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## Why are reactions of 2- and 8-thioquinoline derivatives with iodine different?

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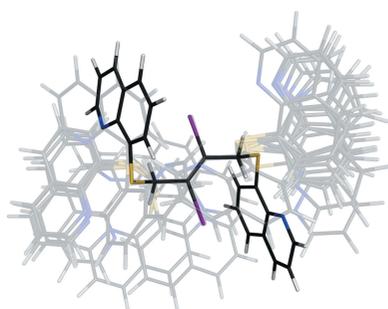
The crystal structures of 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-dium diiodide hemihydrate, C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub><sup>2+</sup>·2I<sup>-</sup>·0.5H<sub>2</sub>O, and 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-dium iodide triiodide, C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub><sup>2+</sup>·I<sup>-</sup>·I<sub>3</sub><sup>-</sup>, obtained during the reaction of 1,4-bis(quinolin-2-ylsulfanyl)but-2-yne (2TQB) with iodine, have been determined at 120 K. The crystalline products contain the dication as a result of the reaction proceeding along the iodocyclization pathway. This is fundamentally different from the previously observed reaction of 1,4-bis(quinolin-8-ylsulfanyl)but-2-yne (8TQB) with iodine under similar conditions. A comparative analysis of the possible conformational states indicates differences in the relative stabilities and free rotation for the 2- and 8-thioquinoline derivatives which lead to a disparity in the convergence of the potential reaction centres for 2TQB and 8TQB.

### 1. Introduction

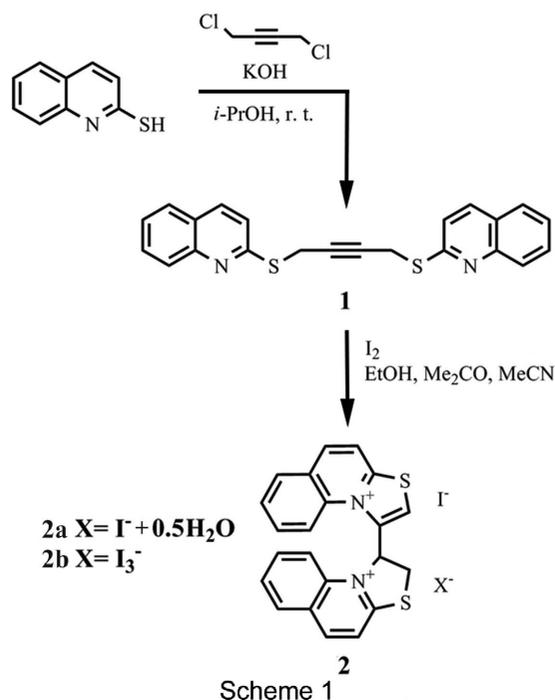
Organic oligo- and polyiodides are well-known structures that prefer to build chains in crystals due to the tendency of iodide anions to form halogen bonds (Desiraju *et al.*, 2013). In most cases, I<sup>-</sup>/I<sub>3</sub><sup>-</sup> anions act as halogen-bond acceptors, while the I<sub>2</sub> molecule behaves like a halogen-bond donor (García *et al.*, 2011). The availability of synthetic methods for organic iodides and the study of their properties is important in many applications due to their specific electric properties, spanning from conduction values typical of insulators to those of metals. Moreover, the unstable polyiodides have been postulated to be the charge-transfer intermediates responsible for the electron-transport mechanism in electrolytes of dye-sensitized solar cells (DSSCs), based on I<sup>-</sup>/I<sub>3</sub><sup>-</sup> (Abate *et al.*, 2010), following a Grotthuss-like process (Kawano & Watanabe, 2005). The chain-like organization of crystal motifs with the highest polarizability and the deficit of protons capable of shifting in a predictable direction under the action of a field can be the reason for such properties as nonlinear optical activity and the conductivity of crystalline materials.

Some structurally ordered organic polyiodides with a chain-like organization of the polyiodide anions have been described (Bartashevich, Stash *et al.*, 2016; Bartashevich, Batalov *et al.*, 2016).

