Comparison of non-covalent interactions and spectral properties in 1-methyl-3-methylthio-5-phenyl-1,2,4-triazinium mono- and tetraiodide crystals

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Abstract
The reaction of 1-methyl-3-methylthio-5-phenyl-1,2,4-triazinium (MTPT) iodide with diiodine in a solution leads to monoiodide crystal structure that in excess of iodine gives the unusual tetraiodide anion with two central iodine atoms in disorder. The bonding within the anion has been characterized as $I^-$...$I_2^-$...$I^-$; the existence of the bound iodine molecule inside has been proven by the characteristic band in experimental and calculated Raman spectra. Non-covalent interactions of MTPT in considered crystal structures are different. Monoiodide anion as a strong electron donor allows the formation of the S...I chalcogen bonds that are absent in tetraiodide structure. The features of halogen bonds within the $I_4^{2-}$ anion also performed.

Keywords 1,2,4-Triazine · 1,2,4-Triaziniumoligosiodide · Tetraiodide · Halogen bond · Chalcogen bond

Introduction
The N-alkyltriazinium iodides are an attractive object of theoretical and practical interest since both the cationic and anionic components of these substances possess a number of various unusual and beneficial properties. On the one hand, heteroaromatic compounds with the 1,2,4-triazine moiety possess a wide spectrum of biological activities such as antifungal [1], anticancer [2], analgesic and antihypertensive [3], antimalarial [4], antiparasitic [5], and anti-inflammatory [6] activities; they are also known as potential blood platelet aggregation inhibitors and estrogen receptor modulators [7], so, for a long time, they have attracted the attention of researchers. The anticonvulsant 6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine (known by the trade name “Lamotrigine”) is used in the treatment of bipolar disorder [8, 9].

The sulfur-containing derivatives of 1,2,4-triazines, in addition to this, are the important classes of organic compounds which exhibit a wide range of biological activities. For example, the thio-indolotriazine derivative is used as a fungicide, 5,6-diphenyle-1,2,4-triazine possessing the thiosemicarbazide moiety is a bactericidal agent, and 3-thio-5-cyclohexenyl-6-oxo-1,2,4-triazine is a pesticide. Herbicidal activity is shown by 4-aminoo-6-tert-buty1-3-methylsulfanyl-1,2,4-triazine-5(4H)-one, sold under the trade names “Sencor” or “Metribuzin,” widely used herbicide [7]. 5,6-Diphenyl-1,2,4-triazine-3-thiol is one of the triazine derivatives that possess anti-inflammatory activity [10].

Quaterytriazinium salts possess high reactivity, are attractive for researchers, and exhibit a series of transformations that are unusual for N-alkylazinium salts. For example, 1-ethyl-3-alkylthio-5-phenyl-1,2,4-triazinium under the action of triethylamine forms 4a,4b,9,10-tetrahydro-1,3,6,8,8a,10a-hexaazaphenanthrenes [11]. The derivatives of 1-alkyl-5-phenyl-1,2,4-triazinium iodides have been found to undergo oxidative dequaternization reaction easily, on treatment with...
triethylamine in alcohol or acetone solutions at room temperature [12], while other N-alkylazinium salts require significantly more severe conditions.

On the other hand, the area of practical use of the compounds containing molecular iodine is rather large [13]. The iodine-saturated compounds composed of an organic cation and a polyiodide anion can be used as iodophors for water disinfection [14]. It is important for the search for efficient and safe bacteriostatic [15] and X-ray contrast compounds [16]. The contemporary practical tasks stimulate permanent interest in studies of the structural and physicochemical properties of new iodine-containing compounds [17].

Some of organic polyiodide compounds are able to exhibit the conductive [18] and nonlinear optical properties [19]. Such crystals usually contain several polyiodide units, such as tri- and oligoiiodide anions. The diversity of their structural disposition provides a great variety of polyiodide structures in the solid state [20]. Polyiodides with organic cations containing sulfur atoms attract particular interest: they are known as effective templates for self-assembly of polyiodide networks. In addition, due to multiple S...I interactions [21] they are promising for drug design [22] and low-temperature conductors [23]. The unusual charge-assisted I...I halogen bonds are observed between the asymmetric triiodide and diiodide units, which include at least two diiodine fragments in some oligoiiodides [24–26].

