Synthesis, spectrophotometry, and X-ray diffraction studies of a new salt: *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide)

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A new salt, *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide) $C_{16}H_{24}I_6S_2$, was prepared. The molecular structure of the salt was studied by X-ray diffraction; the factors that form the crystal packing represented by ...Ct...I_3...I_3...Ct... type chains (Ct is cation) were identified. The stability of *p*-xylylenebis(tetrahydrothiophenium) diiodochlorides and triiodides was estimated by spectrophotometry using the average iodine number function $\bar{n}_{I_2}$.

Key words: *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide), synthesis, UV spectroscopy, ^{1}H NMR spectroscopy, X-ray diffraction analysis, stability constants.

The structural chemistry of triiodides of trialkylsulfonium cations is the subject of vigorous modern research.[1,2] Trialkylsulfonium iodides and triiodides, either molten at room temperature or solid, were proposed as potential new electrolytes for light-sensitive nanocrystalline solar batteries. Triiodides of trialkylsulfonium derivatives demonstrate good electrical conductivity caused by the presence of polyiodide chains.[3,4]

Iodine in organic interhalides exhibits high biological activity; therefore, studies of the molecular structure and equilibrium chemistry of these compounds is of considerable interest.[5]

The features of molecular structure of liquid and solid polyiodides have been characterized using Raman, long-wavelength-IR, UV, NQR, and Mössbauer spectroscopies.[6]

The diverse structures formed by trimethylsulfonium iodide and elemental iodine have been studied by X-ray crystallography. Trimethylsulfonium iodide has been structurally studied.[7] The structure of $(Me)_3SI_3$ has been studied in the solid and liquid states.[8] The shape, the length, and the symmetry of the polyiodide chain have been studied for compounds $[R_3S]I_x$ (R = Me, Et; x = 3—11).[9,10] The presence of intermolecular I...I contacts implies that the triiodide ion is asymmetric, the bond lengths being 2.915 and 2.946 Å for Me_3SI_3 and 2.89—2.95 Å for Et_3SI_3.[8,11]

The bromine-containing interhalide compounds $[R_3S]Br_3$, $[R_3S]IBr_2$, and $[R_3S]I_2Br$ were also investigated.[8—11] A later publication[12] reports the molecular structure of $(Me_3S)_3I_{26}$, which was interpreted as $[Me_3S]_3(I_7)(I_5)_2 \cdot (9/2)I_2$ where the I_5^- and I_7^- anions form a two-layer spatial network.

The scope of this study includes the synthesis and determination of the molecular and crystal structures of *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide) $C_{16}H_{24}I_6S_2$ and comparative estimate of the ability of halides (chlorides, iodides) of a sulfur-containing organic cation to coordinate elemental iodine in chloroform solutions.

Results and Discussion

We synthesized for the first time a new salt, *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide) $C_{16}H_{24}I_6S_2$, by replacing the chloride anion in *p*-xylylenebis(tetrahydrothiophenium) chloride by the triiodide anion.

The equilibrium in the organic halide (chloride, iodide)—molecular iodine system in chloroform was studied by spectrophotometry. The number of iodine molecules coordinated by *p*-xylylenebis(tetrahydrothiophenium) chloride was determined using the average iodine number function $\bar{n}_{I_2}$ (see Ref. 13). The complexation reactions in solution and the stability constants of mono- and bis-complexes can be represented by equations

$$CtX_2 + I_2 \rightleftharpoons CtX_2I_2,\ \beta_1 = \frac{[CtX_2I_2]}{[CtX_2][I_2]}, \quad (1)$$

$$CtX_2 + 2\,I_2 \rightleftharpoons Ct(XI_2)_2,\ \beta_2 = \frac{[Ct(XI_2)_2]}{[CtX_2][I_2]^2} \quad (2)$$

(Ct is cation).

The $\bar{n}_{I_2}$ function was determined for each equilibrium concentration of iodine from the equation

$$\bar{n}_{I_2} = (C_{I_2} - [I_2])/C_{CtX_2}, \quad (3)$$

where C_{CtX_2} is the analytical concentration of the organic halide; C_{I_2} and $[I_2]$ are the analytical and equilibrium concentration of molecular iodine, respectively.

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The stability constants of the mono-complex $CtCl_2I_2$ ($\beta_1 = 2.39 \cdot 10^3$) and bis-complex $Ct(ClI_2)_2$ ($\beta_2 = 1.20 \cdot 10^7$) were calculated by the linear least-squares method using the equation

$$\frac{\bar{n}_{I_2}}{(1-\bar{n}_{I_2})[I_2]} = \beta_1 + \beta_2 \frac{(2-\bar{n}_{I_2})}{(1-\bar{n}_{I_2})}[I_2], \quad (4)$$

which describes the simultaneous coordination of two iodine molecules by an organic halide molecule.

