1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-*c*]thiophenium Bis(tetrafluoroborate): X-ray Crystal Structure of a Stable Thieno[3,4-*c*]thiophene Dication

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The structure of the 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene dication (**2**) prepared from 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**) by two-electron oxidation was investigated by X-ray crystallographic analysis. The results revealed that the positive charges are largely delocalized on the two *i*-PrS-C-C-C-SPr-*i* moieties.

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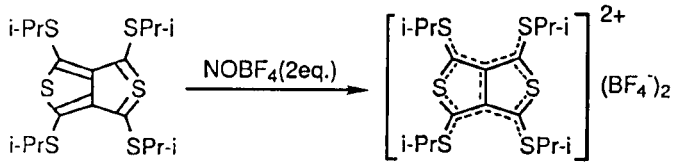
Introduction.

Thieno[3,4-*c*]thiophenes are of considerable interest in having the nonclassical structure which can not be represented by the normal valence bond [1]. Previously we have investigated the molecular structure of 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**), which can be isolated as a stable form, by X-ray crystallographic analysis and showed that the thieno[3,4-*c*]thiophene ring is planar and the π-electrons are delocalized [2]. This observation is consistent with that of 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene [3]. Recently we have found that two-electron oxidation of **1** with nitrosonium tetrafluoroborate ($NOBF_4$) yields the dication **2** as stable crystals [4].



1 **2**

This dication is of interest as the first example of a sulfur analog of pentalene with 8 π–electrons and in investigating the molecular structural change by removal of two electrons from **1**. We performed its X-ray crystallographic analysis and now report our findings that the conjugation is expanded to the sulfur atoms of the substituents and the positive charges are largely delocalized on two *i*-PrS-C-C-C-SPr-*i* moieties.

Results and Discussion.

The dication **2** was prepared from **1** by reaction with $NOBF_4$ (2 equiv) in acetonitrile at -30° and its single crystals suitable for the X-ray structure determination were obtained by diffusion of ether vapor into the acetonitrile solution of **2**. The molecular structure of **2** is illustrated in Figure 1. Table 1 shows the atomic parameters, and Tables 2 and 3 the bond distances and angles. The crystal structure of **2** consists of the thieno[3,4-*c*]thiophene molecule and tetrafluoroborate anion (BF_4^-) in a 1:2 ratio. The

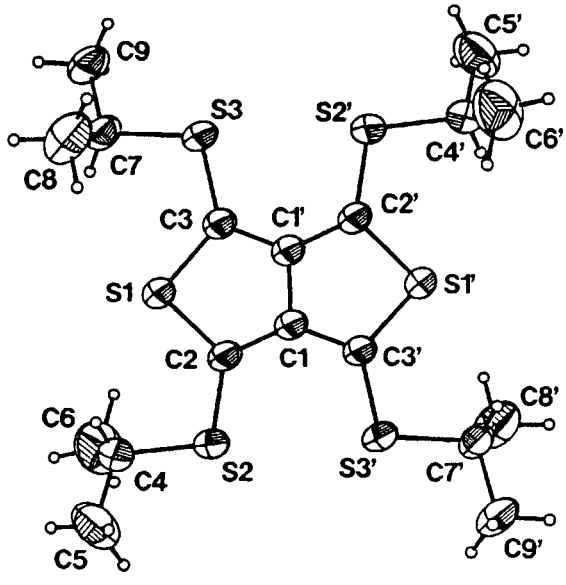


Figure 1. ORTEP drawing and atomic numbering scheme of the dication moiety in **2**.

thieno[3,4-*c*]thiophene dication moieties occupy the crystallographic inversion center. The BF_4^- anions disorder about B-F1 bond with occupation factor of 0.7 and 0.3 for F2, F3, F4 and F2', F3', F4' respectively. The thieno[3,4-*c*]-