Alkylammonium cations have been used successfully for the dimensional caging of polyiodides. In fact, the known tendency of these cations to organize into lamellar structures forces the polyiodide anions to be confined in the vicinity of positive charges (Reiss & Engel, 2002; Reiss & Engel, 2004; Svensson *et al.*, 2008). Crystalline compounds containing



pyridinium dications are of longstanding interest from a diverse range of perspectives, including applications in analytical chemistry, nonlinear optical devices, *etc.* (Sliwa *et al.*, 2006; Coe *et al.*, 2010). The studies of some research groups have shown that heterocyclic dications, for example, viologens, are useful building blocks in supramolecular chemistry (Ong *et al.*, 2005; Chas *et al.*, 2006; Branowska *et al.*, 2005) and crystal engineering.



One of the major obstacles of this approach is the lack of synthetic control over the system due to the unpredictable balance of a large number of parameters, which frequently influence the structure of the solid polyiodides formed in a given synthesis (*e.g.* the stoichiometry of the reagents, the nature of the organic compounds and solvents, *etc.*) (Tebbe & Rheingold, 1997; Svensson & Kloo, 2003; Blake *et al.*, 1998; Coppens & Miller, 1982; Marks *et al.*, 1982). Metal complexes containing  $I^-$  and  $I_3^-$  anions have been used in the cation-templated synthesis of polyiodide and polycationic systems to solve the problem. However, the structure of the metal-ion complex is also complicated and coordination effects can significantly change the nature of the interactions with the  $I^-$  and  $I_3^-$  fragments in the polyiodide chain (Kloo *et al.*, 2002; Svensson *et al.*, 1999; Svensson & Kloo, 1999).

Dicationic substances recently emerged as interesting candidates for the design of ion-containing polymers. For example, the dicationic derivatives of 1,4-diazabicyclo[2.2.2]octane (Zhang *et al.*, 2016) exhibited superior thermo-mechanical properties.

Currently, the well-known heterocyclic dications have the properties of viologens and are of great interest as functional materials in a wide array of applications, including electrochromic devices, molecular machines and organic batteries (Striepe & Baumgartner, 2017; Benniston *et al.*, 2012; Chas *et al.*, 2006).

Thus, the selective preparation of organic polyiodide and polycationic salts using crystal engineering approaches is an attractive goal that can possibly lead to the development of a new electron-affinic cationic system. To this end it was proposed to direct studies towards various types of azinium dications, such as quinolinium derivatives, with polyiodide anions.

The possibility of a chain-like organization of a structure with heterocyclic cations was discovered previously by us for single crystals of polyiodides based on chalcogenazo(azino)-containing heterocycles. In the single crystal of (*E*)-8-[[2,3-diiodo-4-(quinolin-8-ylsulfanyl)but-2-en-1-yl]sulfanyl]quinoline triiodide (Bartashevich, Stash *et al.*, 2016),  $I \cdots I$  halogen bonds, formed between the *I* atoms of the *trans*-1,2-diiododiviny moiety and the *I* atoms of the triiodide anions, play a binding role, allowing the formation of a chain in which the proton of the quinolinium cation is dynamically disordered.

This fact was established experimentally based on the characteristic changes in the difference Fourier difference maps of the electron density obtained at room temperature and at 100 K (Bartashevich, Stash *et al.*, 2016).

1,4-Dichlorobut-2-yne was used as an alkylating agent for 8-thioquinoline as the starting compound in the synthesis. The aim of this work was an evaluation of the possibility of obtaining structurally ordered motifs in single crystals using 2-thioquinoline as the starting compound.

As shown previously, the reaction of 8TQB with iodine led to (*E*)-8-[[2,3-diiodo-4-(quinolin-8-ylsulfanyl)but-2-en-1-yl]sulfanyl]quinolin-1-ium triiodide (Bartashevich, Stash *et al.*, 2016). However, under the same conditions, the reaction of 1,4-bis(quinoline-2-ylsulfanyl)but-2-yne (*i.e.* **1**) (see Scheme 1) with iodine does not lead to an iodine addition product, but to the bithiazoloquinolinium dication (*i.e.* **2**), as the product of iodocyclization reactions. The present work covers a description of the crystal structures of 1,2-dihydro[1,1'-bithiazolo[3,2-*a*]quinoline]-10a,10a'-dium iodides **2a** and **2b** (Fig. 1), with a difference in the stoichiometry of the iodide anions and the presence of a water molecule in **2a**.

