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The Crystal Structure of 1,5-Dithioniabicyclo[3.3.0]octane Bis(trifluoromethanesulfonate). The First Structural Characterization of Dithionia Dication and Strong S···O Interactions between Cations and Anions

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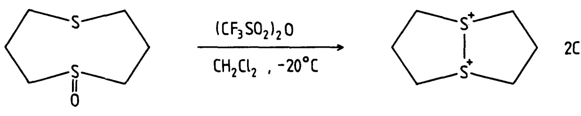
The crystal structure of 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) has been determined by the X-ray method to elucidate the structure of a dithionia dication. Crystal data; $C_6S_2H_{12}{}^{2+}\cdot 2CF_3SO_3{}^-$, F_w=446.43, orthorhombic, Pccb, a=16.775(2), b=9.893(3), c=19.592(3) Å, V=3251(1) Å^3, Z=8, D_x=1.825 Mg m^{-3}. There are two independent dications, **A** and **B**, in the crystals, each of which has a crystallographic twofold axis. The mean S^+–S^+ distance is 2.124 Å. The conformation of the eight-membered ring is a distorted chair–chair form. Very strong interactions were observed between S^+ of dications and O atoms of counter anions. The average distance of $S^+\cdots O$ is 2.724 Å and colinear arrangements of O···S–S···O are formed with the central twofold axis. Other weak S···O interactions (2.903—3.153 Å) were also observed between dications and anions. The coordination around S is a roughly distorted octahedron with two C and two O atoms in a plane and apical S and O atoms.

The presence of cyclic dithionia dications was reported by means of spectroscopic studies.[1] No crystallographic studies of these salts have been reported because of the difficulties to obtain stable crystals. Recently the title salt could be isolated from a reaction of 1,5-dithiacyclooctane *S*-oxide and $(CF_3SO_2)O$ in CH_2Cl_2.[2] The X-ray analysis was undertaken to confirm the existence of a dication and to reveal a structural feature of a transanuular effect between sulfurs. Some sulfur-bonded 1-thionia-5-thiacyclooctane salts and 1,5-dithiacyclooctanes have been found to have a relatively short transannular S···S contact in the range 3.121—3.271 Å[3] because of the hypervalency of the sulfur atom.[4] It is also interesting to compare the structure of 1,5-dithioniacyclooctane with those of 1,5-dithiacyclooctanes. This is the first report about the structure of a cyclic dithionia dication.



Experimental

Colorless plate with dimension of 0.45×0.30×0.15 mm was sealed in a thin glass capillary because crystals were unstable in air. Crystal data and some experimental conditions are listed in Table 1. Intensities were collected on a Rigaku automatic diffractometer with graphite-monochromated Mo*Kα* (λ=0.71073 Å) radiation, using ω–2θ scan technique. At both ends of the scan range 10 s background counts were taken for each reflection. Three reflections were monitored for each 50 reflections. Variation of intensities of the monitored reflections were within 2%. Reflections with $|F_o|\geq 3\sigma(F)$ were considered to be observed. No absorption nor extinction corrections were applied. Three S atoms were picked up from the E-map obtained by MULTAN78.[5] The other atoms were obtained from the succesive F- and D-maps. Block-diagonal least-squares were carried out with anisotropic temperature factors for non-H and isotropic ones for H atoms. Four strong reflections considered to be affected by an extinction effect

Table 1. Crystal Data and Some Experimental Conditions

	$C_6H_{12}S_2{}^{2+}\cdot 2CF_3SO_3{}^-$
F_w	446.43
Crystal system	Orthorhombic
Space group	Pccb
a/Å	16.775(2)
b/Å	9.893(3)
c/Å	19.592(3)
V/Å^3	3251.2(11)
Z	8
D_x/Mg m^{-3}	1.825
F(000)	1808
Temperature/K	292
Crystal size/mm	0.45×0.30×0.15
Radiation	Mo*Kα*
μ/mm^{-1} (Mo*Kα*)	0.646
$2\theta_{max}$/°	55
Scan width $\Delta\omega$/°	1.3+0.5 tan θ
Scan speed 2θ/° min^{-1}	4
Max. h,k,l	21, 12, 25
No. of reflections	
measured	3966
unique	3735
observed	2200
refined	2196
R (Observed)	0.069
R (Refined)	0.065
wR (Refined)	0.071

were omitted from the final refinement. $\sum w(|F_c|-k^{-1}|F_o|)^2$ was minimized with $w=1/(9.1852-0.1234|F_o|+0.0013|F_o|^2)$. The final R was 0.065 for 2196 refined reflections and an R value for 2200 reflections with $|F_o|\geq 3\sigma(F)$ was 0.069. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[6] All computations were performed on a HITAC M260 Computer of the Data Processing Center of the University of Electro-Communications with the programs UNICS III,[7] ORTEP II.[8]

