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CRYSTAL, MOLECULAR, AND π-ELECTRONIC STRUCTURE OF 1,3,2-BENZODITHIAZOLIUM CHLORIDE

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X-Ray diffraction examination and MNDO calculations have shown that 1,3,2-benzodithiazolium chloride (I) is ionic, with a planar heteroaromatic 10π-electron cation. The π–MO of the cation (I) is isolobal with the p-MO of benzo-2,1,3-thiadiazole. In the cation of (I), as in the latter compound, the p-AO of nitrogen and sulfur contribute for the most part to π-MO of differing symmetry (b_1 and a_2, respectively). This has the consequence that although both nitrogen and sulfur participate in the formation of a single π-system in the thiazolium cation of (I), there is virtually no π-bonding between them. Generally speaking, the π-MO of the (I) cation shows a tendency to localization on separate molecular fragments. The charge on the cation is localized at the SNS group, and the five-membered ring is strongly polarized. These features all reduce the heteroaromaticity of the system.

1,3,2-Benzodithiazolium chloride (I), a rational synthesis of which is by reaction of 1,2-bis(chlorosulfenyl)benzene with trimethylsilazane [1], is readily reduced to the 1,3,2-benzodithiazyl radical, which forms with tetracyanoquinodimethane a CTC with the properties of a synthetic metal [1, 2]. Benzobis(1,3,2-dithiazolium) salts (II) behave similarly [3, 4]. Neither the synthetic metals incorporating the benzodithiazolium system, nor the salts (I) and (II) have, however, been examined with respect to structure.

The cation of (I) is isomeric with that of Herz salts (1,2,3-benzothiadiazolium halides [5-7]). Unlike Herz salts, however, which are unstable to atmospheric moisture, light, and heat, (I) is very stable. It is stable on storage under normal conditions for periods of a year, and according to thermogravimetry, it melts at 220°C without decomposition (the maximum for the exothermic decomposition on the DTA plot occurs at 270°C). The most closely related analog of the (I) cation to have been examined, the 4-methyl-1,3,2-dithiazolium hexafluoroarsenate cation (III), has a planar structure [8]. The PMR and ^{13}C NMR spectra of (I) [9] likewise do not conflict with a planar structure for the cation with C_{2v} symmetry; the PMR chemical shifts, which are substantially greater than those for 1,2,3-benzodithiazolium chloride [7] and 1,3-benzodithiolium perchlorate (IV) [10], could indicate considerable charge delocalization in the (I) cation. It my be assumed that the (I) cation, which has ten π-electrons, is heteroaromatic, whereas the cations of Herz salts (which likewise have not been investigated structurally up to the present time) are not heteroaromatic, for example as a result of their nonplanar geometry.

The aim of the present investigation was to examine the crystal, molecular, and π-electronic structure of (I), previously obtained by us [9] by reacting N,N,N',N'-tetrakis(trimethylsilyl)-1,2-bis(sulfenylamino)benzene with selenium tetrachloride.

An x-ray diffraction examination of (I) was carried out (Figs. 1 and 2; Tables 1 and 2). The nonhydrogen atoms in the (I) cation lie in the same plane to within ±0.037 Å. The five- and six-membered rings are individually planar to within ±0.018 Å, the angle between their planes being 1.8°. The mean C–C bond length is 1.396 Å, ranging from 1.366(6) to 1.413(5) Å,

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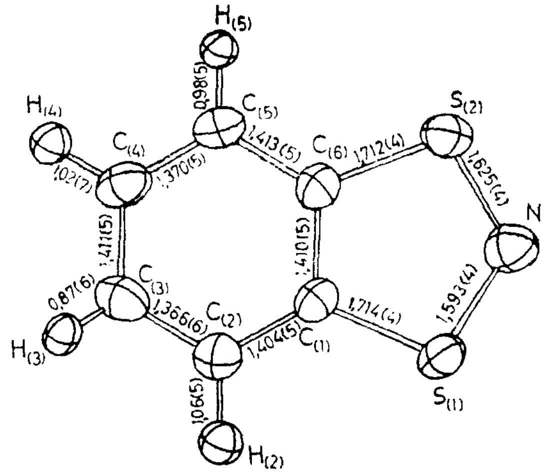

Fig. 1. Geometry of the (I) cation (bond lengths in Å; for valence angles, see Table 1).