It is known that in a similar reaction, 2-(allylsulfanyl)quinoline forms 1-iodomethyl-1,2-dihydro[1,3]thiazolo[3,2-*a*]quinolinium polyiodides of various stoichiometric composition (Kim *et al.*, 2015). This fact suggests that the formation of the bithiazoloquinolinium dication apparently proceeds according to a mechanism similar to the known halogen-cyclization reactions of *S*-allyl (Kim *et al.*, 1996, 2008, 2015) and *S*-propargyl derivatives of thioquinolines.

The bithiazoloquinolinium dication has not been observed previously. In the present study, we have tried to understand the causes of the differences of two similar substrates differing only in the position of the thio group in the quinoline system.

## 2. Materials and methods

### 2.1. Synthesis and crystallization

The 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-dium iodides **2a** and **2b** were synthesized in two steps from quinoline-2-thiol *via* 2TQB.

**Table 1**  
Experimental details.

	<b>2a</b>	<b>2b</b>
Crystal data		
Chemical formula	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> S <sub>2</sub> <sup>2+</sup> ·2I <sup>-</sup> ·0.5H <sub>2</sub> O	C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> S <sub>2</sub> ·I <sup>-</sup> ·I <sub>3</sub> <sup>-</sup>
<i>M<sub>r</sub></i>	635.29	880.09
Crystal system, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	120	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	21.3218 (16), 8.6006 (6), 25.2773 (19)	8.4090 (4), 11.1793 (5), 15.0322 (7)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 112.768 (2), 90	100.233 (1), 105.798 (1), 100.372 (1)
<i>V</i> (Å <sup>3</sup> )	4274.2 (5)	1298.61 (10)
<i>Z</i>	8	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.15	4.97
Crystal size (mm)	0.21 × 0.14 × 0.14	0.15 × 0.15 × 0.12
Data collection		
Diffractometer	Bruker SMART APEX DUO	Bruker SMART APEX DUO
Absorption correction	Analytical ( <i>SADABS</i> ; Bruker, 2013)	Numerical ( <i>SADABS</i> ; Bruker, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.637, 0.762	0.565, 0.674
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	38462, 10030, 7369	24022, 11866, 8210
<i>R<sub>int</sub></i>	0.054	0.035
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.834	0.834
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.044, 0.116, 1.02	0.048, 0.135, 1.00
No. of reflections	10030	11866
No. of parameters	259	271
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	2.34, -1.57	3.29, -3.21

Computer programs: *APEX2* (Bruker, 2013), *SAINTE* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *SHELXTL* (Bruker, 2013).

**2.1.1. 1,4-Bis(quinolin-2-ylsulfanyl)but-2-yne (2TQB).** Quinoline-2-thiol (0.321 g, 2.0 mmol) was suspended in water (30 ml) containing potassium hydroxide (0.114 g, 2.0 mmol), to which a solution of 1,4-dichlorobut-2-yne (0.116 g, 0.94 mmol) in propan-2-ol (2.0 ml) was added dropwise. The reaction mixture was stirred for 1 h. The precipitate was filtered off and dried in air, yielding 0.285 g (81%) of crude 2TQB. The product was washed with acetone (2 ml). The resulting precipitate of **1** was recrystallized from chloroform (3 ml), yielding 0.195 g (55%) of target 2TQB.

**2.1.2. 1,2-Dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-diium iodides.** 2TQB (0.185 g, 0.5 mmol) was dissolved under moderate heating in a chloroform–ethanol–acetone mixture (10:2:1 *v/v/v*, 20 ml) and mixed at room temperature with an iodine solution (0.130 g, 0.51 mmol) in the same acetone–acetonitrile–ethanol system (10:2:1 *v/v/v*, 8 ml). The resulting mixture was kept in an open flask at room temperature for 24 h. A brown precipitate of **2** formed, the solution was decanted and the precipitate was washed with dichloromethane (5 ml).

