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## The Structure and Energy Minimization of Two Benzothiazolium Iodides

BY DIETER ZOBEL AND GERHARD RUBAN

*Institut für Kristallographie der Freien Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany*

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### Abstract

The structures of 3-methyl-2-(2-thienylvinyl)benzothiazolium iodide ( $C_{14}H_{12}NS_2^+ \cdot I^-$ ) (I) and 3,6-dimethyl-2-(2-thienylvinyl)thiazolo[4,5-*f*]benzothiazolium iodide ( $C_{16}H_{13}N_2S_3^+ \cdot I^-$ ) (II) were determined by X-ray structure analysis. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a = 15.765$  (7),  $b = 16.966$  (7),  $c = 5.496$  (5) Å and  $Z = 4$  for (I), and triclinic, space group  $P\bar{1}$  with  $a = 10.712$  (7),  $b = 12.945$  (7),  $c = 7.421$  (2) Å,  $\alpha = 102.12$  (7),  $\beta = 100.01$  (4),  $\gamma = 99.14$  (5)° and  $Z = 2$  for (II). The structures were solved by Patterson methods and refined by block-matrix least-squares

methods to  $R$  values of 5.3 and 6.2% for 1640 and 3211 reflexions, respectively. Disorder was found for (II) with respect to the terminal thiophene ring which was treated by group refinement. In addition, ethanol was found to be crystallized in the structure of (II). Energy minimization by variation of the torsion angle between the terminal thiophene ring and the rest of the structure led to results which are in good agreement with those obtained from the X-ray analysis.

### Introduction

A large number of different monomeric and polymeric benzothiazolium systems containing  $\pi$ -electron systems

were synthesized by Bocionek (1978) to study the possible influence of the ionic character of the benzothiazolium system on their electrical properties. The title compounds were selected for X-ray structure determination to determine the steric properties and molecular arrangements. Since iodine salts of these compounds show interesting semiconduction properties (Kossmehl, Bocionek & Manecke, 1979), the purpose of this work was to determine the existence of intermolecular or ionic interactions possibly favouring charge transfer.

### Experimental

Orange-red parallelepipeds for (I) and red-brown ones for (II) were obtained by recrystallization from ethanol (Bocionek, 1978). Oscillation and Weissenberg photographs revealed the crystals to be orthorhombic for (I) and triclinic for (II). Systematically absent reflexions uniquely indicated the space group  $P2_12_1$  for (I). Additional crystal data are given in Table 1. The accurate cell dimensions, as well as the intensities, were obtained from diffractometer measurements using a  $\theta/2\theta$  scan. An automatic diffractometer (Siemens AED) and nickel-filtered  $\text{Cu } K\alpha$  radiation were used with a  $\theta$  range between 3 and  $70^\circ$ . The data for both compounds were corrected for absorption. The atom form factors for N, S, C and  $\text{I}^-$  were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). All computations were performed on a CDC Cyber 1175 computer with XRAY 76 (Stewart, 1976).

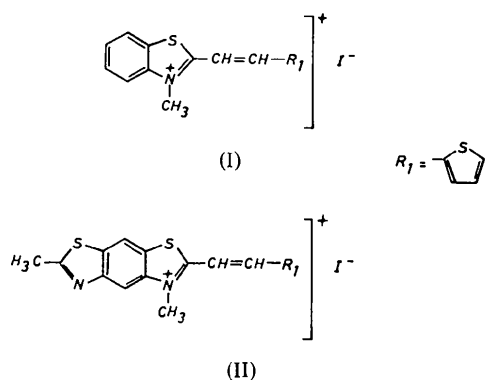


Table 1. Additional crystal data

	(I)	(II)
$M_r$	385.30	456.40 (+46.07)
$V$	1470.01 $\text{\AA}^3$	946.69 $\text{\AA}^3$
$Z$	4	2
$F(000)$	752	448 (+52)
$D_m$	1.70 $\text{Mg m}^{-3}$	1.61 $\text{Mg m}^{-3}$
$D_x$	1.7474	1.6381
$\mu(\text{Cu } K\alpha)$	19.85 $\text{mm}^{-1}$	16.449 $\text{mm}^{-1}$
Crystal size	0.06 $\times$ 0.17 $\times$ 0.20 mm	0.04 $\times$ 0.05 $\times$ 0.21 mm

### Structure determination

Both structures were solved by the heavy-atom method using a three-dimensional Patterson function. For (I) this led to the correct structural model without any complications. The anomalous-dispersion correction for  $\text{I}^-$  and S (*International Tables for X-ray Crystallography*, 1968) was introduced and eight low-order reflexions were excluded from refinement because of probable extinction effects. The extinction parameter was allowed to vary.