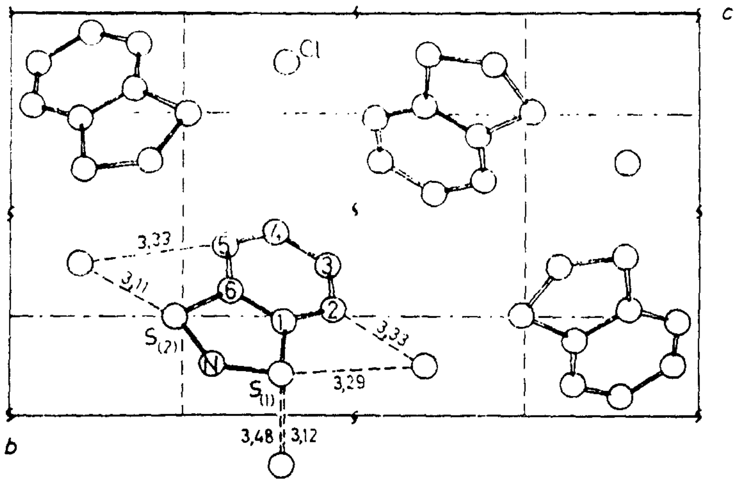

Fig. 2. Packing of (I) in the crystal.

TABLE 1. Valence Angles in the (I) Cation

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(1)}S_{(1)}N$	98,7 (2)	$C_{(6)}S_{(2)}N$	98,2 (2)	$S_{(2)}NS_{(1)}$	117,1 (2)
$C_{(2)}C_{(1)}S_{(1)}$	126,0 (3)	$C_{(6)}C_{(1)}S_{(1)}$	113,1 (3)	$C_{(6)}C_{(1)}C_{(2)}$	120,9 (3)
$C_{(3)}C_{(2)}C_{(1)}$	118,0 (3)	$C_{(4)}C_{(3)}C_{(2)}$	121,3 (4)	$C_{(5)}C_{(4)}C_{(3)}$	121,7 (4)
$C_{(6)}C_{(5)}C_{(4)}$	117,8 (3)	$C_{(1)}C_{(6)}S_{(2)}$	112,8 (3)	$C_{(5)}C_{(6)}S_{(2)}$	127,1 (3)
$C_{(5)}C_{(6)}C_{(1)}$	120,1 (3)	$H_{(2)}C_{(2)}C_{(1)}$	118 (3)	$H_{(2)}C_{(2)}C_{(3)}$	123 (3)
$H_{(3)}C_{(3)}C_{(2)}$	117 (4)	$H_{(3)}C_{(3)}C_{(4)}$	121 (4)	$H_{(4)}C_{(4)}C_{(3)}$	119 (3)
$H_{(4)}C_{(4)}C_{(5)}$	119 (3)	$H_{(5)}C_{(5)}C_{(4)}$	121 (3)	$H_{(5)}C_{(5)}C_{(6)}$	121 (3)

in agreement with the C_{2v} symmetry indicated by the PMR and ^{13}C NMR spectra. The C–S bonds are equivalent, but their lengths (1.712(4) and 1.714(4) Å) are less than expected for the C_{sp^2}–S bond [12]. The S–N bond lengths are intermediate between 1.53 Å for S=N and 1.76 Å for S–N [13, 14], their differing values (1.593(4) Å for $S_{(1)}$–N and 1.625(4) Å for $S_{(2)}$–N) being due to the crystal packing in (I) (this was confirmed by MNDO-optimization of the geometry of the (I) cation – see below). Thus, as compared with the sum of the van der Waals radii (3.74 Å [15]), atom $S_{(1)}$ has three markedly shortened contacts with the chlorine anions: $S_{(1)}$...Cl (x, 1 + y, z) 3.12; $S_{(1)}$...Cl (0.5 + x, 1 – y, 1 – z) 3.29; $S_{(1)}$...Cl (1 + x, 1 + y, z)

TABLE 2. Atom Coordinates in (I) (cell fraction × 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
$C_{(1)}$	1875(8)	7663(3)	3988(2)	$C_{(2)}$	0284(10)	7347(4)	4704(2)
$C_{(3)}$	−1572(10)	6276(4)	4629(2)	$C_{(4)}$	−1847(9)	5479(4)	3864(2)
$C_{(5)}$	−0376(8)	5797(4)	3149(2)	$C_{(6)}$	1525(8)	6917(4)	3209(2)
$S_{(1)}$	4322(0)	8951(1)	3939(1)	$S_{(2)}$	3594(4)	7527(1)	2416(1)
Cl	−0208(3)	1258(1)	3966(1)	N	5222(8)	8730(2)	2970(2)
$H_{(2)}$	0628(129)	7917(61)	5281(31)	$H_{(4)}$	−3149(157)	4632(59)	3847(31)
$H_{(3)}$	−2596(166)	6116(52)	5068(29)	$H_{(5)}$	−0794(117)	5358(50)	2593(31)