To obtain the crystals, 0.05 g of the crude product was dissolved in an acetone–acetonitrile–ethanol (1:1:1 *v/v/v*, 5 ml) mixture. The resulting solution was placed in a test tube of 15 mm diameter, which was closed with a stopper with a hole of 3 mm, allowing the solvent to evaporate freely at room temperature. Four weeks later, two types of crystals had formed, *i.e.* pale-red–orange prisms of **2a** and dark-brown needles of **2b**.

The structures **2a** and **2b** was determined by X-ray analysis. The structure of the reaction products is based on the 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-diium dication with a different composition of iodine anions.

## 2.2. Powder X-ray diffraction

The powder X-ray diffraction analysis of the crude product isolated from the reaction mixture before the crystallization procedure was performed on a Rigaku Ultima IV (Cu *K* $\alpha$  radiation) powder diffractometer at 293 K. The elemental analysis was carried out with an EDX spectrometer (Oxford INCA X-max 80) attached to a scanning electron microscope (Jeol JSM-7001F).

Powder X-ray diffraction analysis of the crude product confirms the formation of a single phase of **2b**. The diffraction pattern is in good agreement with that obtained from the structure solved from a single crystal (Fig. 1S in the supporting information). The **2a** peaks are absent on its diffractogram. There is some conversion to **2a** during the crystallization procedure which follows the isolation of the crude material, probably associated with some loss of molecular iodine from the crystallization mixture.

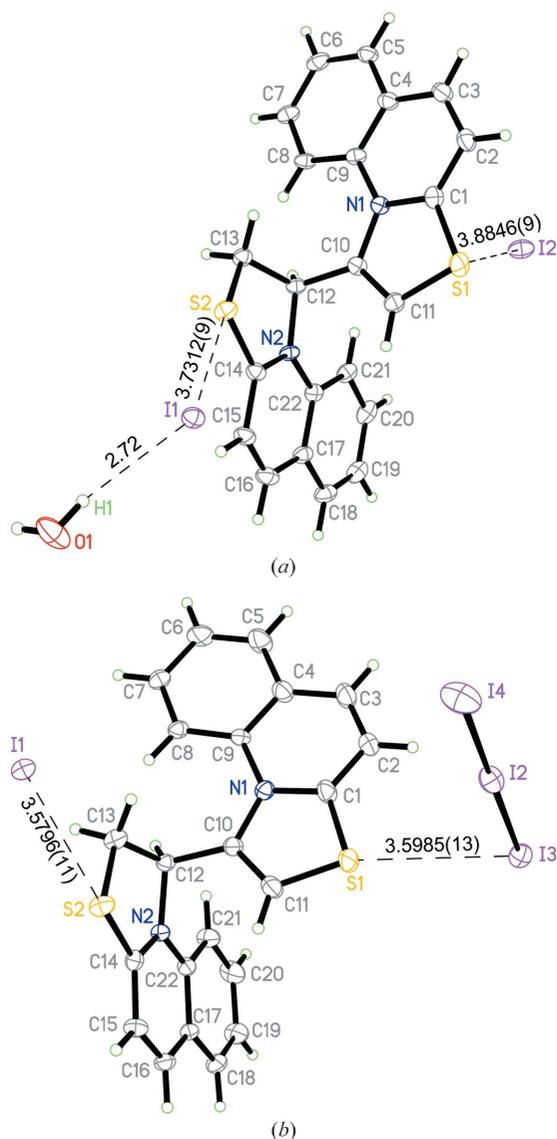
## 2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The water molecule in **2a** (Fig. 1) is located on a twofold axis. The H atom of the water

molecule was found from a difference Fourier synthesis and was refined with an isotropic displacement parameter at fixed coordinates. The remainder of the H atoms were placed in geometrically calculated positions and included in the structure-factor calculations in the riding-motion approximation, with C–H = 0.99 Å for methylene H atoms and 0.95 Å otherwise, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

#### 2.4. Calculations

The geometry optimization of the crystalline structures of **2a** and **2b** were carried out by the Kohn–Sham method with the periodic boundary conditions in *CRYSTAL14* (Dovesi *et al.*, 2014). The experimental crystallographic data were taken as initial data in the procedure of geometry optimization that was performed for all atomic coordinates and without the unit-cell parameters changing.



