

COMPLEX STRUCTURE Tri- AND POLYIODIDES OF IODOCYCLIZATION PRODUCTS OF 2-ALLYLTHIOQUINOLINE

E. V. Bartashevich,¹ I. D. Yushina,¹ E. A. Vershinina,¹
P. A. Slepukhin,² and D. G. Kim¹

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Iodocyclization products of 2-allylthioquinoline are obtained in the form of polyiodides with different stoichiometric compositions. X-ray crystallography data are analyzed for two different crystal structures of 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium polyiodides: triiodide $C_{12}H_{11}INS^+I_3^-$ and complex polyiodide $2(C_{12}H_{11}INS^+I_3^-) \cdot I_2$. A comparison is made of the nonbonding interactions of dihydrothiazoloquinolinium with atoms of the triiodide anion and complex polyiodide to show the crystal structure features attributed to the participation of molecular iodine.

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INTRODUCTION

The fundamental interest in iodine-containing organic compounds, in particular polyiodides [1, 2], is explained, on the one hand, by the features of their electronic structure and the diversity of their structural organization in crystals. Polyiodides with three or more iodine atoms in their composition are known to form chain, layered, and other motifs with various patterns of packing and mutual orientation of iodine fragments in the crystals.

On the other hand, iodine-containing heterocyclic compounds are of great practical value and may have biological activity. For example, the complexes of quinoline derivatives with radioactive iodine (^{123}I , ^{125}I , and ^{131}I isotopes) can be used to diagnose various kinds of melanoma tumors and neutral iododerivatives of quinoline can be effective in diagnosing Alzheimer's disease lesions [3, 4]. The biological activity of iodine-containing heterocyclic compounds is largely determined by their capability of nonbonding interactions [5].

It is known that halogens that are part of molecules can be involved in a whole variety of interactions [6]. First, it can be halogen bonds [7], i.e., nonbonding electrostatic interactions whereby the halogen atom functions as an electron density acceptor. Compared with other halogens, iodine is the most polarizable and, hence, potentially most capable of forming relatively strong halogen bonds, with iodine functioning as an electron density acceptor. This type of interaction is attributed to the existence of a pole with an electron-deficient area (called a σ -hole) formed on the extension of the iodine atom covalent bond [8]. In another case the electron-donor properties of iodine crystals can be manifest in crystals in dispersive interactions due to the negative values of the electrostatic potential encircling the equatorial region of the bound

¹South Ural State University, Chelyabinsk, Russia; kbartash@yandex.ru. ²I. Ya. Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 55, No. 1, pp. 117-124, January-February, 2014. Original article submitted December 27, 2012.

atom. It is of interest to study the diversity of interactions involving iodine for the engineering of crystals with desired properties [9].

Currently, a lot of attention is paid to theoretical studies on the electronic structure of polyiodide anions, which are characterized by great structural diversity [10, 11]. However, only a few works draw an analytical comparison between the interactions in the structures of crystals formed by an invariable organic cation and polyiodide anions with different stoichiometric compositions [12-14].

The focus of this study is on polyiodides with different stoichiometric compositions obtained by the iodocyclization reaction [15]. These are two salts: the previously synthesized [16] 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium triiodide ($C_{12}H_{11}INS^+I_3^-$) and a new complex polyiodide $2(C_{12}H_{11}INS^+I_3^-) \cdot I_2$. To find out how the number of iodine atoms in the complex anion affects the properties of nonbonding interactions in crystals, we consider shortened contacts in polyiodides with different stoichiometric compositions from the Cambridge Structural Database (CSD) v.5.33.

EXPERIMENTAL

Synthesis technique: iodination of 2-allylthioquinoline. A 1:2 solution of 0.051 g (0.20 mmol) iodine in 5 ml glacial CH_3COOH was added to a solution of 0.020 g (0.10 mmol) 2-allylthioquinoline in 3 ml glacial CH_3COOH . The precipitate formed during 24 h was filtered and dissolved in acetone; then diethyl ether was added to the mixture until it became turbid and 1-iodomethyl-1,2-dihydrothiazolo[3,2-*a*]quinolinium triiodide (**1**) crystals began to form. After a while, needle-like crystals of complex 1-iodomethyl-1,2-dihydrothiazolo[3,2-*a*]quinolinium polyiodide (**2**) were observed to form in the filtrate. The corresponding triiodide was obtained by the reaction of 2-allylthioquinoline with iodine in ether. The triiodide was treated with a NaI solution to obtain monoiodide, which was confirmed by elemental analysis. The use of glacial acetic acid made it possible to obtain crystalline products.