The stability of *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide) was estimated by stoichiometric dilution in a chloroform solution containing 5% acetonitrile. The stability constants of the mono-complex CtI_4 and bis-complex CtI_6 were calculated by the linear least-squares method using Eq. (4) ($\beta_1 = 4.93 \cdot 10^4$, $\beta_2 = 3.88 \cdot 10^8$) and nonlinear least-squares method using the equation

$$\bar{n}_{I_2} = \frac{\beta_1[I_2] + 2\beta_2[I_2]^2}{1 + \beta_1[I_2] + \beta_2[I_2]^2} \quad (5)$$

($\beta_1 = 2.34 \cdot 10^4$; $\beta_2 = 6.05 \cdot 10^8$).

The results obtained by linear and nonlinear least-squares calculations are in good agreement.

Previously, we elucidated the relationship between the cation structure, the anion nature, and the anion ability to coordinate molecular iodine using quantum-chemical calculations for the gas phase and a spectrophotometric study of the stability of iodohalides of quaternary ammonium salts[14,15] and their phosphorus analogs[16] in solutions. The $Ct^+...XI_2^-$ electrostatic interaction weakened in the sequence organic cation diiodochloride—diiodobromide—triiodide, along with the strengthening of the $X...I_2$ bond; this stabilized the anion and decreased the possibility of liberation of molecular iodine from the $CtXI_2$ complex (X = Cl, Br, I). The same trend in the stability was found on going from *p*-xylylenebis(tetrahydrothiophenium) diiodochloride to triiodide.

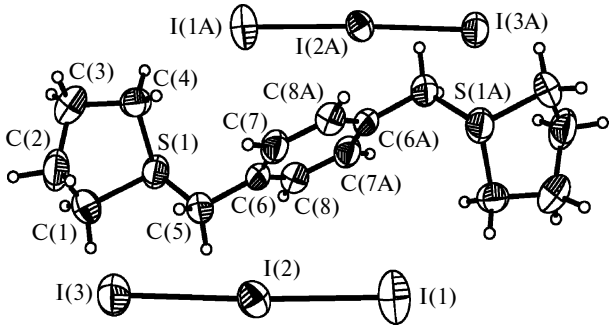

Fig. 1. Structure of the $C_{16}H_{24}I_6S_2$ molecule.

The structure of *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide) is composed of separate, almost linear I_3^- anions and *p*-xylylenebis(tetrahydrothiophenium) cations (Fig. 1). The triiodide ion is located in a general position and slightly deviates from $D_{\infty h}$ symmetry, the I—I—I angle is equal to 176.75(2)°, and the d_{I-I} distances are 2.9199(9) and 2.9123(9) Å. These values are in good agreement with those found previously for the triiodides of N-, S-, and As-containing organic cations.[8,17,18] The cation is located in a special position at the inversion center (0.5, 0.5, 0.5), which coincides with the center of the benzene ring.

The cations and the anions form ...Ct...I_3...I_3...Ct... type chains (Fig. 2) through the shortened $I(3)...H(2B)_{1-x,-y,2-z}$ contact (3.03 Å) and the weak anion—anion contact $I(1)...I(1)_{-x,2-y,1-z}$ (3.794(1) Å), which are shorter than the sum of the van der Waals radii