**Figure 1**  
The structures of the crystalline 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-diium iodides (a) **2a** and (b) **2b**.

The calculation level was HSE06/6-31G\*\* (for H, C, N, O and S atoms)/DZVP (for I atoms) (Perdew *et al.*, 1996; Krukau *et al.*, 2006; Francel *et al.*, 1982; Godbout *et al.*, 1992).

The investigated quinoline derivatives were modelled by the molecular dynamics simulation method using GAFF (general amber force field) (Wang *et al.*, 2004) and the program *GROMACS* (Version 5.1.4; van der Spoel *et al.*, 2005; Hess *et al.*, 2008). The integration time step was 2 fs in all simulations and the coordinates were recorded into the trajectory file every 5 ps. In order to limit the lengths of the covalent bonds with H atoms, the LINCS algorithm was applied (Hess *et al.*, 1997). All simulations were run at  $T = 298.15$  K, with a 0.1 ps coupling time controlled by a velocity rescaling thermostat with an additional stochastic correction (Bussi *et al.*, 2007) and under constant-volume boundary conditions. Optimized three-dimensional structures and molecular electrostatic potentials were found by quantum chemical Hartree–Fock calculations with the 6-31G\* basis set. Partial charges were evaluated with the RESP model (Bayly *et al.*, 1993). Electrostatic interactions were computed using the particle mesh Ewald method (PME) (Darden *et al.*, 1993) with a 0.1 nm grid step and the sixth-order interpolation.

Computation of bias exchange (Domene *et al.*, 2015) well-tempered metadynamics (Barducci *et al.*, 2008) of the title compounds was performed with the *PLUMED* software (Version 2.3; Tribello *et al.*, 2014) working in conjunction with the *GROMACS* software. Biasing potentials depending on the corresponding torsion angles of simulated compounds were adjusted by the addition of Gaussians with a 4 kJ mol<sup>−1</sup> height and a 10° width every 2500 steps (5 ps), until the Gaussian height reached approximately 0.1 kJ mol<sup>−1</sup>. The bias factor was 2. The simulation used one replica for each biasing potential.