X-ray crystallography technique. A single-crystal XRD analysis of **1** and **2** was made using an Xcalibur 3 automatic four-circle X-ray diffractometer by the standard procedure (MoK_α radiation, graphite monochromator, 295(2) K, and $\omega/2\theta$ -scanning). A crystal fragment with dimensions 0.099×0.066×0.025 mm was used to analyze compound **1**, and a crystal fragment of 0.111×0.059×0.013 mm was used to analyze **2**. The absorption correction was made analytically [17] using a multifaceted crystal model. The structure was solved and refined in SHELX97 [18]. All nonhydrogen atoms were refined in an anisotropic approximation; hydrogen atoms were placed in geometrically calculated positions and included into the refinement using a rider model with dependent isotropic thermal parameters. The main crystallographic data and refinement parameters are given in Table 1; selected bond lengths and valence angles are shown in Table 2. The results of the single-crystal XRD analysis (CIF-files) have been deposited with the Cambridge Crystallographic Data Centre under Nos. CCDC 815955 and 815956. These data are in public domain and can be obtained upon request at www.ccdc.cam.ac.uk/data_request/cif.

Compounds **1** and **2** crystallize in a centrosymmetric triclinic space group. The crystal structures of iodides **1** and **2** differ in composition and features of iodine motif packing and organization (Figs. 1 and 2).

RESULTS AND DISCUSSION

There is a number of reviews [1, 2] focused on the attempts to systematize the great structural diversity of polyiodide anions. A common point of these reviews is the observation that, in triiodide crystals, triiodide anions can occur in a relatively isolated (from one another) state more often than other polyiodides. However, triiodide anions are quite often packed in patterns whereby the "stacked" anions fill channels or form layers of *T*-shaped structures. Triiodide anions are, as a rule, linear and can be classified into two types: asymmetric $[I-I \dots I]^-$ and symmetric $[I \dots I \dots I]^-$. According to the diagrams in [1], the former can be characterized by the limit values of the bond lengths: $d_{\min} = 2.7 \text{ \AA}$ and $d_{\max} = 3.2 \text{ \AA}$. The average internuclear $I \dots I$ distance is observed in the neighborhood of the value 2.92 Å [1].

TABLE 1. Main Crystallographic Data and Structure Refinement Parameters

Compound	1	2
Formula	C ₁₂ H ₁₁ I ₄ NS	C ₁₂ H ₁₁ I ₅ NS
Molecular weight	708,88	835,78
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	7.3740(7), 8.5051(8), 14.833(2)	7,8769(9), 9,4099(14), 14,0669(13)
α , β , γ , deg	76.454(10), 75.725(10), 89.155(8)	76.342(11), 80.532(9), 81.626(11)
<i>V</i> , Å ³	875.57(17)	993.1(2)
<i>Z</i>	2	2
<i>d</i> _x , g/cm ³	2.689	2.795
μ , mm ⁻¹	7.222	7.924
θ scan region, deg	2.85 < θ < 28.28	2.85 < θ < 30.51
Measured/independent reflections (<i>R</i> _{int})	5432/4320 (0.0160)	6788/5700 (0.0260)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2684	2983
Completeness (for θ), %	99.6 (26.00°)	96.3 (26.00°)
Number of refined parameters	163	172
<i>S</i>	1.011	1.000
<i>R</i> ₁ / <i>wR</i> ₂ (for <i>I</i> > 2 σ (<i>I</i>))	0.0275/0.0563	0.0344/0.0605
<i>R</i> ₁ / <i>wR</i> ₂ (for all reflections)	0.0529/0.0586	0.0887/0.0655
$\Delta\rho_{\text{e}}$, e/Å ⁻³	0.598/−0.967	1.545/−1.416