Table 1

Positional Parameters with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B(Å) [a]
S1	0.41688 (5)	0.40424 (5)	0.2292 (1)	3.74 (2)
S2	0.34297 (5)	0.59230 (5)	0.1676 (2)	4.49 (2)
S3	0.54887 (5)	0.28467 (5)	0.4854 (1)	4.11 (2)
C1	0.4747 (2)	0.5374 (2)	0.4626 (5)	3.38 (6)
C2	0.4115 (2)	0.5170 (2)	0.2936 (5)	3.42 (6)
C3	0.5020 (2)	0.3841 (2)	0.4276 (5)	3.28 (6)
C4	0.2688 (2)	0.5279 (2)	-0.0174 (6)	4.39 (7)
C5	0.2444 (3)	0.5876 (3)	-0.2090 (7)	6.7 (1)
C6	0.1919 (3)	0.4937 (3)	0.0967 (8)	8.1 (1)
C7	0.4901 (2)	0.2060 (2)	0.3007 (6)	3.94 (7)
C8	0.5252 (3)	0.2096 (3)	0.0768 (7)	6.6 (1)
C9	0.5041 (3)	0.1162 (2)	0.4109 (7)	5.58 (9)
H4	0.300 (2)	0.486 (2)	-0.067 (5)	5.0(7)*
H5A	0.291 (3)	0.608 (3)	-0.268 (7)	11 (1)*
H5B	0.207 (3)	0.643 (3)	-0.144 (7)	11 (1)*
H5C	0.204 (2)	0.554 (2)	-0.281 (6)	6.8 (9)*
H6A	0.215 (3)	0.446 (3)	0.241 (7)	11 (1)*
H6B	0.153 (2)	0.467 (3)	-0.004 (6)	9 (1)*
H6C	0.160 (2)	0.538 (2)	0.123 (5)	5.3 (8)*
H7	0.428 (2)	0.222 (2)	0.297 (5)	4.5 (7)*
H8A	0.484 (3)	0.168 (3)	-0.015 (7)	11 (1)*
H8B	0.591 (2)	0.200 (2)	0.083 (6)	7 (1)*
H8C	0.512 (3)	0.268 (3)	0.010 (6)	8 (1)*
H9A	0.469 (2)	0.074 (2)	0.308 (6)	7.5 (9)*
H9B	0.569 (2)	0.102 (2)	0.435 (6)	8 (1)*
H9C	0.470 (2)	0.113 (3)	0.543 (6)	8 (1)*
B	0.7922 (3)	0.1969 (3)	0.7022 (8)	5.8 (1)
F1	0.8588 (2)	0.1349 (2)	0.7270 (4)	7.60 (6)
F2	0.8171 (3)	0.2668 (2)	0.5929 (7)	9.9 (1)
F3	0.7657 (3)	0.2190 (3)	0.8985 (6)	11.0 (1)
F4	0.7223 (3)	0.1560 (4)	0.5978 (9)	12.9 (2)
F2'	0.8283 (8)	0.2667 (9)	0.820 (3)	17.7 (5)
F3'	0.7166 (5)	0.1851 (6)	0.781 (1)	9.6 (2)
F4'	0.7782 (7)	0.2200 (7)	0.493 (1)	13.0 (3)

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times B(1,1) + b^2 \times B(2,2) + c^2 \times B(3,3) + ab(\cos\gamma) \times B(1,2) + ac(\cos\beta) \times B(1,3) + bc(\cos\alpha) \times B(2,3)]$.

thiophene ring including the sulfur atoms of the substituents is planar. The distances of the S1-C2 and C1-C2 bonds are nearly equal to those of the S1-C3 and C1'-C3 bonds respectively, thus indicating that the ring possesses approximate D_{2h} symmetry. This result is different from those in the cases of 1,3,5-tri-*t*-butylpentalene [5] and dimethyl 4,6-di-*t*-butylpentalene-1,2-dicarboxylate [5] which possess C_{2h} symmetry with 8 π-electrons and exhibit a bond alternation. The distance of the C1-C1' bond becomes shorter than those of **1**, 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene and thiophene [6] by 0.028, 0.033 and 0.004 Å respectively, but is longer than those of the C1-C2 and C1'-C3 bonds, which have *ca.*

Table 2

Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Bond	Distance	Bond	Distance
S1-C2	1.747 (3)	S1-C3	1.741 (3)
S2-C2	1.687 (3)	S2-C4	1.823 (3)
S3-C3	1.682 (3)	S3-C7	1.833 (3)
C1-C1'	1.419 (4)	C1-C2	1.400 (4)
C1-C3'	1.397 (4)	C4-C5	1.513 (5)
C4-C6	1.475 (6)	C4-H4	0.86 (3)
C5-H5A	0.86 (4)	C5-H5B	1.09 (5)
C5-H5C	0.88 (3)	C6-H6A	1.18 (4)
C6-H6B	0.92 (4)	C6-H6C	0.85 (3)
C7-C8	1.508 (6)	C7-C9	1.522 (5)
C7-H7	0.97 (3)	C8-H8A	1.03 (4)
C8-H8B	1.00 (3)	C8-H8C	0.99 (4)
C9-H9A	0.98 (3)	C9-H9B	1.00 (4)
C9-H9C	0.99 (3)	B-F1	1.366 (5)
B-F2	1.316 (6)	B-F3	1.338 (6)
B-F4	1.345 (6)	B-F2'	1.37 (2)
B-F3'	1.266 (9)	B-F4'	1.34 (1)