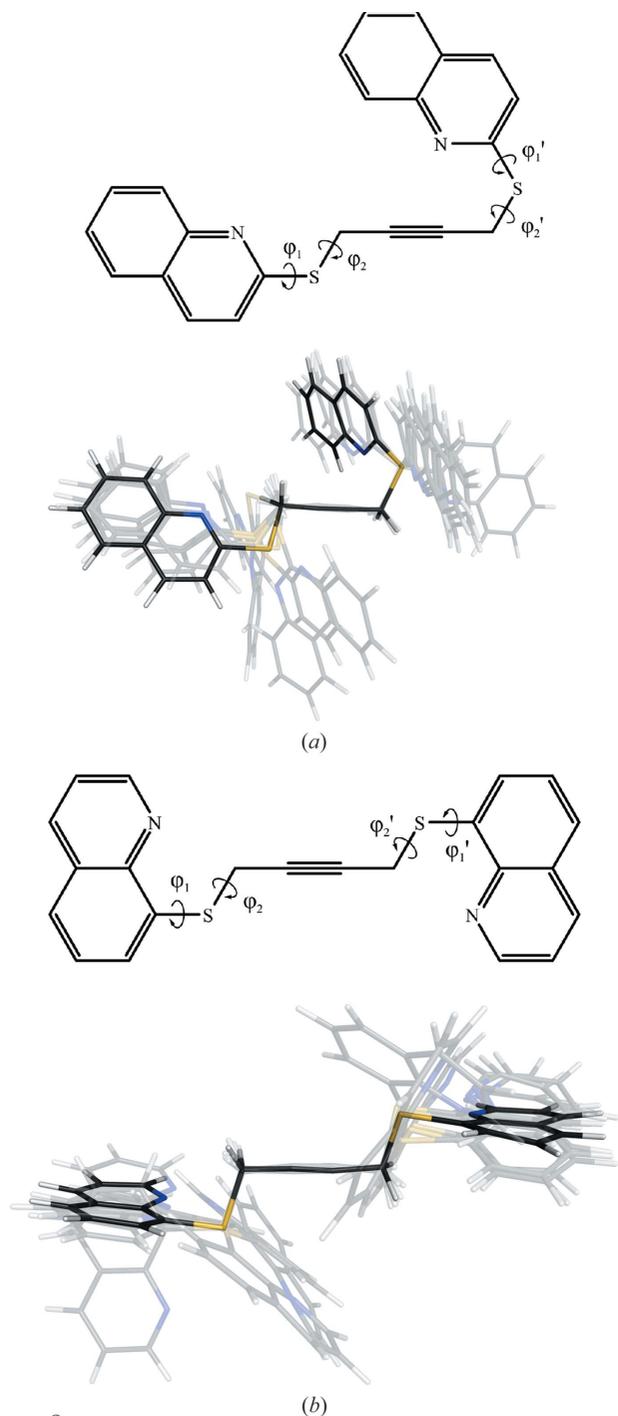
### 3. Results and discussion

#### 3.1. Structures and noncovalent interactions

In both cases, the chiral bithiazoloquinolinium dication in **2a** and **2b** crystallize as the racemates.

The angles between the quinoline fragments in the two structures, calculated between the planes through atoms N1/C1–C9 and N2/C14–C22 (not taking H atoms into account), were 74.0 (2)° for **2a** and 85.8 (3)° for **2b**. This geometry does not allow for extended  $\pi$ -stacking in the crystal structures. Nevertheless, there are  $\pi$ -stacking arrangements between the dihydrothiazoloquinolinediium fragments of neighbouring centrosymmetrically related enantiomers. The distance between the centroids of the N2/C14–C22 rings is 3.584 Å for **2a** and 3.609 Å for **2b**.

The most important noncovalent interactions between the iodide anions and dication are the chalcogen I···S bonds, in which the S atom participates due to its electrophilic site in attractive interactions with the mono- or triiodide anions. The chalcogen I2···S2 bond, with a distance of 3.7313 (9) Å, formed by the S atom of the dihydrothiazoloquinolinediium ring in **2a** is longer than the chalcogen bonds I1···S2



**Figure 2**  
The torsion angles in the top ten stable conformers for (a) 1,4-bis(quinolin-2-ylsulfanyl)but-2-yne and (b) 1,4-bis(quinolin-8-ylsulfanyl)but-2-yne.

[3.5796 (11) Å] and I3···S1 [3.5985 (13) Å] in **2b**. Also, the monoiodide anion forms a hydrogen bond, of length 2.72 Å, with the water molecule. The water molecule, which occupies a crystallographic twofold axis, bridges two iodide anions [I1 and I1(−*x*, *y*, −*z* +  $\frac{3}{2}$ )] by O—H···I hydrogen bonds, with an O···I distance of 3.562 Å and an O—H···I angle of 167°.

Comparing the electronic properties of the bithiazoloquinolinium dication in the crystalline structures of **2a** and **2b**, we have observed the following differences in the atomic

**Table 2**

The free energy (kJ mol<sup>−1</sup>) and interatomic distances (Å) of the most and least stable conformers for the intermediate iodine-derivative products. Free energy was estimated by the well-tempered metadynamics method with GAFF.