In our research, we managed to synthesize the product of N-alkyl-derived 1,2,4-triazinum salt and the rather rare tetraiodide anion I₄⁻. The similar type of polyiodide anion organization was previously described in the series of works [27–31]. Tetraiodides can be either symmetric with equal I...I distances or asymmetric with non-equivalent distances. Such structures are intermediate on the way to the I₃⁻...I⁻ type of tetraiodide; such reversible phase transition has been previously observed in the solid state under cooling for dipirazolium salt and has been thoroughly discussed in the work [28]. From the theoretic standpoint, the authors of the paper [26] identify the following factors controlling asymmetry of the tetraiodide anion: the crystal surrounding, especially the localization and the value of positive charges nearby and the possibility of electron delocalization.

Materials and Methods

Synthesis and crystallization

3-Methylthio-5-phenyl-1,2,4-triazine

3-Methylthio-5-phenyl-1,2,4-triazine 1 was synthesized in two steps from thiosemicarbazide and phenylglyoxal hydrate via S-methylthiosemicarbazide hydriodide (Scheme 1).

Stage A. Thiosemicarbazide (4.55 g, 50 mmol) was heated with methyl iodide (8.52 g, 60 mmol) at reflux in ethanol (30 mL) for 8 h. The reaction mixture was cooled and the precipitate was filtered off and dried in air, yielding 10.28 g.
(88%) of crude S-methylthiosemicarbazide hydroiodide.
Stage B. The crude S-methylthiosemicarbazide hydroiodide
obtained in stage A (6.44 g, 27.6 mmol) and 4.20 g (27.6
mmol) of phenylglyoxal hydrate were dissolved under mod-
crate heating in 30 mL of water, then 2.52 g (27.6 mmol) of
sodium bicarbonate was added to the resulting solution with
stirring.

The obtained precipitate was filtered off and recrystallized
from ethanol to yield 4.92 g (88%) of 1 as yellow solid with
m.p. 98-99°C. 1H NMR in CDC13: 2.67 (3H, s, methylthio
groups), 9.32 (1H, s, H-6), 7.53, 8.11 ppm (5H, m, phenyl
groups).

1-Methyl-3-methylthio-5-phenyl-1,2,4-triazinium iodide

Methyl iodide (1.06 g, 7.5 mmol) was added to a suspension of
(1.01 g, 5.0 mmol) 3-methylthio-5-phenyl-1,2,4-triazine 1 in
20 mL of ethanol and the reaction mixture was heated at reflux
for 15h. The obtained precipitate was filtered off and recryst-
tallized from ethanol to yield 1.2 g (69%) of 2 as dark red
prisms with m.p. 185-188°C. 1H NMR in CD3OD: 2.70 (3H,
s, methylthio group), 4.80 (3H, s, N-methyl group), 10.25
(1H, s, H-6), 7.4-7.8, 8.10-8.35 ppm (5H, m, phenyl
group). To obtain the crystals, 0.05 g of 1-methyl-3-
methylthio-5-phenyl-1,2,4-triazinium iodide was dissolved
in 3 mL of acetonitrile. The resulting solution was placed in
a test tube of 15 mm diameter, which was closed with a stop-
per with a 3 mm hole, allowing the solvent to evaporate freely
at room temperature. Two weeks later dark red prisms were
formed. The structure 2 was determined by X-ray analysis.

1-Methyl-3-methylthio-5-phenyl-1,2,4-triazinium polyiodide

Iodide of 1-methyl-3-methylthio-5-phenyl-1,2,4-triazinium
(MTPT) 2 (0.172 g, 0.5 mmol) was dissolved under moderate
heating in 5 mL of ethanol and mixed with iodine (0.127 g, 0.5
mmol), then the reaction mixture was heated at reflux for 5 h
and left overnight at room temperature. The obtained precip-
itate was filtered off and recrystallized from ethanol with the
yield 0.274 g (91.63%) of MTPT polyiodide 3 as dark red
needles of good diffraction quality.