TABLE 2. Comparative Table of Selected Bond Lengths and Bond Angles

1		2	
I(1)–I(2)	2.9024(6)	I(3)–I(2)	2.8630(7)
I(1)–I(3)	2.9329(6)	I(3)–I(4)	2.9377(7)
—	—	I(5)–I(5) ^{#1}	2.7646(9)
C(11)–S(1)	1.796(5)	S(1)–C(10)	1.817(6)
C(2)–S(1)	1.725(4)	S(1)–C(1)	1.720(6)
N(1)–C(12)	1.492(4)	N(1)–C(11)	1.498(6)
I(4)–C(1)	2.140(4)	I(1)–C(12)	2.147(5)
I(2)–I(1)–I(3)	178.246(14)	I(2)–I(3)–I(4)	177.672(18)
C(12)–C(1)–I(4)	113.4(3)	C(11)–C(12)–I(1)	110.3(4)
C(2)–S(1)–C(11)	90.5(2)	C(1)–S(1)–C(10)	90.8(2)

Symmetry transformation: ^{#1} [−*x*+2, −*y*+1, −*z*+1].

According to its characteristics, the structure of triiodide **1**, which is discussed in this article, belongs to the second group because the lengths of the I...I bonds in the anion are close to each other (2.902 Å and 2.933 Å) and the angle is only slightly deviated from the straight angle by 1.76°.

Complex structure polyiodide anions in which triiodide anions are observed to be stacked directly with one or more iodine molecules [I₃[−]...I₂] are quite common. If we use the systematization proposed by Kloo [1], then these polyiodide anions can be described as two series with two common formulas: I_{2*n*+1}^{1−} and I_{2*n*+2}^{2−}. The representatives of the first series are, e.g., penta-, hepta-, and enneaiodides. Pentaiodide anions, in their turn, are also classified into several structural types differing in the ratio of I...I bond lengths. However, there are no pentaiodide anions in which all the four bonds are close

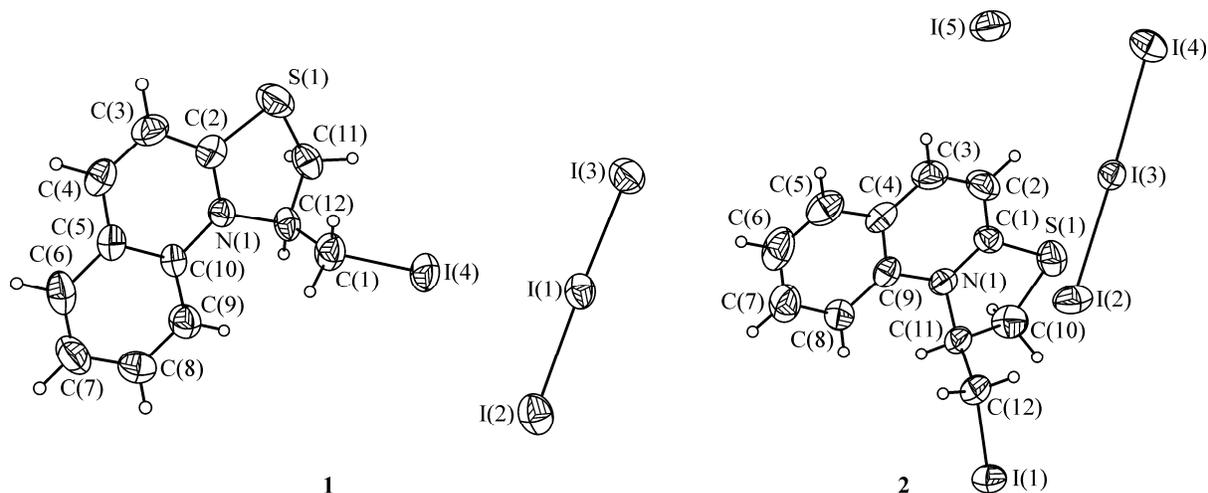


Fig. 1. Compounds **1** and **2** in 50% probability thermal ellipsoids.