	( <i>E</i> )-2,3-Diiodo derivatives of 2TQB	( <i>E</i> )-2,3-Diiodo derivatives of 8TQB
$E_{\min}$	−260.9	−292.8
$E_{\max}$	−227.7	−261.2
$R_{\min}(\text{N}\cdots\text{C})$	3.794	3.333
$R_{\max}(\text{N}\cdots\text{C})$	4.499	5.542
	2TQB derivatives	8TQB derivatives
$E_{\min}$	−162.6	−159.0
$E_{\max}$	−153.5	−133.5
$R_{\min}(\text{N}\cdots\text{C})$	3.226	3.629
$R_{\max}(\text{N}\cdots\text{C})$	4.428	5.736

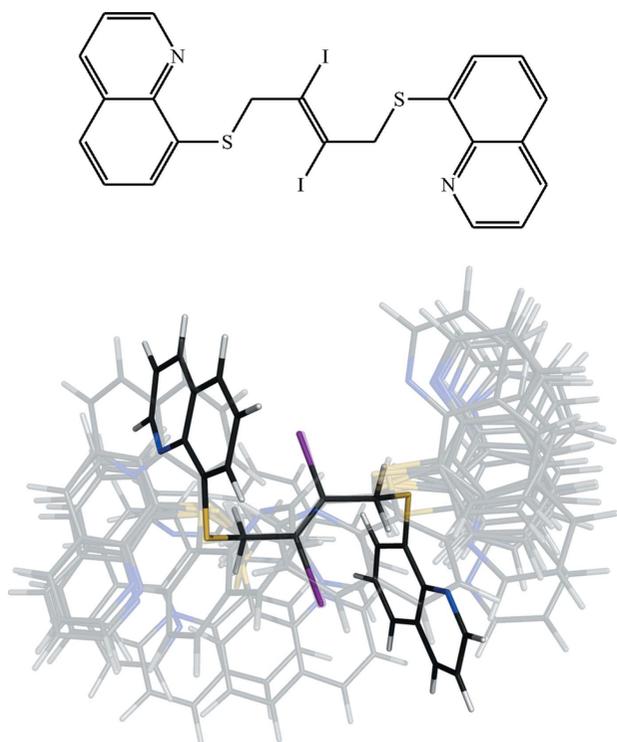
charges. In general, the total positive charges of the dications are higher in the crystal of monoiodide triiodide **2b**. The total charges of the dication are +1.70 and +1.75 e, respectively (Table 1S in supporting information). This occurs owing to the more positive S atom and the less negative N atom in **2b**. The largest difference in the charges for the C atoms is observed on atoms C1 and C9, which are covalently bonded to the N atom of the quinolinium ring. These atoms have the more positive charges ( $\Delta = +0.05$  and +0.07 e, respectively) in dimonoiodide hemihydrate **2a**. This is facilitated by the direct interaction of atoms C1 and C9 with the different anions. In particular, the electrophilic site of the triiodide anion in **2b**, located on the extension of the I—I bond and called the  $\sigma$ -hole, is oriented strictly towards the C9 atom. The length of the I3···C9(−*x* + 1, −*y* + 1, −*z* + 1) contact is 3.532 (4) Å. At the same time, in **2a**, the C1 atom interacts with the nucleophilic monoiodide anion atom I2, and the length of the I2···C1 contact is 3.650 (4) Å. Also, in **2a**, atoms C5 and C19 of the quinoline rings have the more negative atomic charges. Thus, a larger separation of the charges between the dication and the anions is observed in **2a**. Note that despite the interactions with the water molecule, the higher negative charge is concentrated on both monoiodide anions in **2a**, while the negative charge on the triiodide anion is more spread over the three atoms.

### 3.2. Comparative analysis of conformers based on 2- and 8-thioquinoline derivatives

Conformational analysis of a number of molecular structures was carried out to gain some insight into of the influence of possible steric factors on the cyclization reaction of 8-thioquinoline and 2-thioquinoline derivatives.

The energy of the generated conformers 2TQB and 8TQB and the relative proximity of the reaction centres for a possible cyclization reaction, namely the N atom of the quinoline ring and the acetylenic C atom (N···C), have been analyzed. Moreover, we have tested how the iodide-addition products of the 2TQB and 8TQB isomers differ in the conformational stability and in the cyclization ability.