Five H atoms were located and calculated positions were used for the remaining H atoms. A final  $R$  value of 5.3% and an extinction parameter (Larson, 1967) of  $1.2(1) \times 10^{-4}$  were obtained. A final electron density map showed a few residual maxima of about  $0.5 \text{ e \AA}^{-3}$ , most of which belonged to the heavy atom  $\text{I}^-$ . Fig. 1 shows a line diagram with the numbering, and bond lengths and angles including e.s.d.'s. Table 2 contains the final nonhydrogen-atom positional parameters. Fig. 2 shows an ORTEP plot (Johnson, 1976) of the cell contents.

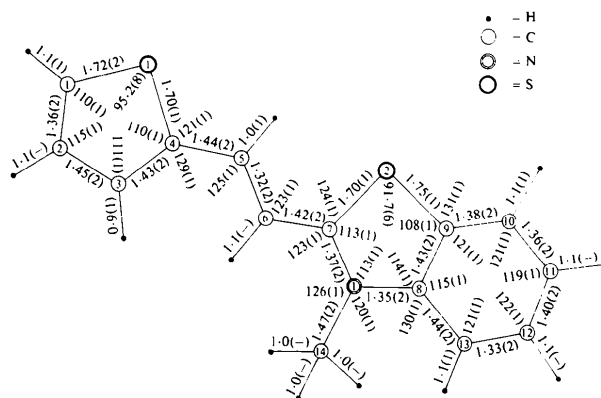


Fig. 1. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) of (I) (with e.s.d.'s).

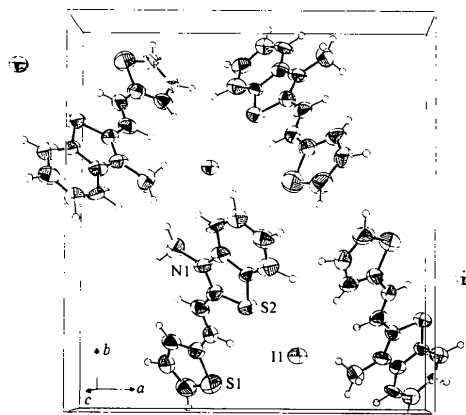


Fig. 2. ORTEP projection of the cell for (I) on the  $ab$  plane. Thermal ellipsoids for non-H atoms are at 50% probability.

Table 2. Fractional coordinates and isotropic thermal parameters for (I) with e.s.d.'s in parentheses

The temperature factors  $U_{eq}$  are calculated after Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} (\times 10^2)$ or $U (\times 10^3)$
I <sup>-</sup>	0.6297 (1)	0.1407 (1)	1.5226 (2)	7.2 (6)
N(1)	0.3754 (7)	0.3643 (5)	1.036 (2)	6.2 (5)
S(1)	0.3849 (3)	0.0664 (2)	0.325 (1)	10.0 (3)
S(2)	0.4944 (2)	0.2616 (2)	1.0572 (8)	7.1 (2)
C(1)	0.310 (1)	0.0563 (9)	0.101 (3)	9 (1)
C(2)	0.2534 (9)	0.1172 (9)	0.113 (3)	8 (1)
C(3)	0.272 (1)	0.1751 (8)	0.300 (3)	7.5 (9)
C(4)	0.3462 (9)	0.1533 (7)	0.433 (3)	7.6 (9)
C(5)	0.3879 (8)	0.1937 (7)	0.629 (3)	6.7 (8)
C(6)	0.361 (1)	0.2598 (7)	0.731 (3)	6.6 (9)
C(7)	0.4043 (8)	0.2971 (7)	0.926 (3)	6.1 (8)
C(8)	0.4248 (8)	0.3887 (7)	1.223 (8)	5.3 (7)
C(9)	0.4961 (8)	0.3389 (6)	1.269 (3)	5.4 (7)
C(10)	0.5523 (9)	0.3552 (8)	1.454 (3)	7.2 (8)
C(11)	0.541 (1)	0.4186 (8)	1.603 (3)	7.1 (8)
C(12)	0.4717 (9)	0.4687 (8)	1.561 (3)	7 (1)
C(13)	0.415 (1)	0.4546 (6)	1.385 (3)	7.0 (9)
C(14)	0.2982 (8)	0.4081 (8)	0.973 (4)	8.0 (9)

For (II) the *E*-value statistics did not distinguish between *P*1 or *P*1̄. Some vectors which could be interpreted as I<sup>-</sup>-S from their peak height were found in a centrosymmetric arrangement with respect to the I<sup>-</sup>-I<sup>-</sup> vector. So we first started with *P*1 and the position of I<sup>-</sup>, which led to *R* = 40%. A  $\Delta F$  map revealed the positions of two S atoms clearly but not the third. In addition, 12 C atoms could be located, two of which later turned out to be N atoms. Further refinement with isotropic and then anisotropic temperature parameters for I<sup>-</sup> led to *R* = 22%. A  $\Delta F$  map showed all the remaining non-hydrogen atoms. Block-matrix least-squares refinements including all atoms with anisotropic temperature parameters gave *R* = 9.8% after three cycles.