Results and Discussion

Crystal Structure. The final atomic parameters are listed in Table 2.[9] There are two independent dications, **A** and **B**, in the crystals, each of which has a crystallographic twofold symmetry as shown in Fig. 1(a). Thus there are two halves of the dications and two independent anions in an asymmetric unit. These two independent dications are related with each other by a local pseudo mirror at x=0.125. The molecules are stacked along the a axis in a manner of **AABBAA**.... The environment of the anion **A** is different from that of **B**: the anions **A** are located between methylene groups of the two dications while the anions **B** are located between sulfur atoms. Figure 1(b) shows the molecular arrangement viewed along the a axis.

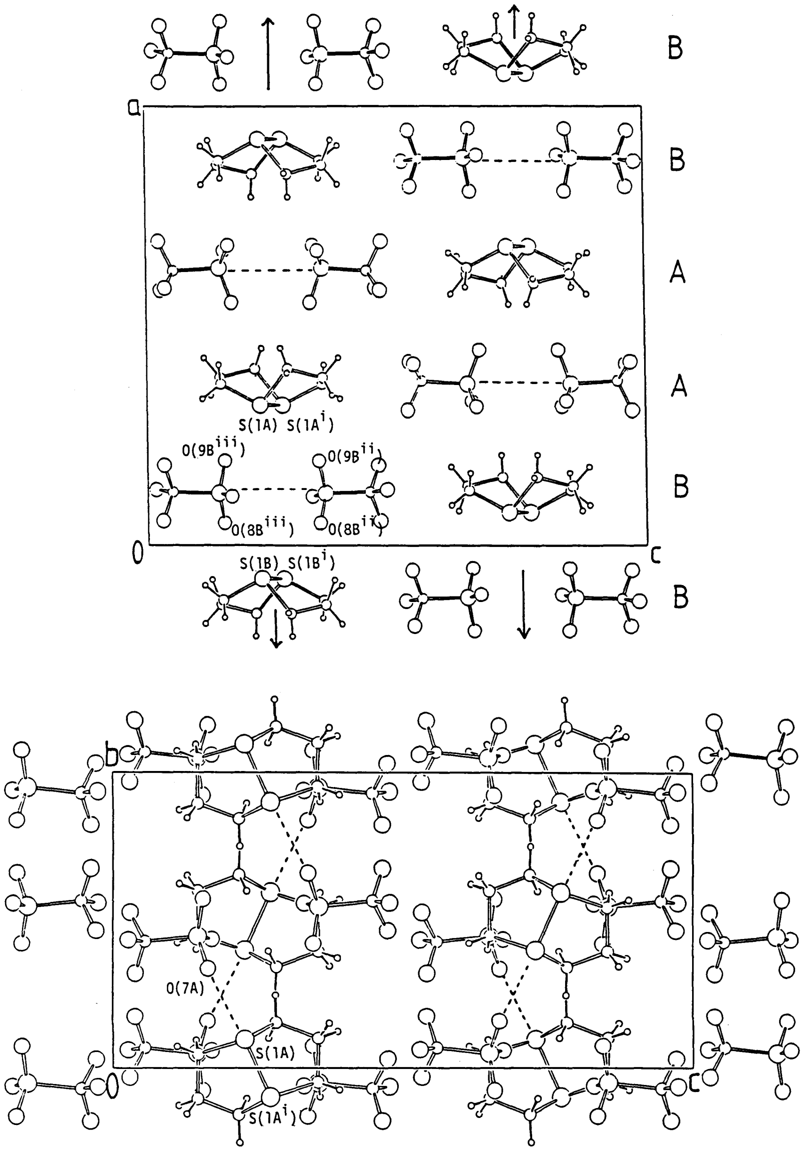


Fig. 1. The projection of the crystal structure, (a) viewed along the b axis within the range from x=0.0 to 0.5. Dotted lines show the pseudo local mirror between the dications **A** and **B**. (b) Viewed along the a axis within the range from x=0.25 to 0.75. Only dications **A** and anions **A** are shown in this range. Dotted lines show the S···O interaction between dications **A** and anions **A**.