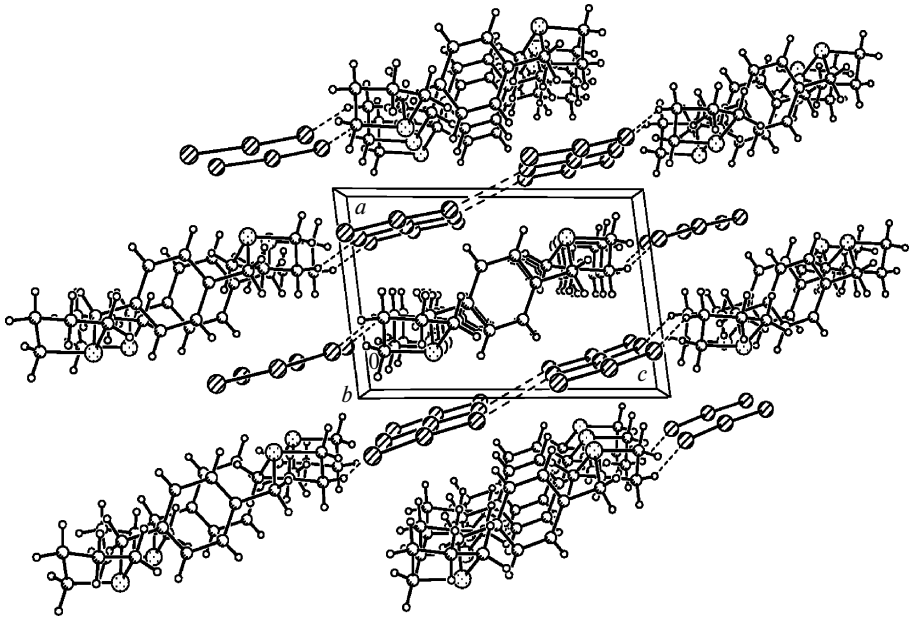

Fig. 2. Fragment of the crystal packing, projection along the *b* axis of the crystal of $C_6H_{24}I_6S_2$.

of the elements (r_I = 2.03 Å and r_H = 1.1 Å).[19] The other intermolecular distances I...H are longer than 3.2 Å. The shortest I...S distance is 3.887 Å, which is comparable with the corresponding value for the simplest sulfonium salt triiodide Me_3SI_3 (3.81 Å).

A structural analysis of the triiodides of organic cations, which are represented rather comprehensively in the Cambridge Structural Database,[20] allows one to reveal the key factors that affect the interatomic distances in the anion, namely, the cation bulk and symmetry, the presence of strong interatomic contacts, and crystal lattice features.

Both triiodide anions present in the molecular structure of $C_{16}H_{24}I_6S_2$ are almost symmetrical, and the distance d_{I-I} is close to that in a free triiodide anion (d_{I-I} = 2.90 Å, I—I—I angle 176.4°).[18] This may be a consequence of coordination of the I_3^- anions linked by weak intermolecular contacts (3.794(1) Å) by the bulky *p*-xylylenebis(tetrahydrothiophenium) cation. The size of the organic cation is apparently the crucial factor. In the known[21] bis(2-*N*,*N*,*N*-trimethylammonioethyl)succinate bis(triiodide) structure, both I_3^- anions are asymmetric, although they are linked by even weaker intermolecular contacts (4.084(3) Å).

Thus, we performed the first X-ray diffraction study of the molecular and crystal structures of *p*-xylylenebis(tetrahydrothiophenium) bis(triiodide). Both triiodide anions present in the molecular structure of $C_{16}H_{24}I_6S_2$ are symmetric due to coordination of the anions by the bulky *p*-xylylenebis(tetrahydrothiophenium) dication in the absence of strong intra- and intermolecular contacts of the I_3^- anions. A comparative estimate of the ability of the interhalide and the triiodide of a sulfur-containing organic cation to retain molecular iodine was carried out by spectrophotometry.

Experimental

p-Xylylenebis(tetrahydrothiophenium) bis(triiodide) was prepared by replacing the chloride ions in *p*-xylylenebis(tetrahydrothiophenium) chloride (98%, Aldrich) by triiodide ions upon mixing of ethanol solutions of the salt (0.3514 g, 1 mmol) and potassium triiodide (0.8396 g, 2 mmol) at ~20 °C. The finely crystalline precipitate of $C_{16}H_{24}I_6S_2$ was decanted from the mother liquor, washed with a small amount of EtOH, and dried in air. The product was formed in a quantitative yield. Recrystallization was carried out by slow saturation of an acetonitrile solution with ether vapor at ~20 °C. The product $C_{16}H_{24}I_6S_2$ was a dark-red solid, m.p. 137—138 °C.

The product $C_{16}H_{24}I_6S_2$ was identified by the ^{1}H NMR spectrum recorded in DMSO-d_6 on a Bruker DPX-250 spectrometer. ^{1}H NMR, δ: 2.07—2.30 (m, 8 H_β, $C_4H_8S^+$); 3.28—3.52 (m, 8 H_α, $C_4H_8S^+$); 4.55 (s, 4 H, CH_2); 7.63 (s, 4 H, C_6H_4).

The electronic absorption spectra of chloroform solutions containing organic dication chloride and elemental iodine in different concentration ratios were recorded on a Specord UV—Vis spectrophotometer in 1.0-cm (in the 30000—50000 cm^{-1} range) and 5.0-cm (in the 14000—30000 cm^{-1} range) cells. As initial solutions, $1.0 \cdot 10^{-3}$ *M* solutions of *p*-xylylenebis(tetrahydrothiophenium) chloride and elemental iodine in chloroform were used. The concentration of elemental iodine in the reaction series was varied from deficiency to a 5-fold excess, the organic chloride concentration remaining invariable ($5.0 \cdot 10^{-5}$ mol L^{-1}).