TABLE 3. MNDO-Optimized Geometry of the (I) Cation*

Bond	*d*, Å	Angle	ω°
$N—S_{(1)}$ $(N—S_{(2)})$	1,569	$S_{(2)}NS_{(1)}$	119,4
$S_{(1)}—C_{(1)}$ $(S_{(2)}—C_{(6)})$	1,682	$NS_{(1)}C_{(1)}$ $(NS_{(2)}C_{(6)})$	96,8
$C_{(1)}—C_{(2)}$ $(C_{(6)}—C_{(5)})$	1,408	$S_{(1)}C_{(1)}C_{(2)}$ $(S_{(2)}C_{(6)}C_{(5)})$	127,3
$C_{(2)}—C_{(3)}$ $(C_{(5)}—C_{(4)})$	1,407	$C_{(1)}C_{(2)}C_{(3)}$ $(C_{(6)}C_{(5)}C_{(4)})$	119,1
$C_{(3)}—C_{(4)}$	1,415	$C_{(1)}C_{(2)}H_{(2)}$ $(C_{(6)}C_{(5)}H_{(5)})$	120,7
$C_{(1)}—C_{(6)}$	1,442	$C_{(2)}C_{(3)}H_{(3)}$ $(C_{(5)}C_{(4)}H_{(4)})$	119,6
$C_{(2)}—H_{(2)}$ $(C_{(5)}—H_{(5)})$	1,092		
$C_{(3)}—H_{(3)}$ $(C_{(4)}—H_{(4)})$	1,093		

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*Heat of formation, 241.0 kcal/mole.

**The remaining valence angles were calculated from the parameters given in the table and the C_{2v} symmetry of the cation.

3.48 Å. In contrast, $S_{(2)}$ has a shortened contact with only one chlorine anion: $S_{(2)}$...Cl (x, 0.5 + y, z) 3.11 Å. Comparing the other contacts with the sum of the van der Waals radii (3.60 Å [15]), $C_{(2)}$...Cl (0.5 + x, 1 − y, 1 − z) and $C_{(5)}$...Cl (x, 0.5 + y, 0.5 − z) are shortened to 3.33 Å. The shortest N...Cl distance (1 + x, 1 + y, z) is 3.63 Å, which is greater than the sum of the van der Waals radii of 3.38 Å [15]. These findings confirm that (I) is ionic in structure.

MNDO-optimization of the geometry of the (I) cation (Table 3) also shows it to be planar, with the C_{2v} symmetry. The bond lengths and valence angles differ slightly from those found experimentally. In particular, the S–N and C–S bonds are shorter, and the C–C bonds, especially $C_{(1)}$–$C_{(6)}$ and $C_{(2)}$–$C_{(3)}$ ($C_{(4)}$–$C_{(5)}$) are lengthened. In the optimized geometry, the C–C bonds alternate to a much lesser extent than in the experimental geometry, and this may be regarded as the principal difference between them.

Comparison of the experimental geometry of the thiazolium cation of (I) with data for the cation of salt (III) [8] shows the bond lengths in the S–N–S fragment to be the same (1.58(1) and 1.62(1) Å). The C–S bond in the (I) cation is longer than the corresponding bonds in the dithiazolium cation (III) (1.673(11) and 1.696(11) Å). The SNS valence angles in the cations of (I) and (III) differ markedly, being 117.1(2) and 112.4(6)°, respectively. This is partly due to the different C–C bond lengths in the dithiazole ring, namely 1.410(5) Å in the (I) cation and 1.365(14) Å in the (III) cation.

MO calculations for the (I) cation by the MNDO method satisfactorily convey its structure, which was confirmed by comparing the theoretical results with the experimental x-ray fluorescence data for the SK_β spectrum of (I), found to be in good agreement (Fig. 3). The calculations show that the (I) cation does in fact contain a multicentered π-MO system typical of aromatic compounds (Table 4).

The occupied π-MO in (I) are isolobal with the π-MO of benzo-2,1,3-thiadiazole (V) [16], i.e., their numbers, sequence, and shapes are identical. On the energy scale, the π-MO of the thiazolium cation of (I) are shifted relative to the π-MO of (V) toward higher energies almost in parallel (Table 4) apart from the $2b_1$ MO, which contain a large contribution from the atom in the 2-position. Accordingly, the energy interval by which the occupied π-MO are shifted (the difference between the energies of MO $2a_2$ and $1b_1$, Table 4) is 5.84 eV for the (I) cation, and 5.88 eV for (V).