Structure of Dication. The structure of the dication with the atom-numbering is shown in Fig. 2 and the bond distances and angles are listed in Table 3. The S(1)-S(1^{i}) (i=x,$-y$,1/2$-z$) lengths are 2.126(3) and 2.122(3) Å,10) for **A** and **B**, respectively, which are only slightly longer than the normal S-S single bond (2.08 Å). Therefore a bond formation of S$^+$-S$^+$ is confirmed unequivocally and the structure of the dication is not an open cyclooctane ring but a bicyclooctane. On the other hand relatively short transannular S···S contacts in some sulfur-bonded 1-thionia-5-thiacyclooctane salts and 1,5-dithiacyclooctanes are in the range of 3.121—3.271 Å.2) The S-C lengths are 1.842(7) and 1.828(6) Å for the dication **A** and 1.829(7) and 1.830(6) Å for **B**. These values are also slightly longer than the normal S-C single bond length, while C-C lengths are slightly shorter than the normal Csp^3-Csp^3 bond. The bond angles of C-S-C are 104.1(3)° and 104.6(3)° for **A** and **B**, respectively and those of S-S-C are 92.7(2)—95.9(2)°. The torsion angles of the dications are listed in Table 4. The conformation of the eight-membered ring is a

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors$^{a)}$ for Non-H Atoms

The esd's in parenthses refer to last digits.

Atom	x	y	z	B_{eq}/Å^2
S(1A)	3205(1)	982(1)	2280(1)	2.52(3)
C(2A)	4036(4)	1553(6)	2824(3)	3.1(1)
C(3A)	3836(4)	1026(7)	3526(3)	3.6(2)
C(4A)	3687(3)	−478(6)	3517(3)	2.9(1)
S(1B)	−752(1)	984(1)	2285(1)	2.41(3)
C(2B)	−1555(4)	1570(6)	2844(3)	3.2(2)
C(3B)	−1351(4)	1023(7)	3546(3)	3.4(1)
C(4B)	−1254(4)	−511(6)	3509(3)	2.9(1)
S(5A)	3681(1)	4500(2)	1468(1)	3.4(1)
C(6A)	3749(6)	4308(10)	553(4)	5.9(3)
O(7A)	3166(3)	3390(5)	1652(3)	5.0(2)
O(8A)	3288(4)	5758(6)	1561(4)	7.2(2)
O(9A)	4460(3)	4393(11)	1715(4)	10.2(3)
F(10A)	4139(5)	3232(8)	385(4)	12.4(3)
F(11A)	3081(4)	4371(12)	261(3)	13.3(4)
F(12A)	4189(5)	5309(9)	293(4)	12.5(3)
S(5B)	−1194(1)	4775(1)	1431(1)	2.6(1)
C(6B)	−1216(5)	4507(9)	518(4)	5.1(2)
O(7B)	−1125(3)	3446(5)	1697(3)	5.3(2)
O(8B)	−515(2)	5631(5)	1540(3)	4.2(1)
O(9B)	−1947(2)	5437(5)	1558(2)	3.8(1)
F(10B)	−1838(3)	3726(7)	346(3)	8.0(2)
F(11B)	−558(4)	3863(8)	315(3)	9.7(2)
F(12B)	−1272(4)	5620(7)	178(3)	9.3(2)

a) $B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_ia_j$.

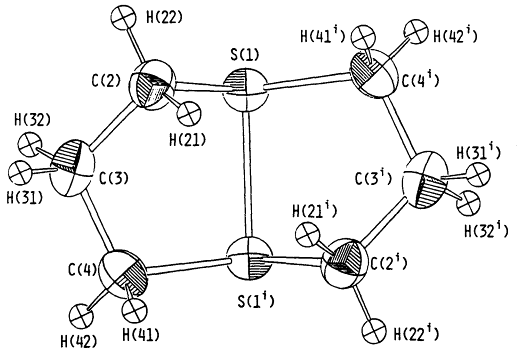


Fig. 2. The structure of dication **A** with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 3. Bond Lengths (l) and Angles (θ)