X-ray diffraction study

Single-crystal X-ray diffraction experiments were carried out
with a Bruker SMART APEX DUO diffractometer equipped
with an Oxford cryosystem Cobra (graphite monochromated
Mo-Kα radiation, λ = 0.71073 Å, ω-scan technique, T = 120
K). The APEX II software [32] was used for collecting frames
of data, indexing reflections, determination of lattice con-
stants, integration of intensities of reflections, scaling and ab-
sorption correction while the SHELXTL program package
[33] was applied for the space group and structure
determination, refinements, graphics, and structure reporting.
The structures were solved by direct methods and refined
by the full-matrix least-squares technique against F² with the an-
isotropic thermal parameters for all non-hydrogen atoms. The
hydrogen atoms were placed in the geometrically calculated
positions and included in the structure factors calculation in
the riding motion approximation, with the 0.98 Å length for
methylene H atoms with Uiso(H) = 1.5Ueq(C) and 0.95 Å
otherwise, and with Uiso(H) = 1.2Ueq(C). Crystal data, data
collection and structure refinement details are summarized in
Table 1; CCDC 1909732 and 1909733 contain supplementary
crystallographic data for 2 and 3, correspondently, which can
be obtained free of charge from The Cambridge Crystallographic Data Centre.

Spectral experiment

Raman spectra were recorded with a NT-MDT NTegra
Spectra spectrometer using 632.8 nm line of a He-Ne* laser
for spectra excitation. The laser power on the sample surface
was about 0.2 μW or less. We had to take into consideration
that the laser power had to be thoroughly controlled in order
to avoid decomposition under laser exposition, due to decreasing
thermal stability of higher polyiodides.

Theoretical calculations

Periodical boundary conditions methodology implemented
in CRYSTAL17 program [34] was fulfilled during the atom
position optimization with fixed cell parameters for crystal struc-
tures 2 and 3 using the hybrid B3LYP exchange-correlation
functional, TZVP basis set for C, H, N, S atoms [35] and
DZVP for I atoms [36]. K-point sampling was done using a
Monkhorst-Pack grid of 8 × 8 × 8. All optimized structures did
not detect negative modes in the Hessian matrix and thus
could be attributed to energy minimum and equilibrium state.
The calculated Raman spectra were obtained using couple-
perturbed Kohn-Sham procedure as implemented in
CRYSTAL17 [37]. Calculations of the electron density distribu-
tions, eigenvalues of electron density Hessian matrix, poten-
tial and kinetic energy densities, and the electron localiza-
tion function (ELF) [38] were performed using TOPOND14
[39].

Discussion

Crystal structure and description of non-covalent
interactions

Non-covalent interactions and crystal packing of MTPT with
iodine moieties in monoiiodide 2 and triiodide 3 differ in 2, the
<table>
<thead>
<tr>
<th>Compound</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C14H12N3S</td>
<td>C14H12N3S, I, 0.5 I2</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>345.20</td>
<td>880.09</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
<td>Monoclinic, P21/n</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>120(2)</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.2809(4)</td>
<td>10.2363(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.7753(4)</td>
<td>7.0620(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.5905(5)</td>
<td>20.9001(9)</td>
</tr>
<tr>
<td>α (°)</td>
<td>68.010(1)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>69.096(1)</td>
<td>102.881(8)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>77.617(1)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1298.44(9)</td>
<td>1472.82(11)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo-Kα, λ = 0.71073 Å</td>
<td></td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>2.600</td>
<td>4.396</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.439 × 0.378 × 0.344</td>
<td>0.486 × 0.102 × 0.080</td>
</tr>
</tbody>
</table>

| Data collection | Bruker SMART APEX II | |
| Diffraecometer | | |
| Absorption correction | Numerical (SADABS-2014/5. Bruker, 2013) | |
| Tmin, Tmax | 0.448, 0.586 | 0.188, 0.778 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 25,981, 9591, 8931 | 28,618, 5591, 4619 |
| Rint | 0.0157 | 0.0289 |
| (sinθ/λ)max (Å⁻¹) | 0.781 | 0.781 |
| Refinement | | |
| R(F² > 2σ(F²)), wR(F²), S | 0.0179, 0.0412, 1.074 | 0.0275, 0.0658, 1.038 |
| No. of reflections | 9591 | 5591 |
| No. of parameters | 294 | 166 |
| H-atom treatment | H-atom parameters constrained | |
| Δρmax, Δρmin (e Å⁻³) | 0.579, −0.515 | 1.329, −1.585 |

MTPT cations form almost planar sheets, while in 3 the packing slightly more reminds the wave-like layers.