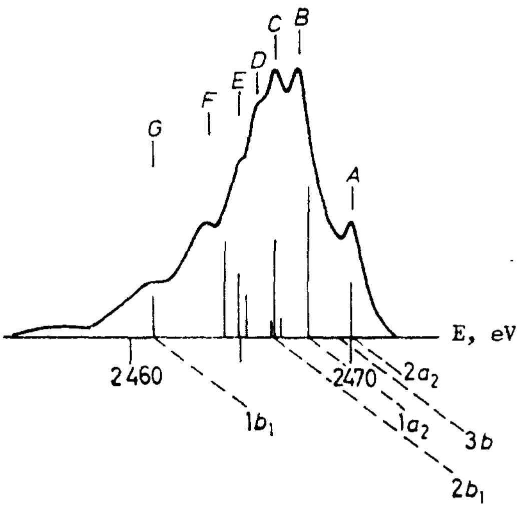

Fig. 3. Experimental SK_β spectrum for (I) on the energy transfer scale. Positions of maxima: 2470.1 (A), 2467.6 (B), 2466.6 (C), 2465.8 (D), 2465.0 (E), 2463.5 (F), ~2460.8 eV (G). Vertical lines correspond to relative intensities of individual spectral transitions according to the MNDO data. The positions of the transitions with π-MO are shown. The strong transition at maximum C is due not to MO $2b_1$, which does not contain a contribution by the sulfur 3p-AO, but to the σ-MO randomly degenerate therewith. The energy transfer scale is combined with the one-electron MO energies by comparing the maximum A with the HOMO $2a_2$ transition.

TABLE 4. π-Electronic Structure of the Thiazolium Cation in (I) and (V) according to MNDO Calculations

π-MO	$-\varepsilon$, eV**		Composition***	π-MO	$-\varepsilon$, eV**		Composition***
	I	V [16]			I	V [16]	
$1b_1$	20,20	15,62	π_5	$2a_2$ (B3MO)	14,36	9,74	$e_{1g}S-2\pi$
$2b_1$	17,82	12,46	$a_{2u}-1\pi$	$4b_1$ (HCMO)	7,43	1,32	$e_{1g}A-3\pi$
$1a_2$	16,40	12,29	$e_{1g}S+2\pi$	$3a_2$	5,12	−0,25	$e_{2u}A$
$3b_1$	14,87	10,08	$e_{1g}A-\pi_2$				

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*The occupied and two lower virtual π-MO were taken into account.

**MO energy with a reciprocal sign.

***1π, 2π, and 3π are the quasiallyl group π-orbitals for the heteroarotomic fragment (bonding, nonbonding, and repulsive, respectively); a_{2u}, $e_{1g}S$, $e_{1g}A$, and $e_{2u}A$ are the group π-orbitals for the carbocycle, correlating with the benzene π-MO $1a_2$, $1e_{1g}$, and $1e_{2u}$, respectively; π_2 is the p-AO of the atom in the 2-position, and π_5 is the bonding combination of AO of atoms in the five-membered ring.

As in (V) [16], in the thiazolium cation of (I) the sulfur 3p-AO and the nitrogen 2p-AO contribute mainly to π-MO of differing symmetry: the nitrogen 2p-AO to MO $2b_1$ and $3b_1$, and the sulfur 3p-AO to MO $1a_2$ and $2a_2$. Only in the deepest π-MO $1b_1$ are the p-AO of nitrogen and sulfur participating simultaneously. This has the result that although the p-AO of both nitrogen and sulfur participate in the formation of a single π-system in the (I) cation, π-bonding between them is virtually nonexistent.

The energies of the p-MO of the (I) cation and their shapes within the carbocycle differ considerably from those in benzene, indicating effective intramolecular interaction with the heteroatomic moiety. Using the fragmental approach, there is a correspondence between the π-MO of the thiazolium cation in (I) and the π-MO of benzene (Table 4). The efficiency of intramolecular interactions in the (I) cation is given by the difference in energy between the MO $2a_2$ and $1a_2$, corresponding to bonding and repulsive combinations of one set of fragment orbitals (Table 4), equal to 2.04 eV. The value for (V) is slightly higher (2.55 eV) [16].

As in (V) [16], the π-MO of the thiazolium cation in (I) show a tendency to localization on the individual molecular fragments. For example, MO $1b_1$, as in (V), is completely localized in the five-membered ring, MO $1a_2$ is 70% localized on the sulfur atoms, and MO $2b_1$ on the nitrogen atom.