Cation Distance	**A** l/Å	**B** l/Å	Cation Angle	**A** θ/°	**B** θ/°
S(1)-S(1^{i})	2.126(3)	2.122(3)	S(1^{i})-S(1)-C(2)	92.6(2)	93.1(2)
S(1)-C(2)	1.842(7)	1.829(7)	S(1^{i})-S(1)-C(4^{i})	95.6(2)	95.9(2)
S(1)-C(4^{i})	1.828(6)	1.830(6)	C(2)-S(1)-C(4^{i})	104.1(3)	104.6(3)
C(2)-C(3)	1.509(9)	1.516(9)	S(1)-C(2)-C(3)	104.7(4)	105.3(4)
C(3)-C(4)	1.509(9)	1.527(9)	C(2)-C(3)-C(4)	111.5(5)	109.6(5)
			C(3)-C(4)-S(1^{i})	110.6(4)	110.1(4)
Anion Distance	**A** l/Å	**B** l/Å	Anion Angle	**A** θ/°	**B** θ/°
S(5)-C(6)	1.807(10)	1.809(9)	C(6)-S(5)-O(7)	101.9(4)	103.2(4)
S(5)-O(7)	1.443(6)	1.419(6)	C(6)-S(5)-O(8)	104.4(4)	104.5(4)
S(5)-O(8)	1.419(7)	1.435(5)	C(6)-S(5)-O(9)	106.0(6)	102.7(4)
S(5)-O(9)	1.397(11)	1.444(5)	O(7)-S(5)-O(8)	111.0(4)	115.3(3)
C(6)-F(10)	1.292(13)	1.340(11)	O(7)-S(5)-O(9)	114.6(5)	115.4(3)
C(6)-F(11)	1.259(15)	1.335(12)	O(8)-S(5)-O(9)	117.2(6)	113.6(3)
C(6)-F(12)	1.336(13)	1.291(11)	S(5)-C(6)-F(10)	111.8(7)	110.4(6)
			S(5)-C(6)-F(11)	112.9(8)	110.3(7)
			S(5)-C(6)-F(12)	109.6(7)	112.7(7)
			F(10)-C(6)-F(11)	112.1(10)	107.1(8)
			F(10)-C(6)-F(12)	103.5(9)	107.9(8)
			F(11)-C(6)-F(12)	106.3(10)	108.2(8)

Superscript (i) x, $-y$, $1/2-z$.

distorted chair–chair form, while in the case of 1-thionia-5-thiacyclooctanes and 1,5-dithiacyclooctanes a chair–boat conformation is dominant.

S···O Interaction between Cations and Anions. Very strong interactions were observed between S^{+} of the dications and O(7) atoms of the counter anions. The distance of S^{+}···O are 2.682(6) and 2.766(6) Å for **A** and **B**, respectively, which are remarkablely shorter than the van der Waals contact of 3.35 Å. The angles of S–S···O are 176.3(2) and 166.8(1)°, for **A** and **B**, respectively. Nearly colinear interactions of O···S–S···O, especially in **A**, are formed with the central two fold symmetry as shown in Fig. 3. A linear O···S–S arrangement with a short S···O distance is a typical feature of the hypervalent sulfur compounds.[4] Intramolecular interactions with such a linear O···S–S···O interaction have been reported in 3,5-diacetamido-1,2-dithiolium bromide,[11] bis(*o*-nitrophenyl) disulfide,[12] dimethyl 2,2′-dithiodibenzoate,[13] and N,N′-dimethyl-2,2′-dithiodibenzamide.[14] The S···O distances of these compounds are 2.52—2.89 Å.

Other short nonbonded interactions between dications and anions are also shown in Fig. 3. S(1**A**) has nonbonded contacts to O(9**B**^{ii}) and O(9**B**^{iii}) (ii=$-x$, $y-1/2$, $1/2-z$; iii=$-x$, $1/2-y$, z) at the distances of 3.151(5) and 2.903(5) Å, respectively. These oxygen atoms, in turn, have bifurcate contacts with S(1**A**) and S(1**A**^{i}). The similar situation is observed between S(1**B**) and O(8**B**). The distances of S(1**B**)···O(8**B**^{ii}) and S(1**B**)···O(8**B**^{iii}) are 3.153(5) and 3.034(5) Å, respectively. Thus the coordination around S(1) is a roughly distorted octahedron with two C and two O atoms in a plane and an apical S–S bond and S···O contact. Some interatomic distances and angles related with the S···O interactions are summalized in Table 5. S(1**A**) deviates by 0.277 Å from the plane defined by four atoms C(2**A**), C(4**A**^{i}), O(9**B**^{ii}), and O(9**B**^{iii}). The angle between this plane and S(1**A**)···O(7**A**) is 67.9°. The corresponding deviation and the angle for the dication **B** are 0.260 Å and 56.1°, respectively.