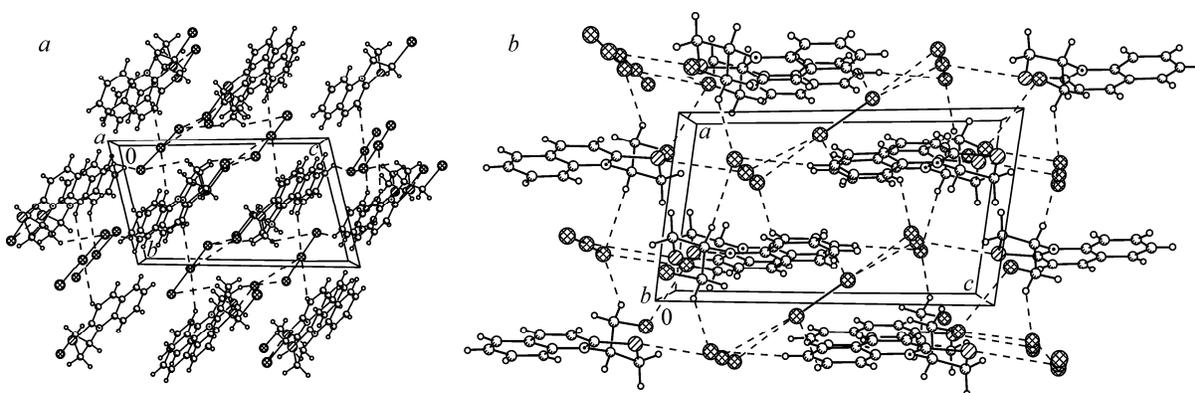


Fig. 2. Molecular packing fragment for compounds **1** (a) and **2** (b).

in length. The representatives of the other series of complex structure polyiodide anions often form continual crystal motifs $[I_3^- \dots I-I \dots I_3^- \dots]$, but can occur as isolated tetra-, hexa-, octa-, etc., iodides. It is the orientation of the σ -hole in the iodine molecule to the area of electron density localization in the equatorial zone of the terminal atoms of triiodide anion that leads to the formation of stable zigzag structures with $I \dots I$ halogen bonds. To visualize the structure of these anions, researchers often use letter designations: Z (zigzag), V-, and L-shaped structures.

The iodine motif in the crystal of **2** can be seen to contain centrosymmetric zigzags $\{[I(2)-I(3)-I(4)]^- \dots I(5)-I \dots [I-I-I]^-\}$ (Fig. 1), which can be regarded as a complex of two triiodide anions with molecular iodine. The atoms of each zigzag belong to the same plane; the zigzags are symmetric with respect to the bond center in the iodine molecule. The distance $I(4) \dots I(5)$ is much larger (3.444 \AA) than the one typical of isolated pentaiodide anions (3.147 \AA) [1]; however, it is much shorter than the observed contacts between the stacked triiodide anions. The zigzag angle $I(3)-I(4)-I(5)$ is 80.44° . Thus, the iodine molecule participates in halogen bonding whereby the terminal atom of the triiodide anion is the electron density donor. There are shortened contacts between the terminal atoms of the triiodide anions belonging to the neighboring zigzags. Thus, there is one more iodine motif in the crystal that can be described as a continual stacking of triiodide anions with shortened $I \dots I$ contacts of 3.864 \AA between the terminal atoms of triiodide anions. In the case of the structure of **2**, there is a more significant difference between the $I(2)-I(3)$ and $I(3)-I(4)$ bond lengths in the triiodide anion. The difference in the bond lengths is 0.075 \AA (compare with 0.031 \AA in the structure of **1**).

In organic crystals of the series of I_{2n+2}^{2-} polyiodides, either one or two particles can act as a cation. A relatively common example of the first case is alkyl diammonium salts described in [14, 19]. The cations in the studied crystals of **1** and **2** are enantiomers of 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium.

To gain an understanding of which crystal interactions are typical of polyiodides containing an invariable organic cation and anions of different stoichiometry, we analyzed samples of C,H,N,S,I-containing structures from the CSD v.5.33 crystallographic database [20, 21]. The sampling conditions ruled out the presence of other molecules except for the organic cation and tri- or polyiodide anion in the crystals. Neither organometallic compounds nor neutral complexes with molecular iodine were included in the study. Thus, we achieved the search conditions providing to the greatest resemblance of the selected compounds to **1** and **2**.

We assumed that heterocyclic cations containing only C, H, N, or S atoms might be the most similar to compounds **1** and **2** in their ability to form different packing patterns with different polyiodide anions. However, the crystallographic database was found to contain data only on three such organic cations, each of which can form both triiodide and polyiodide with a large number of iodine atoms in their composition. Among organic cations containing C, H, or S atoms only, these polyiodides were found only for tetrathiofulvalene derivatives. The largest number — 14 polyvariant packing patterns with tri- and polyiodides of different stoichiometry—were found only for C,H,N-containing cations. These are mainly alkyl- and arylammonium and alkyl-substituted urotropinium salts. The data on the compounds used for comparison, their gross formulas, and references to the original literature sources are given in Table 3.