It is noteworthy that the thiazolium cations in (I) and (V) are connected by a formal transformation: when the number of π-electrons is the same (10), they are interconvertible by replacing the sulfur atoms by nitrogen, and vice versa. The invariance of the shape and sequence of the π-MO to this transformation appear to indicate that they are of a topological nature. If this conclusion is valid, it should be extensible to the other isostructural systems examined, for example the (IV) cation and the indenyl anion. This observation requires further study.

The charge on the (I) cation is, according to the MNDO data, distributed very unequally, being concentrated on the heteroatomic fragment: q(SNS) = 1.11 e, $q(C_6H_4) = -0.11$ e. The q(SNS) value is virtually the same as the π-charge on this fragment, $q_\pi(SNS) = 1.09$ e. The charge on nitrogen is –0.41 e ($q_\pi(N) = -0.13$ e), and on each sulfur atom 0.76 e ($q_\pi(S) = 0.61$ e). Of the remaining atoms of the cation, higher charges are borne only by the carbon atoms forming the five-membered ring (–0.30 e each). The charges on the other carbons are close to zero, and on the hydrogen atoms, 0.1 e. Since the $q(C_6H_4)$ of the (I) cation and the analogous fragment of the benzene molecule (according to the MNDO data, in C_6H_6, q(C) = –0.06 e, q(H) = 0.06 e), it may be concluded that no integral transfer of electron density between the SNS and C_6H_4 fragments in the (I) cation takes place, but the system is strongly polarized, which is in accordance with the considerable descreening of the ^1H nuclei mentioned above.

The thiazolium cation of (I) is even more polarized in its optimized geometry than in the experimental geometry: q(N) = –0.48 e, q(S) = 0.82 e, $q(C_{(1)}, C_{(6)}) = -0.35$ e, apparently as a result of the shortening of the S–N and C–S bonds and the lengthening of the $C_{(1)}C_{(6)}$ bond in the optimized, as compared with the experimental geometry.

The nonquantum chemical charge method of equalizing electronegativity, calculated as in [17] for sulfur and chlorine from the shifts of the SK_α and ClK_α peaks for (I) (0.126(6) relative to S_8, and –0.196(7) Å eV relative to Cl_2) were 0.15(2) and –0.13(2), respectively. For comparison, the charge on chlorine in KCl, calculated by the same method, is –0.20(3) e, and the charge on sulfur in (V) is 0.21(1) e [17].

The factors enumerated above, namely the predominant participation of the p-AO of nitrogen and sulfur in π–MO of differing symmetry, the tendency to localization of the π–MO on separate fragments, and localization of the cationic charge on the heteroatomic grouping, all of which operate in the same sense, must weaken the heteroaromaticity of the (I) cation, as in (V) [16]. However, the great stability of (I) indicates that the heteroaromaticity of its cation, which is shown by the planarity of its structure and the presence of a single 10π electron system, has not been completely lost.

EXPERIMENTAL

The x-ray structural investigation was carried out on a Syntex $P2_1$ diffractometer with Mo irradiation and a graphite monochromator. The crystals were rhombic, with $a = 5.013(1)$, b = 9.272(2), c = 15.618(5) Å, space group $P2_1nb$, $d_{calc} = 1.74$ g/cm^3, Z = 4, $\mu = 9.8$ cm^{-1}. The intensities of 1167 independent reflections were measured by 2θ/θ scanning in the range 20-60°, and 1058 reflections with $I > 2\sigma$ were used in the calculations. Corrections were made for absorption using an experimental transmittance plot, and for the drift of the control reflections. The structure was calculated using the SHELX-86 program, and refined using the SHELX-76 program. The coordinates of the hydrogen atoms were found from the difference synthesis. Final structure refinement was carried out in block diagonalanisotropic or isotropic (for H atoms) approximation to R = 0.035 and $R_w = 0.041$, where $w^{-1} = \sigma_F^2 + 0.000928F^2$. The atom coordinates are shown in Table 2.

X-Ray fluorescence spectra were obtained on a Stearat spectrometer at 77 K. The spectra were excited by AgL irradiation, and analyzed with a quartz crystal (rhombohedral plane) and recorded on a continuous proportional counter filled with argon-methane. The operating conditions for the x-ray tube were: 0.8 A, 10 kV. The sample was prepared by rubbing into a grooved copper support.

Thermogravimetry was carried out on an MOM derivatograph in air, heating rate 5°/min.

The MNDO calculations were carried out using the AMPAC program [18] for the experimental geometry, idealized to C_{2v} symmetry (Table 4 and Fig. 3), and optimized for C_{2v} geometry.

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