Table 4. Torsion Angles (τ) of Dications

Torsion angle	**A** τ/°	**B** τ/°
C(2)-S(1)-S(1^{i})-C(2^{i})	−81.6(3)	85.1(3)
C(4)-S(1)-S(1^{i})-C(4^{i})	127.2(3)	−124.9(3)
C(2)-S(1)-S(1^{i})-C(4^{i})	22.8(3)	−19.9(3)
C(4^{i})-S(1)-C(2)-C(3)	−140.3(4)	140.1(4)
S(1^{i})-S(1)-C(2)-C(3)	−43.8(4)	43.3(4)
S(1)-C(2)-C(3)-C(4)	54.2(5)	−55.9(5)
C(2)-C(3)-C(4)-S(1^{i})	−34.8(6)	38.7(5)
C(3)-C(4)-S(1^{i})-S(1)	2.1(4)	−6.6(4)
C(3)-C(4)-S(1^{i})-C(2^{i})	96.3(4)	−101.3(4)

Superscript (i) x, $-y$, $1/2-z$.

All the O atoms of the anion **B**, which is located between S atoms of both dications **A** and **B**, coordinate

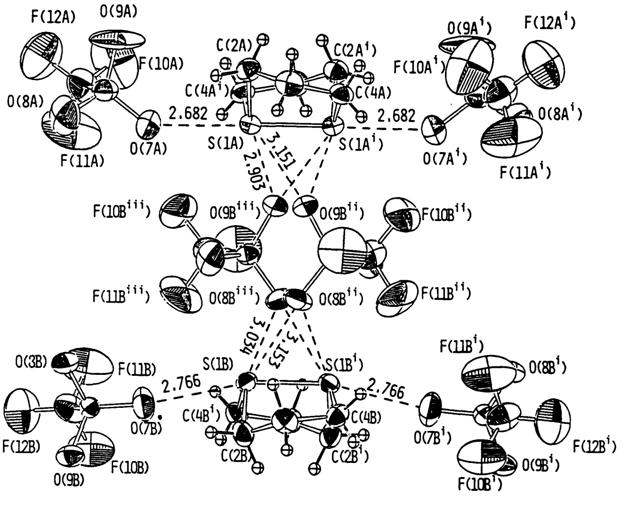


Fig. 3. S···O interactions between dications and anions.

Table 5. S···O Interactions between Cations and Anions Distances (l) and Angles (θ)

	Cation **A**	Cation **B**
Distance	l/Å	l/Å
S(1)···O(7)	2.682(6)	2.766(6)
Angle	θ/°	θ/°
S(1^{i})-S(1)···O(7)	176.3(2)	166.8(1)
C(2)-S(1)···O(7)	90.7(2)	78.7(2)
C(4^{i})-S(1)···O(7)	82.0(2)	76.5(2)

	Cation **A**		Cation **B**	
X	O(9**B**^{ii})	O(9**B**^{iii})	O(8**B**^{ii})	O(8**B**^{iii})
Distance	l/Å	l/Å	l/Å	l/Å
S(1)···X	3.151(5)	2.903(5)	3.153(5)	3.034(5)
Angle	θ/°	θ/°	θ/°	θ/°
S(1^{i})-S(1)···X	63.3(1)	75.8(1)	67.0(1)	73.0(1)
C(2)-S(1)···X	98.1(2)	168.5(2)	95.4(2)	166.1(2)
C(4^{i})-S(1)···X	150.1(2)	76.9(2)	154.5(2)	77.2(2)
O(7)···S(1)···X	117.8(2)	100.9(2)	123.7(2)	114.9(2)
X···S(1)···X′	77.4(1)		79.7(1)	

Superscript (i) x, $-y$, $1/2-z$, (ii) $-x$, $-1/2+y$, $1/2-z$, (iii) $-x$, $1/2-y$, z.

to the sulfur atoms. On the other hand for the anion **A** only O(7) is used for the coordination. These facts relate with a larger deviation from the linearity of O···S–S···O and a longer S···O distance in the case of **B** rather than those of **A**. The temperature factors of O atoms of the anion **B** and O(7**A**) are smaller than those of the other O and F atoms. This is another evidence of the strong interactions between S^+ and O. It may be attributed to these strong interactions between the dications and the anions to obtain the crystals of this salt successfully, since an attempt to obtain stable crystals with different anions such as $H_2SO_4^{2-}$ and BF_4^- was failed.

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