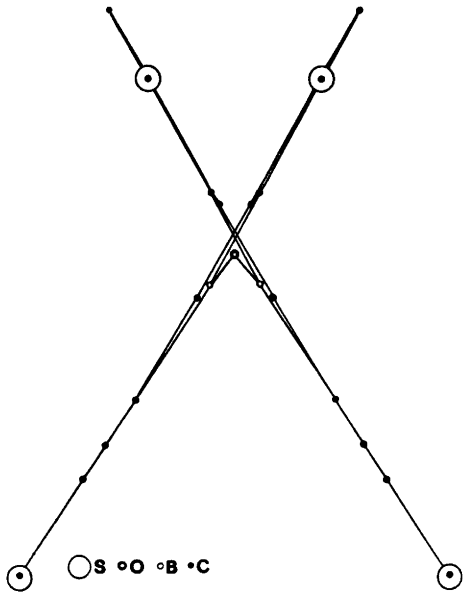

Fig. 3. Projection of one molecule of $(C_{10}H_6BS_2)_2O$ on a plane perpendicular to the line of intersection between the best planes of the $C_{10}H_6BS_2$ parts. Only non-hydrogen atoms are shown. Carbon atoms overlap sulfur atoms in four cases in the projection.

angles in complex borates.

Planarity of the different rings. The best plane through the $C_{10}H_6BS_2$ part was calculated using only the positions of the 13 non-hydrogen atoms, giving them all unit weight. The largest deviation from the plane occurred for the boron atom, amounting to 0.09 Å, whereas the deviations of the sulfur atoms were 0.04–0.05 Å. As mentioned in Ref. 3, the same calculations were made for the dithienotropylium cation, where deviations of 0.04 – 0.05 Å were found for the sulfur atoms, while all other atoms were closer to the best plane. Similar least-squares calculations were performed for the borepinyl ring only, using the positions of the 7 non-hydrogen atoms, and giving them unit weight. The largest departure from planarity, 0.038 Å, was found for the boron atom and the smallest one, 0.015 Å, for C(8). Calculations of the same kind for the tropylium ring[3] showed that no atom was more distant from the plane than 0.015 Å. Considering the *e.s.d.*'s of the atomic positions, it is concluded that neither the dithienoborepinyl parts, $C_{10}H_6BS_2$, nor the borepinyl parts, C_6B, of the present compound $(C_{10}H_6BS_2)_2O$, are planar from a statistical point of view. It also seems probable that the 7- and 13-membered rings of the borepinyl compound are less planar than the corresponding rings in the dithienotropylium cation.[3]

A projection of one molecule $(C_{10}H_6BS_2)_2O$ on a plane perpendicular to the common line to the best planes of the $C_{10}H_6BS_2$ parts is given in Fig. 3, which shows that the dithienoborepinyl parts have boat forms. However, the best planes were calculated for the two thiophene rings separately and the angle between the normals to these planes was found to be 4(2)°. Thus the boat form has no statistical significance.

Intermolecular distances. No intermolecular distances occurring in the crystal structure are shorter than the respective sums of the van der Waals radii. The shortest hydrogen-hydrogen interaction is 2.6 Å.

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