In the crystal structure of compound 2 (Fig. 1) the monoiodide anions and MTPT cations have symmetrically inequivalent positions in the asymmetric part of a crystal cell. The most evident difference in crystal surrounding can be observed in interatomic distances for the I(1) and I(2) anions (Fig. 1a). Two symmetrically inequivalent positions remain in the calculated structure after the equilibrium state localization: I(1)" and I(2)" have different Mulliken charges: −0.88 e and −0.91 e, respectively. The common feature of both monoiodide anions is that they form the short contacts with a great number of hydrogen atoms (Fig. 1a). Moreover, both monoiodide anions are located in front of sulfur atoms, on the extension of the C–S covalent bond of the thiol group and form the chalcogen bonds. Note that the most pronounced σ-hole of sulfur manifests itself on the extension of the covalent bond with triazinium heterocycle. Although, I(1)…S(1) and I(2)…S(1A) interactions are longer than the sum of Van der Waals radii (3.939 Å and 4.149 Å), and in the equilibrium crystal structure these distances are slightly increased but still the corresponding bond critical point (bcp) and bond path for the chalcogen bond are observed (Fig. 3). As it can be seen from Fig. 3, the monoiodide anion also participates in a hydrogen bond with the atom of the CH₂-group.

A chalcogen bond is observed only in the case of monoiodide 2 while in tetraiodide 3 structure the anion is shifted away from the sulfur atom and the cation…anion interactions are implemented mainly via I…H interactions.

Monoiodide I(1)⁻ is situated above and below C(4) and C(4A) atoms of triazinium ring (Fig. 1b), but the position of I(2)⁻ is shifted, so that I(2)⁻ interacts with the hydrogen located above and below the atoms of CH₃-groups instead.
Fig. 1 MTPT monoiodide: a in-layer and b inter-layer interactions in crystal structure 2

The I(1)...C(4) and I(1)...C(4A) interactions are presented in experimental geometry with distances 3.305 and 3.415 Å, respectively. In the calculated structure these interactions are aligned to 3.263 and 3.292 Å.
In the crystal structure of 3 (Fig. 2), oligoiodide anions $I_4^{2-}$ are stretched along MPTT, and the H(4) and H(10) atoms, just as in compound 2, form the short contacts with $I(1)^{-}$. The interlayer interactions between the oligoiodide anion and MTPT are represented by interactions $I(2)\ldots N(1)$ and $I(1)\ldots$ C(4) (Fig. 2b).

For the oligoiodide $I_4^{2-}$ anion of 3, the central atoms have two alternative positions. The symmetry and disorder of the
I(2) and I(3) atoms are revealed using X-ray diffraction data. According to the literature data concerning typical I$_2$-I$_2$ structures [40, 41], we can interpret it as I(1)$^-$-I(2)$^-$-I(2)$^-$ with the inversion in the middle of the central I(2)-I(3) bond. The problem of an unambiguous model of crystal structure 3 is as follows: if we treat edge positions of central iodine atoms, we get unreal I-I bond lengths for a diiodine molecule in both cases: firstly, 2.301 Å, which is extremely short; secondly, 3.340 Å, which is very long. Thus, we perform spectral investigation in order to reveal structural units within the I$_2$-$I_2$ anion, as well as theoretic simulation in order to achieve reasonable atomic positions corresponding to the equilibrium state, and then analyze the resulting electronic and spectral characteristics.

The experimental and theoretical observations concerning the existence of a bound diiodine molecule inside the tetraiodide anion can be supplemented by the values of bond descriptors based on calculated electron density at the bond critical points, $\rho(r_{icp})$, in crystals for the typical oligoiodide subunits (Table 2). The distances and the values of electron density $\rho(r_{icp})$ obtained within one theoretical level of calculations allow us to characterize the shorter I-$I^-$ bond in the tetraiodide anion as the one close to the shorter I-$I^-$ bond in the asymmetric triiodide unit, and it can definitely be characterized as the elongated bond of the diiodine molecule. However, the longer I-$I^-$ bond in the tetraiodide anion is longer and weaker than the one in symmetric triiodide (Fig. 3). One of the reasons for this fact may be formation of two halogen bonds instead of one bond in the asymmetric triiodide unit.

According to [43] the ratio of potential and kinetic energy densities, $\left| \frac{V(r_{icp})}{G(r_{icp})} \right|$, the relations for all considered I-I/I-I bonds can be interpreted as intermediate ones between closed-shell interactions and covalent bonds. The descriptor based on the ratio of maximal and minimal eigenvalues of electron density Hessian $\lambda_1(r_{icp})/\lambda_3(r_{icp})$ [44] for all studied polyiodide subunits gives values much less than 1 (typical for closed-shell interactions), which is consistent with the previously given interpretation for halogen bonding [45].