Some fairly diffuse electron density maxima between 2.0 and 1.0 e Å<sup>-3</sup>, not related to the molecule, could be interpreted as ethanol, which had been used as the solvent. Taking the 'best' three maxima into account, with isotropic temperature parameters, the *R* value dropped to 8%. In an extra run, the population parameter converged to 0.5. Additionally remaining maxima in the neighbourhood showed that only in every second cell was a solvent molecule included with some uncertainty in position. During that procedure, electron density maxima were also found close to S(1) and C(3). This, together with a 'poor' geometry for the S(1)-C(4) thiophene ring and large, divergent anisotropic temperature parameters for C(1) and C(2), led us to assume a disordered terminal thiophene ring. We introduced a second ring at this position but rotated 180° around the axis through C(5) and C(4) (IIb). This was included in the refinement with a positional-constraint condition (identical molecule programming)

in *CRYLSQ* (XRAY76) and a population parameter of 0.7 (0.3 respectively) for each atom belonging to the different groups in accordance with the relative heights of the maxima. This gave an improvement with respect to the ring geometry and accounted for the remaining electron density sufficiently. The population parameters, refined separately, converged to 0.78 and 0.22, respectively, with an *R* value of 7.9%.

Six H atoms could be found and were refined isotropically. For the remaining H atoms the theoretical positions were used and kept invariant. The final *R* value was 6.2%.

The last electron density map showed a few, fairly diffuse, maxima between 0.6 and 0.9 e Å<sup>-3</sup>. Two belonged to the heavy atom I<sup>-</sup>, and the rest to the poorly defined solvent molecule.

An attempt was made to describe the structure in *P*1 instead of *P*1̄ to avoid the disorder problems and as the *E* statistics did not favour either space group. This, however, resulted in a deterioration of the molecular geometry. Fig. 3 shows a line diagram with the atomic numbering and the bond lengths and angles including e.s.d.'s. Table 3 contains the final positional parameters. Fig. 4 shows the positions of the molecules in

Table 3. Fractional coordinates and isotropic thermal parameters for (II) with e.s.d.'s in parentheses

The temperature factors  $U_{eq}$  are calculated after Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq} (\times 10^2)$ or $U (\times 10^3)$
I <sup>-</sup>	0.29860 (6)	0.29783 (8)	0.0238 (1)	8.6 (5)
S(2)	-0.0640 (2)	0.9627 (2)	0.0237 (3)	6.2 (1)
S(3)	0.2047 (2)	0.6285 (2)	0.2586 (4)	7.1 (1)
N(1)	0.1599 (6)	1.0801 (5)	0.364 (1)	5.6 (4)
N(2)	0.3991 (6)	0.7874 (5)	0.408 (1)	6.0 (4)
C(5)	-0.1270 (8)	1.1938 (7)	0.233 (1)	6.5 (5)
C(6)	0.0003 (8)	1.1866 (7)	0.290 (1)	6.6 (5)
C(7)	0.0368 (8)	1.0870 (7)	0.292 (1)	6.1 (5)
C(8)	0.1755 (7)	0.9741 (6)	0.345 (1)	5.5 (4)
C(9)	0.0627 (7)	0.8975 (7)	0.260 (1)	6.0 (5)
C(10)	0.0590 (7)	0.7889 (6)	0.226 (1)	5.9 (5)
C(11)	0.1759 (9)	0.7576 (6)	0.283 (1)	5.7 (4)
C(12)	0.2890 (7)	0.8318 (7)	0.367 (1)	6.1 (5)
C(13)	0.2934 (7)	0.9433 (6)	0.403 (1)	5.8 (5)
C(14)	0.3686 (8)	0.6845 (8)	0.360 (1)	7.2 (5)
C(15)	0.4640 (9)	0.6124 (7)	0.377 (2)	8.8 (7)
C(16)	0.2666 (8)	1.1719 (7)	0.460 (1)	7.4 (5)
S(1)	-0.0699 (4)	1.4102 (4)	0.2690 (9)	7.8 (1)
C(1)	-0.189 (2)	1.483 (1)	0.235 (3)	9.7 (6)
C(2)	-0.298 (1)	1.420 (2)	0.196 (4)	11.2 (7)
C(3)	-0.308 (1)	1.307 (1)	0.182 (2)	7.6 (3)
C(4)	-0.167 (1)	1.292 (1)	0.221 (3)	5.6 (4)
S(101)	-0.33 (-)	1.283 (-)	0.157 (-)	8.7 (3)
C(101)	-0.323 (-)	1.413 (-)	0.191 (-)	5.2 (8)
C(102)	-0.201 (-)	1.466 (-)	0.274 (-)	7 (1)
C(103)	-0.106 (-)	1.404 (-)	0.323 (-)	4.8 (7)
C(104)	-0.180 (-)	1.287 (-)	0.257 (-)	7 (2)
O(50)	0.432 (2)	0.077 (1)	-0.013 (2)	9.1 (4)
C(51)	0.505 (2)	-0.005 (2)	0.084 (3)	9.9 (7)
C(53)	0.624 (4)	-0.025 (3)	0.009 (6)	15 (1)