Table 3

Bond Angles (°) with Estimated Standard Deviations in Parentheses

Bond	Angle	Bond	Angle
C2-S1-C3	92.9 (1)	C2-S2-C4	105.2 (1)
C3-S3-C7	105.4 (1)	C1'-C1-C2	113.1 (2)
C1'-C1-C3'	113.6 (3)	C2-C1-C3'	133.3 (3)
S1-C2-S2	125.6 (2)	S1-C2-C1	110.2 (2)
S2-C2-C1	124.2 (2)	S1-C3-S3	125.7 (2)
S1-C3-C1'	110.2 (2)	S3-C3-C1'	124.1 (2)
S2-C4-C5	106.5 (2)	S2-C4-C6	110.4 (3)
S2-C4-H4	107.0 (2)	C5-C4-C6	115.0 (3)
C5-C4-H4	106.0 (2)	C6-C4-H4	111.0 (2)
C4-C5-H5A	112.0 (3)	C4-C5-H5B	106.0 (2)
C4-C5-H5C	110.0 (2)	H5A-C5-H5B	109.0 (4)
H5A-C5-H5C	122.0 (4)	H5B-C5-H5C	106.0 (3)
C4-C6-H6A	111.0 (2)	C4-C6-H6B	108.0 (2)
C4-C6-H6C	106.0 (2)	H6A-C6-H6B	113.0 (3)
H6A-C6-H6C	119.0 (3)	H6B-C6-H6C	98.0 (3)
S3-C7-C8	111.5 (2)	S3-C7-C9	104.4 (2)
S3-C7-H7	106.0 (2)	C8-C7-C9	113.3 (3)
C8-C7-H7	111.0 (2)	C9-C7-H7	110.0 (2)
C7-C8-H8A	105.0 (3)	C7-C8-H8B	111.0 (2)
C7-C8-H8C	110.0 (2)	H8A-C8-H8B	120.0 (3)
H8A-C8-H8C	102.0 (3)	H8B-C8-H8C	109.0 (3)
C7-C9-H9A	104.0 (2)	C7-C9-H9B	111.0 (2)
C7-C9-H9C	110.0 (2)	H9A-C9-H9B	110.0 (3)
H9A-C9-H9C	107.0 (3)	H9B-C9-H9C	114.0 (3)
F1-B-F2	112.3 (4)	F1-B-F3	108.7 (4)
F1-B-F4	106.3 (4)	F2-B-F3	111.8 (4)
F2-B-F4	110.8 (4)	F3-B-F4	106.6 (4)
F1-B-F2'	101.7 (6)	F1-B-F3'	121.4 (5)
F1-B-F4'	110.9 (6)	F2'-B-F3'	103.7 (8)
F2'-B-F4'	110.2 (9)	F3'-B-F4'	108.1 (7)
F2-B-F2'	62.8 (7)	F2-B-F3'	126.3 (6)
F2 -B-F4'	48.1 (5)	F3-B-F2'	57.1 (7)
F3-B-F3'	51.1 (5)	F3-B-F4'	140.3 (6)
F4-B-F2'	151.2 (7)	F4-B-F3'	55.5 (5)
F4-B-F4'	65.4 (6)		

50% double-bond character, by 0.019 and 0.022 Å respectively. On the other hand, the distance (1.744 Å, average) of the C-S bond of the ring is longer than those of **1**, 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene and thiophene by 0.043, 0.038 and 0.030 Å, respectively and is close to that (1.748 Å) of the C(sp^2)-S single bond of methyl vinyl sulfide [7]. Furthermore, the distance (1.685 Å, average) of the *i*-PrS-C bond is significantly shorter than those of the C(sp^2)-S single bond of methyl vinyl sulfide and the C-S bond in the ring of **2**.