Strong covalent interaction index, SCI [46], which is the reciprocal value of $\left[ 1 - \frac{\eta(r_{icp})}{\eta(r_{icp})} \right]^{1/2}$, where $\eta(r_{icp})$ corresponds to ELF in the bond critical point, allows us to distinguish the I-I bonding in diiodine from the I-I bond in symmetric I$^-$ and especially from the I-I bond in asymmetric triiodide or tetraiodide anions. In Fig. 4, in terms of the ELF distribution in the plane of a polyiodide anion, the typical representatives of the symmetric triiodide and the studied tetraiodide are considered. It can clearly be seen (Fig. 4b) that the bonding between the central I(2) and I(2A) atoms is significantly stronger than that between the atoms in triiodide (Fig. 4a) resulting in the existence of the separate I$_2$ unit in the center of the

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**Table 2** Iodine-iodine bonding characteristics in the typical oligoiodide subunits obtained from calculations of electron density for equilibrium geometry of listed crystals

<table>
<thead>
<tr>
<th>t2.1</th>
<th>Symmetric triiodide anion in IVOVOG [42]</th>
<th>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t2.2 Bond</td>
<td>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</td>
<td></td>
</tr>
<tr>
<td>t2.4 Distance</td>
<td>2.9875</td>
<td>2.9875</td>
</tr>
<tr>
<td>t2.5 $\rho(r_{icp})$</td>
<td>0.0440</td>
<td>0.0440</td>
</tr>
<tr>
<td>t2.6 $\lambda_1(r_{icp})/\lambda_3(r_{icp})$</td>
<td>0.297</td>
<td>0.297</td>
</tr>
<tr>
<td>t2.7 $</td>
<td>V(r_{icp})/G(r_{icp})</td>
<td>$</td>
</tr>
<tr>
<td>t2.8 SCI</td>
<td>0.940</td>
<td>0.940</td>
</tr>
<tr>
<td>t2.9 Asymmetric triiodide anion in SEJQAC [23]</td>
<td>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</td>
<td></td>
</tr>
<tr>
<td>t2.10 Bond</td>
<td>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</td>
<td></td>
</tr>
<tr>
<td>t2.11 Distance</td>
<td>2.8666</td>
<td>3.1174</td>
</tr>
<tr>
<td>t2.12 $\rho(r_{icp})$</td>
<td>0.0538</td>
<td>0.0344</td>
</tr>
<tr>
<td>t2.13 $\lambda_1(r_{icp})/\lambda_3(r_{icp})$</td>
<td>0.345</td>
<td>0.247</td>
</tr>
<tr>
<td>t2.14 $</td>
<td>V(r_{icp})/G(r_{icp})</td>
<td>$</td>
</tr>
<tr>
<td>t2.15 SCI</td>
<td>1.121</td>
<td>0.731</td>
</tr>
<tr>
<td>t2.16 Symmetric tetraiodide anion in 3 (this work)</td>
<td>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</td>
<td></td>
</tr>
<tr>
<td>t2.17 Bond</td>
<td>$I^\cdots I^\cdots I^\cdots I^\cdots I^-$</td>
<td></td>
</tr>
<tr>
<td>t2.18 Distance</td>
<td>2.8924</td>
<td>3.3690</td>
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<tr>
<td>t2.19 $\rho(r_{icp})$</td>
<td>0.0529</td>
<td>0.0230</td>
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<tr>
<td>t2.20 $\lambda_1(r_{icp})/\lambda_3(r_{icp})$</td>
<td>0.358</td>
<td>0.201</td>
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<tr>
<td>t2.21 $</td>
<td>V(r_{icp})/G(r_{icp})</td>
<td>$</td>
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<tr>
<td>t2.22 SCI</td>
<td>1.168</td>
<td>0.537</td>
</tr>
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</table>
tetaiodide anion (Fig. 4b), while two I–I bonds in the triiodide anion (Fig. 4a) is almost identical. The terminal
I(1) and I(1A) atoms in the triiodide anion (Fig. 4b) tend
to be spherically symmetric like the iodide anion and dem-
strate anisotropy of electronic shells only at the inner
side, due to formation of the halogen bond with the iodine
molecule. A similar question of differentiation between I–I
and I…I bonding has recently been considered for the
halogen-bonded complexes from the standpoint of electron
delocalization indices [47]. The SCI values for the bound
diiodine give significantly higher values than for the
above-mentioned cases and thus help to define the I₂ mol-
ecule as the separate unit within complex oligoiodides of
different stoichiometry and composition. The identification
of the I₂ subunit within oligoiodides is a very important
question in tasks of interpretation of experimental and cal-
culated Raman spectra, as tri- or pentaiodides demonstrate
spectral behavior that is significantly different from the
bound iodine [19]. Moreover, the existence of I₂ dictates
the features of thermal stability and decomposition paths
[48], which is important in the design of organic matrices
for dye-sensitized solar cells.