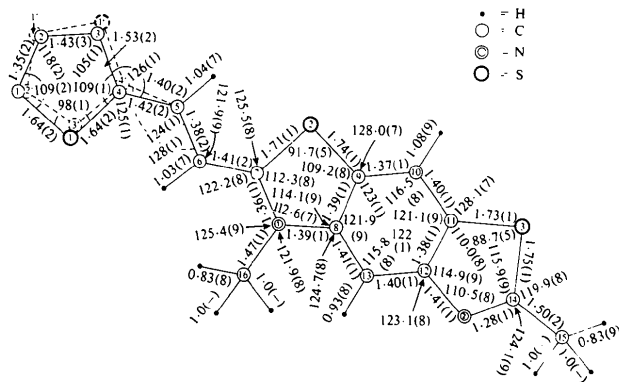


Fig. 3. Bond lengths (Å) and angles (°) of (II) (with e.s.d.'s).

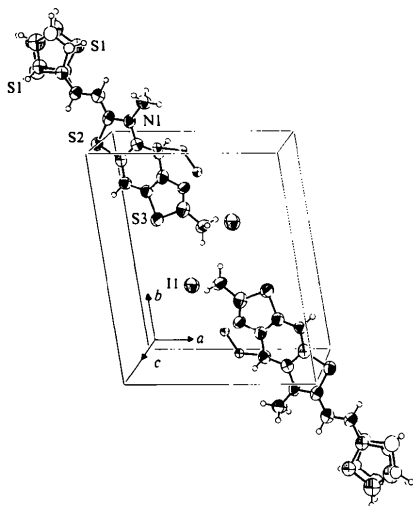


Fig. 4. ORTEP projection of cell contents for (II) on the *ab* plane. Thermal ellipsoids for non-H atoms are at 50% probability except those for the solvent molecule.

the cell including the  $I^-$  and the solvent molecules with arbitrarily small thermal ellipsoids for clarity.\*

### Energy calculation

To confirm the two positions of the terminal thiophene ring for (II) we calculated the energy of the molecule by varying the torsion angle  $C(6)-C(5)-C(4)-C(3)$  with respect to the packing arrangement. We used a slightly modified version (Labischinski, 1976) of the 'program for molecular packing analysis based on the minimization of the crystal lattice energy' (Williams, 1972). The intention was to determine at which torsion angle

\* Lists of structure factors, thermal parameters and H-atom parameters for both structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36026 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Molecular planarity, angles between planes, and electrical conductivity

	Structure (I)	Structure (II)
Planarity of benzothiazolium group (1) (Å)	within 0.012 (8)	within 0.042 (26)
Planarity of terminal thiophene ring (2) (Å)	within 0.012 (11)	within 0.024 (19)
Angle between (1) and (2) (°)	2.9 (1)	12.3 (2) 183.9 (2)
Angle between (1) and (2) from energy calculation (°)	3.46	10.98 181.35
Energy difference ( $\text{kJ mol}^{-1}$ )	-	19.4
Electrical conductivity ( $\Omega^{-1} \text{m}^{-1}$ )*	$7.8 \times 10^{-15}$	$8.1 \times 10^{-12}$

\* Bocionek (1978).

the molecular energy reaches its minimum, *i.e.* to calculate the energy for the given packing arrangement by rotating the terminal thiophene ring around the axis through  $C(4)-C(5)$ . This was done first for structure (I) using the van der Waals radii published by Bondi (1964) and for  $I^-$  a value of 2.75 Å, since the  $I$  atoms determine the packing arrangement. A formal charge of +1 was assumed to be located at N(1) for both structures.