It follows from the analysis of the Table 3 data that compared with the other polyiodides, alkyl- and arylammonium polyiodides more often occur as either triiodides or pentaoidides. In contrast, C,H,N,S-containing cations are more often observed to occur both as triiodides and complex ion salts containing molecular iodine, e.g., in the form of octa- or heptaoidide.

No shortened contacts are observed between the cation atoms in 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium triiodide **1**; neither there is any interaction between the neighboring triiodide anions (the minimum I...I distance is 4.900 Å). Comparatively large I...I–C internuclear distances (4.045 Å and 4.182 Å) are also observed between the atom of the covalent bonded iodine in the heterocyclic cation and those of triiodide anion. Thus, the interactions between the triiodide anion and the cation of dihydrothiazoloquinolinium occur mainly due to the I...H contacts. Only one of these I...H–C_{Ar} contacts has a length less than the sum of the van der Waals radii 3.175 Å. This is the contact between the central iodine atom in the triiodide anion and the hydrogen atom of the quinoline ring.

In contrast to the above discussed packing of triiodide **1**, the structure of compound **2** is observed to have I...H contacts with the hydrogen atom of the quinoline ring (3.055 Å) and with the hydrogen atoms of the dihydrothiazole ring (3.073 Å and 3.174 Å). All the three contacts are formed by one of the terminal iodine atoms in the triiodide anion. The same iodine atom participates in the interactions with the covalent bonded iodine in the cation (3.886 Å) and with the terminal atom of the neighboring triiodide ion (3.864 Å). As a result, the crystal is observed to have the so-called Hal₃-interactions [46], whereby three halogen atoms form a virtually isosceles triangle. Moreover, the central atom of the triiodide anion in compound **2** has shortened I(3)...S contacts. Such interactions as the single shortened contact I(1)...H in the structure of **1** occur due to the electron excessive area in the equatorial zone of the central atom of the triiodide anion. These iodine interactions are not classified as halogen bonds [7] because the σ -hole of iodine is not oriented to the area of electron pair localization or decreased values of electron donor fragments' electrostatic potential. Among the discussed compounds in Table 3, which contain Z, i.e., the zigzag-shaped complex anion $[I_3^- \dots I \dots I_3^- \dots]$, it is the central atom of the triiodide anion that often has shortened I...S and I...H contacts with the organic cation.

CONCLUSIONS

A comparison is made of new crystal structures in which the 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium cation exhibits the ability to form salts both with triiodide anion and complex structure polyiodide anion.