Although the isopropyl groups of the neutral species **1** are directed out from the molecular plane with the dihedral angle of *ca.* 60° in *i*-Pr-S-$C_{(ring)}$-$S_{(ring)}$, the corresponding dihedral angle of the dication **2** is nearly equal to 0°. In former case, the large dihedral angle brings about the considerable decrease of the resonance interaction

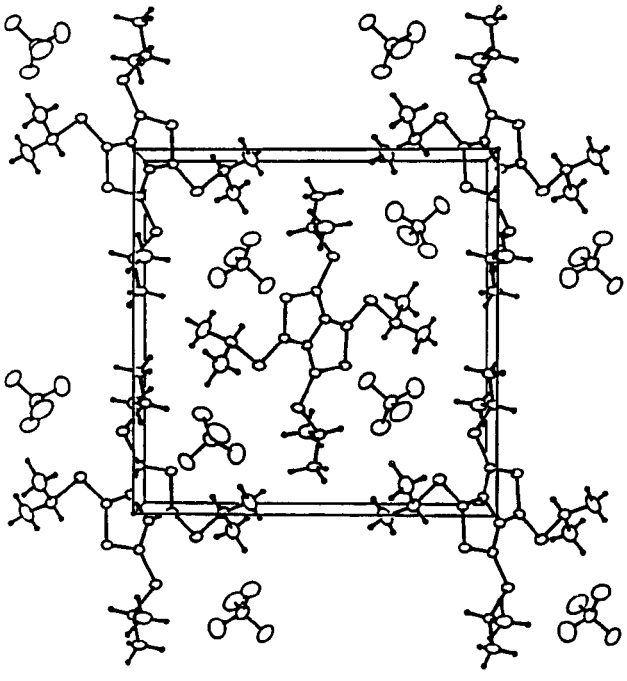


Figure 2. Molecular packing in the unit cell.

between the sulfur atom of the substituent and the thieno[3,4-*c*]thiophene ring [8]. In contrast, the maximum resonance interaction can be achieved in the dication **2**, resulting to the shortening of the *i*-PrS-C bond.

The molecular packing of **2** in the unit cell is shown in Figure 2. There are no intermolecular contacts less than the van der waals distances.

In conclusion, it became apparent by X-ray analysis that the positive charges are largely distributed on the two *i*-PrS-C-C-C-SPr-*i* moieties.

EXPERIMENTAL

Melting point was determined on a Yanaco MP-S3 melting point apparatus and is uncorrected. The ir spectrum was recorded on a Hitachi 215 spectrometer. The uv spectrum was obtained on a Shimadzu UV-160 spectrophotometer. The nmr spectra were recorded on a JEOL JNM-270 FT NMR spectrometer using tetramethylsilane as an internal standard. Elemental analysis was performed on a Yanagimoto MT3 CHN corder. 1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1**) was prepared according to the method described previously [2].

1,3,4,6-Tetrakis(isopropylthio)thieno[3,4-*c*]thiophenium Bis(tetrafluoroborate) (**2**).

Compound **2** was prepared from **1** and $NOBF_4$ according to the method described previously [4], mp 147-148° dec; ir (potassium bromide): ν 2975, 2925, 2860, 1470, 1375, 1310, 1250, 1100-1000, 980 cm^{-1}; uv (acetonitrile): λ max nm (log ε) 274 (4.34), 295 (4.45), 418 (4.24), 579 (4.51); ^1H nmr (270 MHz, acetonitrile-d_3, -30°): δ 1.71 (d, J = 6.7 Hz, 24H, $SCH(CH_3)_2$), 4.26 (br sep, J = 6.7 Hz, 4H, $SCHMe_2$); ^{13}C nmr (68 MHz, acetonitrile-d_3, -30°): δ 22.4, 51.3, 139.5, 176.2.

Anal. Calcd. for $C_{18}H_{28}S_6B_2F_8$: C, 35.4: H, 4.6. Found: C, 35.2; H, 4.7.

X-ray Crystallographic Data of **2** and Structure Determination.

A single crystal of **2** with approximate size of 0.4 x 0.3 x 0.3 mm was employed for the X-ray analysis. The crystal belongs to the monoclinic system, space group $P2_1/a$ (No. 14) with a = 14.937(2), b = 15.059(2), c = 6.172(5) Å, β = 93.29(3)°; Z = 2; V = 1386.0 $Å^3$; D_c = 1.463 g cm^{-3}. The X-ray intensities were measured on an Enraf-Nonious CAD 4 diffractometer by ω/2θ scan mode. The total of 2036 reflections were collected in the range of $1 < \omega < 60°$ utilizing CuKα radiation (λ = 1.5418 Å) and 1548 reflections with $I > 3\sigma(I)$ were used for the the structure determination. The structure was solved by the direct method using SHELXS-86 and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. The potions of hydrogen atoms were obtained from ΔF map and refined isotropically. The final R and Rw values were 0.038 and 0.048 respectively. Further details of the crystal structure investigation are available on request from the authors.

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