For structure (I) only one significant energy minimum was obtained at a torsion angle of 3.46°. As this value agrees very well with the result of the X-ray analysis (see Table 4), we assumed that the van der Waals radii used were satisfactory. For (II) we obtained two fairly flat energy minima of different depths. With respect to the relatively rough approximation of the terminal thiophene ring, the angles of 10.98 and 181.35° compared to 12.3 and 183.9°, respectively, are in very good agreement. The energy increase of 19.4  $\text{kJ mol}^{-1}$  for the second conformation (open spheres in Fig. 4) seems to favour the first position (12.3°) which agrees with a population parameter of 78%.

### Results and discussion

The bond distances and angles in the two title compounds are in good agreement with each other as far as they are comparable. The  $S(2)-C(7)$  bond and the corresponding bond in (II) show the typical double-bond length at 1.70 and 1.71 Å, respectively, while  $S(2)-C(9)$  in both structures and  $S(3)-C(11)$  and  $S(3)-C(14)$  in (II) show typical single-bond character. Because of the disorder the geometry of the terminal thiophene ring for (II) is rather deformed compared to (I).

The maximum distances and standard deviations from a least-squares plane are given in Table 4, together with the angles between these planes. Some remarkably short distances between  $I^-$  and the molecules are listed in Table 5. Intermolecular distances in the range of the usual van der Waals values could not

Table 5. *Intermolecular contact distances (Å) for (I) and (II)*

(I)		(II)	
I <sup>-</sup> -I <sup>-</sup>	5.496 (2)*		
I <sup>-</sup> -S(2)	3.911 (4)	I <sup>-</sup> -S(2)	3.734 (2)
I <sup>-</sup> -S(1)	4.202 (5)	I <sup>-</sup> -S(101)	3.970 (-)
I <sup>-</sup> -H(3)	3.04 (13)	I <sup>-</sup> -H(10)	2.92 (8)
I <sup>-</sup> -H(5)	3.11 (8)	I <sup>-</sup> -N(1)	4.366 (8)
S(1)-S(2)	4.01 (1)	S(1)-S(3)	3.76 (3)
		S(2)-S(2)	3.70 (4)†

\* Symmetry operator  $x, y, 1 + z$ .† Symmetry operator  $-x, 2 - y, -z$ .

be found for (I); the shortest, for S(1)··S(2), is 4.01 Å. For (II), intermolecular contact distances of 3.70 and 3.76 Å (see Table 4) are about twice the van der Waals radii given by Pauling (1969), e.g. 3.70 Å for sulphur in crystalline sulphides.

Molecule-orbital overlap can thus be postulated to a certain degree, the  $\pi$  electrons not being used for the binding of the S atoms. This means that electron transfer is much more possible than with compound (I). Thus the thiophene ring as  $\pi$ -electron donor and also a stronger intermolecular interaction are both responsible for a higher electrical conductivity (Table 4). This effect has been found with several compounds containing thiophene ring systems (Zobel, 1977; Zobel & Ruban, 1978) and supported by electrical measurements on single crystals. There it could be shown that the conductivity in the direction of the shortest intermolecular S-S distance is significantly higher than

in other directions. For the title compounds such measurements on single crystals were not possible because only very small samples were available.

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## Structure of *tert*-Butyl 2-(*tert*-Butylthio)-2-(9-thioxanthenyldene)dithioacetate

BY H. J. BRUINS SLOT AND J. KROON\*

*Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands*

AND A. C. BROUWER AND H. J. T. BOS

*Organisch Chemisch Laboratorium, Rijksuniversiteit, Croesestraat 79, Utrecht, The Netherlands*

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#### Abstract

$C_{23}H_{26}S_4$ ,  $M_r = 430.72$ , is obtained by irradiating a solution of thioxanthenthione and bis(*tert*-butylthio)ethyne. The crystals are monoclinic, space group

$P2_1/n$ , with  $a = 10.899$  (3),  $b = 17.052$  (6),  $c = 12.304$  (6) Å,  $\beta = 98.40$  (4)°,  $V = 2262$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 912$ ,  $D_x = 1.265$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.411$  mm<sup>-1</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å.  $R = 0.038$  for 2695 reflexions. The ratio thiete/unsaturated dithioester found in solution for xanthenyl and thioxanthenyl derivatives is apparently governed by ring strain *versus*

\* Author to whom correspondence should be addressed.