The stability constants for the compound $C_{16}H_{24}I_6S_2$ were studied by 2-, 4-, 8-, 10-, 16-, and 20-fold stoichiometric dilution of the initial $2.0 \cdot 10^{-4}$ *M* solution. The absorbance was measured at the absorption wavelength of molecular iodine (λ = 510 nm, logε = 2.95±0.01) on a SF-46 spectrophotometer in 1.0- and 5.0-cm thick cells. The equilibrium concentration of iodine was calculated from the absorbance at the maximum of the individual elemental iodine band from the equation

$$[I_2] = A_{max}/(l\varepsilon_{I_2}).$$

X-ray diffraction. The crystal data and selected refinement parameters for the structure of $C_{16}H_{24}I_6S_2$ are summarized in Table 1. The experimental set of reflections was collected on an Enraf—Nonius CAD-4 automatic diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å). The absorption correction was applied by azimuthal scanning curves (T_{min}/T_{max} = 0.128/0.178). The structure was solved by the direct method and refined by full-matrix least-squares method on F^2_{hkl} with anisotropic thermal parameters for all nonhydrogen atoms. The H atoms were placed into geometrically calculated positions and included in the refinement by the riding model. All calculations were carried out on a PC using SHELXTL software.[22] The atom coordinates are summarized in Table 2 and selected geometric parameters are in Table 3.

Table 1. Crystal data and refinement parameters for the structure of $C_6H_{24}I_6S_2$

Parameter	Value
Molecular formula	$C_{16}H_{24}I_6S_2$
Molecular weight	1041.87
Space group	$P\bar{1}$
T/K	293
a/Å	7.610(2)
b/Å	7.656(2)
c/Å	11.722(2)
α/deg	94.72(2)
β/deg	97.25(2)
γ/deg	93.49(2)
V/Å^3	673.4(3)
Z	1
d_{calc}/g cm^{-3}	2.569
μ/cm^{-1}	70.75
$2\theta_{max}$/deg	60
The number of independent reflections	3911
R_{int}	0.018
R_1 (on *F* for reflections with $I > 2\sigma(I)$)	0.0318 (2579)
wR_2 (on F^2_{hkl} for all reflections)	0.0904

Table 2. Atom coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters (U_{eq}) for the structure of $C_6H_{24}I_6S_2$

Atom	*x*	*y*	*z*	$U_{eq} \cdot 10^3$/Å
I(1)	1042(1)	8997(1)	6326(1)	74(1)
I(2)	1608(1)	6347(1)	7966(1)	51(14)
I(3)	2295(1)	3608(1)	9514(1)	68(1)
S(1)	7624(2)	2216(2)	7262(1)	55(1)
C(1)	7557(10)	1453(8)	8694(4)	83(2)
C(2)	6066(9)	70(7)	8544(5)	75(2)
C(3)	6168(7)	–986(6)	7420(5)	62(1)
C(4)	6318(6)	311(6)	6531(4)	51(1)
C(5)	6019(9)	3869(7)	7268(4)	65(1)
C(6)	5476(7)	4431(5)	6078(3)	47(1)
C(7)	3777(7)	4069(6)	5535(4)	50(1)
C(8)	6714(7)	5357(6)	5537(4)	54(1)

Table 3. Selected bond lengths (*d*) and bond angles (ω) for the structure of $C_6H_{24}I_6S_2$

Bond	*d*/Å	Angle	ω/deg
I(1)—I(2)	2.9199(9)	I(3)—I(2)—I(1)	176.745(15)
I(2)—I(3)	2.9123(9)	C(4)—S(1)—C(5)	102.6(3)
S(1)—C(4)	1.803(5)	C(4)—S(1)—C(1)	93.6(3)
S(1)—C(5)	1.811(5)	C(5)—S(1)—C(1)	100.8(3)
S(1)—C(1)	1.829(5)	C(2)—C(1)—S(1)	105.2(4)
C(1)—C(2)	1.487(9)	C(1)—C(2)—C(3)	106.6(5)
C(2)—C(3)	1.500(8)	C(2)—C(3)—C(4)	106.6(4)
C(3)—C(4)	1.508(7)	C(3)—C(4)—S(1)	106.5(3)
C(5)—C(6)	1.509(6)	C(6)—C(5)—S(1)	112.2(3)
C(6)—C(7)	1.369(7)	C(7)—C(6)—C(8)	119.7(4)
C(6)—C(8)	1.391(6)	C(7)—C(6)—C(5)	120.9(4)
C(7)—C(8)*	1.379(6)	C(8)—C(6)—C(5)	119.4(5)
C(8)—C(7)*	1.379(6)	C(6)—C(7)—C(8)*	120.2(4)
		C(7)*—C(8)—C(6)	120.1(5)

* Obtained by symmetric transformation $-x + 1, -y + 1, -z + 1$.

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