**Experimental and calculated Raman spectra**

Experimental Raman spectra of both single crystal triazinium
salts were intense and did not demonstrate any significant
luminescence under excitation by 632.8- or 488-nm laser lines
(Fig. 5).

Unlike previously analyzed quinolinium tri- and
diiodides [49], here a series of low-wavenumber bands
in the monoiiodide structure is considered, thus the spec-
trum of tetraiodide 3 can be interpreted only in comparison
with corresponding monoiiodide 2, as some of the bands lie
in the range of typical poloiiodide vibrations 100–180 cm⁻¹.
In Fig. 5, the upper red curve corresponds to the spec-
trum of compound 3, the characteristic band at 170 cm⁻¹
belonging to the I–I vibration is marked by an asterisk. It
can evidently be attributed to the region of bound diiodine
vibration (140–180 cm⁻¹) according to the literature data
[19], which allows us to characterize this molecule as
rather weakly bound: 10 cm⁻¹ shift to lower wavenumbers
in comparison to crystalline I₂ with the band at 180 cm⁻¹.
Other low-wavenumber bands are observed nearly at the
same wavenumbers for structures 2 and 3 and in general
can be attributed to cation…anion, anion…anion and cat-
ion…cation librations as well as deformaional vibrations
of some structural fragments of an organic cation. A more
detailed description has been made using calculated
Raman data for crystals 2 and 3, the comparison of exper-
imental and calculated modes, as well as their detailed
assumption, is presented in Table 3.

Geometry optimization of crystal structure 3 also results
in anion organization of the Γ…I₂…Γ type, which is in
agreement with the experimental Raman data, where only
the characteristic band of the bound diiodine is observed
and no typical triiodide bands are present in the Raman
spectrum of 3.

Thus, experimental, calculated Raman spectra as well as
the descriptors based on calculated electron density allow
us to consistently characterize the bonding within the dis-
ordered tetraiodide anion. The combination of experimental
and computational data identifies the existence of the
bound I₂ unit within the tetraiodide anion.
## Conclusions

Two crystalline products of the synthesis of 1-methyl-3-methylthio-5-phenyl-1,2,4-triazinium iodides have made it possible to analyze the features of non-covalent interactions of the cation in two different crystalline environments: in iodine-excessive and iodine-deficient structures. A strong electron donor, like the monoiiodide anion, allows formation of the S...I chalcogen bonds, while those in the tetraiodide structure do not exist.

Joint consideration of X-ray diffraction data together with experimental and calculated Raman data has helped to describe and characterize the bonding within the $\text{I}_4^{2-}$ anion with the disorder of central iodine atoms in 1-methyl-3-methylthio-5-phenyl-1,2,4-triazinium salts. Reliable interpretation of experimental spectral data of $\text{I}_4^{2-}$ has been carried out in comparison with the corresponding monoiiodide due to several intense bands in the typical range of iodine vibrations. Theoretical structural model of the crystal structure with the disordered anion results in the equilibrium $\text{I}_4^{2-}$ anion of the $\Gamma$...$\text{I}_2$...$\Gamma$ type. Topological characteristics of electron density reveal the existence of the bound diiodine molecule inside the tetraiodide anion structure, which is in consistence with experimental and calculated Raman data.

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### Compliance with ethical standards
All ethical guidelines have been adhered to.

### Conflict of interest
The authors declare that they have no conflict of interest.

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AUTHOR QUERIES

AUTHOR PLEASE ANSWER ALL QUERIES.

Q1. Please check if the caption provided for Scheme 1 is appropriate. Also, a citation for the said scheme was inserted in the sentence "3-Methylthio-5-phenyl-1,2,4-triazine 1 was synthesized..." Kindly check if the insertion is appropriate as well.

Q2. Please check if the tables are presented accordingly.

Q3. A citation for Fig. 3 was inserted in the sentence "However, the longer..." Please check if appropriate.