A comparison of the energy ranges (Table 2),  $\Delta E = E_{\max} - E_{\min}$ , for conformers 2TQB ( $\Delta E = 9.1$  kJ mol<sup>−1</sup>) and 8TQB



**Figure 3**  
The structure and the top ten stable conformers for the (*E*)-2,3-diiodo derivative of 2TQB.

( $\Delta E = 25.5 \text{ kJ mol}^{-1}$ ) counts in favour of a greater stability for the 2TQB isomer. For them, the energy range is narrower, with a slightly lower value of  $E_{\text{min}}$ . We have assumed that the decrease in energy of 2TQB correlates with the free rotation around the C—S bonds between the quinoline system and the butyne chain in 2TQB and 8TQB, determined by the change in the torsion angle  $\varphi_1$ . The rotation barriers,  $\varphi_2$ , around the neighbouring S—C bond are given in the supporting information (Fig. S2). A similar assumption has been made for the symmetric fragments of the molecules and the corresponding angles  $\varphi_1'$  and  $\varphi_2'$ . Fig. S2(a) in the supporting information shows the rotation barriers for the torsion angle  $\varphi_1$ , and for 2TQB we can see only one minimum, while for 8TQB two minima of the free energy are observable (Fig. S2b in the supporting information).

It is important that the N and C atoms are closer together in the structure of the most stable conformers for 2TQB (Fig. 2). The minimum distance between these centres is 3.226 Å, while for the alternative structure of 8TQB, this distance does not exceed 3.629 Å. The high probability of a reduction of the distance between the N and C atoms in free rotation can explain the high probability of the cyclization reaction, in the case of 2TQB leading to the formation of a dication, whose structure is described in this study.

If we compare the energies of the generated conformers of the (*E*)-2,3-iodo derivatives of 2- and 8-thioquinoline, we see that 2,3-diiodo-1,4-bis(quinolin-8-ylsulfanyl)butene demonstrates a greater thermodynamic stability with a clear advantage. This is consistent with the fact that the protonated form of the 8-thioquinoline derivative crystallizes with iodine

during the reaction. We note that in the series of simulated conformers, there is a structure (dark colours marked in Fig. 3) that coincides with the salt form observed in the crystal, which we described previously (Bartashevich, Stash *et al.*, 2016).

#### 4. Conclusion

The interaction of 1,4-bis(quinolin-2-ylsulfanyl)but-2-yne with iodine leads to two different single crystals, namely the diiodide hemihydrate and monoiodide triiodide of 1,2-dihydro-1,1'-bi[thiazolo[3,2-*a*]quinoline]-10a,10a'-dium. Comparing the crystalline products obtained in reactions of butyne-bis-derivatives of 2- and 8-thioquinoline with iodine, which were carried out under identical conditions, we came to the conclusion that these reactions have completely different pathways. Unlike the previously studied reaction for 1,4-bis(quinolin-8-ylsulfanyl)but-2-yne, following the path of the simple addition of iodine to the butyne fragment, in the present study, we obtained and described the structure of a heterocyclic dication which formed during iodocyclization and which crystallized in the forms of a diiodide hemihydrate, **2a**, and a monoiodide triiodide, **2b**.

In both **2a** and **2b**, the interaction of the iodide anions with the dication takes place through chalcogen  $\text{I} \cdots \text{S}$  bonds, assisted by charges. Notwithstanding, the sum of the Mulliken charges of the dication is higher in the case of **2b**, and the shorter and stronger  $\text{I} \cdots \text{S}$  chalcogen bonds are observed in this crystal. This means that the example of these crystals confirms the dominance of the electrostatic nature of charge-assisted chalcogen bonds.

The comparative conformational analysis of butyne-bis-derivatives of 2- and 8-thioquinoline indicates a number of differences, both in the relative stabilities of the structures and in their free rotation, leading to a disparity in the potential reaction centres for the 2- and 8-substituted molecules. The revealed factors can underlie the reasons directing the reactions of butyne-bis-derivatives of 2- and 8-thioquinoline, which have completely different paths that lead to different crystalline products.

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