TABLE 3. Structures Forming Packings with Different Polyiodides

No.	Index	Formula	Ref.	No.	Index	Formula	Ref.
1	AZADPI01*	$2(C_7H_{15}N_4^+, I_8^{2-})$	[22]	11	ZIVXEH	$C_{14}H_{16}N^+, I_3^-$	[33]
	BIWLEY01	$C_7H_{15}N_4^+, I_3^-$	[23]		ZIVXIL	$3(C_{14}H_{16}N^+), 2(I_5^-), I, I_2$	[33]
2	DOVJOO	$2(C_{14}H_{18}N_{22}^+), 2(I_5^-), 2(I_3^-)$	[24]		ZIVXOR	$2(C_{14}H_{16}N^+), 2(I_5^-), I_2$	[33]
	DOVJUJ	$C_{14}H_{18}N_{22}^+, 2(I_3^-)$	[24]		ZIVXUX	$2(C_{14}H_{16}N^+), 2(I_7^-), I_2$	[33]
3	DULZIT01	$C_4H_{12}N^+, I_3^-$	[25]	12	LOQMEK	$C_{38}H_{82}N_{22}^+, 2(I_3^-)$	[34]
	DULZIT03	$C_4H_{12}N^+, I_3^-$	[26]		LOQMIO	$C_{38}H_{82}N_{22}^+, 2(I_5^-)$	[34]
	DULZOZ01	$C_4H_{12}N^+, I_5^-$	[27]	13	NUTSOL	$C_{12}H_{30}N_{22}^+, 2(I^-), I_2$	[14]
4	FIQKUL	$(C_{15}H_{18}N^+)2n, n(I_3^-), n(I_3^-)$	[28]		NURSUR	$C_{12}H_{30}N_{22}^+, 2(I_5^-)$	[14]
	FIQLAS	$C_{15}H_{18}N^+, I_5^-$	[28]		NUTTAY	$C_{12}H_{30}N_{22}^+, 2(I_3^-)$	[14]
5	HILLET	$2(C_8H_{17}N_4^+), I_3^-, I_5^-$	[22]	14	RECKAL	$C_{12}H_{26}N_3^+, I_3^-$	[13]
	ZOYBEU	$C_8H_{17}N_4^+, I_3^-$	[29]		RECKEP	$C_{12}H_{26}N_3^+, I_5^-$	[13]
6	NAGNOY	$C_{12}H_{28}N^+, I_3^-$	[12]	15	CILHIO06	$C_{10}H_8S_8^+, C_{10}H_8S_8, I_3^-$	[35]
	NAGPAM	$C_{12}H_{28}N^+, I_3^-, 2(I_2)$	[12]		CILHIO35	$C_{10}H_8S_8^+, C_{10}H_8S_8, I_3^-$	[36]
7	NALGOW	$C_9H_{19}N_4^+, I_5^-$	[30]		DATREV01	$C_{10}H_8S_8^+, I_3^-, C_{10}H_8S_8$	[37]
	NALGUC	$C_9H_{19}N_4^+, I_7^-$	[30]		DATREV02	$C_{10}H_8S_8^+, I_3^-$	[38]
	ZOYBIY	$C_9H_{19}N_4^+, I_3^-$	[29]		DATRIZ01	$2(C_{10}H_8S_8^+), 2(I_3^-), 0.5(I_2)$	[39]
8	PAZPIP	$C_{11}H_{18}N^+, I_3^-$	[31]		DATRIZ02	$2(C_{10}H_8S_8^+), I_3^-, 0.5(I_8^{2-})$	[40]
	PAZPOV	$C_{11}H_{18}N^+, I_3^-, I_2$	[31]		FENTEX	$2(C_{10}H_8S_8^+), 2(I_3^-), 2(I_2)$	[41]
	PAZPUB	$C_{11}H_{18}N^+, I_3^-, 2(I_2)$	[31]	16	XIVBEJ	$2(C_8H_{11}N_4S_2^+), I_5^-, I_3^-$	[42]
	PAZQAI	$2(C_{11}H_{18}N^+), 2(I_5^-), 3(I_2)$	[31]		XIVBAF	$C_8H_{12}N_4S_{22}^+, 2(I_3^-), I_2$	[42]
	PAZQEM	$C_{11}H_{18}N^+, I_5^-, 2(I_2)$	[31]	17	DUJGEU	$C_{26}H_{30}N_4S_{22}^+, 2(I_3^-)$	[43]
10	YIPYEB	$C_{10}H_9N_2^+, I_3^-$	[32]		DUJGIY	$C_{26}H_{30}N_4S_{22}^+, 2(I^-), 5(I_2)$	[23]
	YIPYOL	$(C_{10}H_9N_2^+)n, n(I_7^-)$	[32]	18	IGEDUT	$C_{11}H_{11}N_2S_2^+, I_3^-$	[44]
					NAKMET	$C_{11}H_{11}N_2S_2^+, I_3^-, 0.5(I_2)$	[45]

*When a structure is included in the CSD as similar records with different indices, priority is given to the structure with the lowest *R* factor.

The presence of molecular iodine in the structure of the complex $2(C_{12}H_{11}INS^+I_3^-) \cdot I_2$ anion increases the number of shortened contacts between the triiodide anion and dihydrothiazoloquinolinium atoms. Having participated in the formation of the Z-shaped complex anion, molecular iodine forms no shortened contacts with the heterocyclic ring.

There is a great structural diversity of organic polyiodides in the CSD v.5.33 crystallographic database; however, for C,H,N,S,I-containing compounds, there are relatively few records characterizing structures whereby one and the same cation forms different polyiodides due to the presence of an iodine molecule in its composition.

In contrast to C,H,N-containing cations, which more often occur as tri- and pentaiodides, C,H,N,S-containing cations exhibit the ability to crystallize both in the form of triiodide and complex polyiodide containing molecular iodine in its composition.

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