Crystals 2020
The 2nd International Online Conference on Crystals
10–20 NOVEMBER 2020 | ONLINE
crystals MDPI

CHALCOGENAZINOQUINOLINIUM MONOIODIDES: PHASE TRANSITION, SPECTRAL PROPERTIES AND NON-COVALENT BONDING

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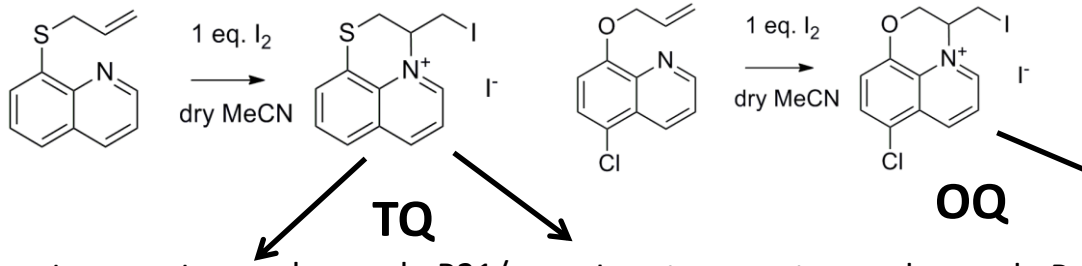
Abstract: The study of phase transitions in organic crystals is a step to tunable modification of their physicochemical properties as a part of modern crystal engineering approaches. Organic crystals with polyiodide anions and S,N-containing heterocycles, such as substituted thiazolo(azino)quinolinium salts [1-3] open possibility for the design of nonlinear optical, semiconductor materials and components of dye-sensitized solar cell devices. The methodology of the present work includes consistent analysis of X-Ray diffraction and the results of periodic quantum-chemical calculations in order to reveal the changes in crystal packing, non-covalent interactions features and electronic properties as a result of undergoing low-temperature phase transition. Objects of the study are two newly obtained crystal structures of substituted thia- and oxazinoquinolinium iodides with the typical I…I halogen bonds. Low-temperature phase transition with decrease of symmetry from P21/c to P-1 is registered by X-Ray diffraction and Raman spectroscopy, the interpretation of the observed spectral changes is made on the basis of theoretic spectra in periodic approximation.

1. Bartashevich E.V.; Yushina I.D.; Stash A.I.; Tsirelson V.G. Crystal Growth & Design, 2014, 14 , P. 5674.
2. Yushina I.D.; Kolesov B.A.; Bartashevich E.V. New Journal of Chemistry, 2015, 39 (8), P. 6163-6170
3. Yushina I.D., Tarasova N.M., Kim D.G., Sharutin V.V., Bartashevich E.V. Crystals, 2019, 9, P. 506.

Keywords: quinolinium iodides; halogen bonding; phase transition; synchrotron radiation; Raman spectroscopy

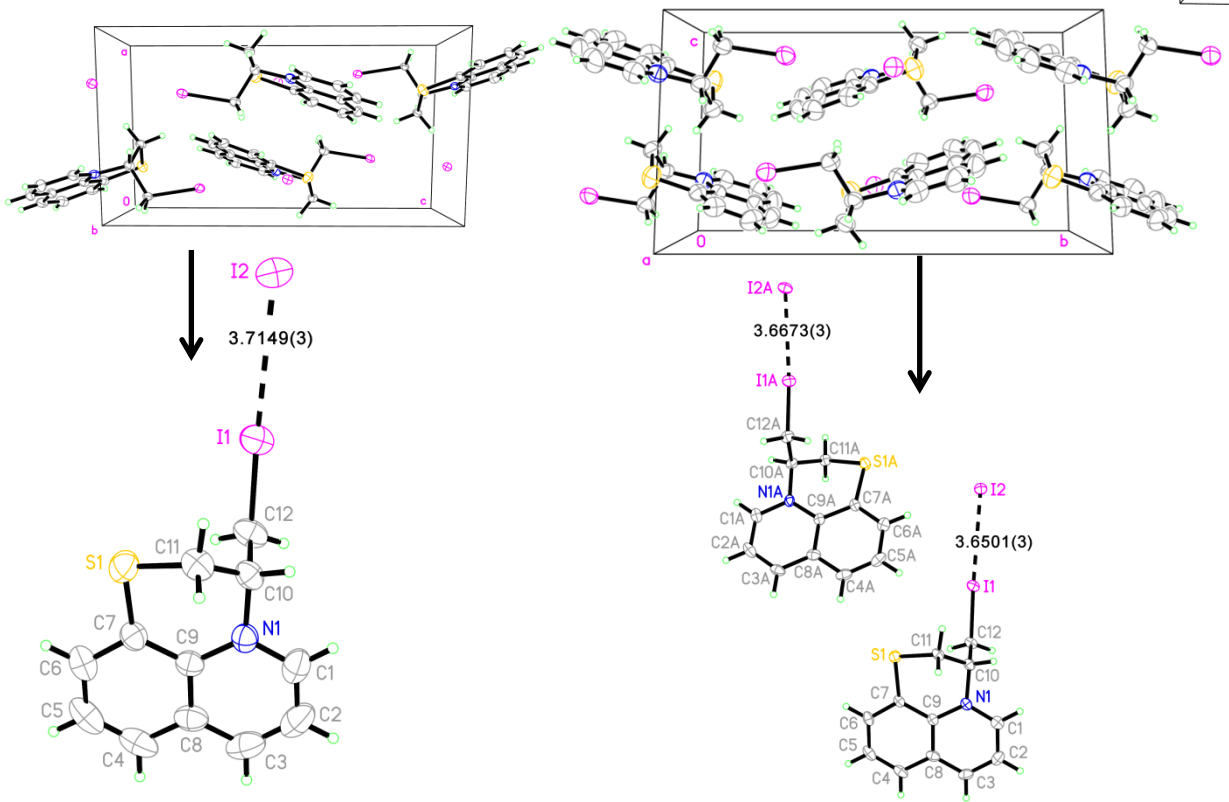
Results and Discussion I

Synthesis & crystallization of chalcogenazinoquinolinium monoiodides



Room temperature polymorph, P21/c

Low temperature polymorph, P-1



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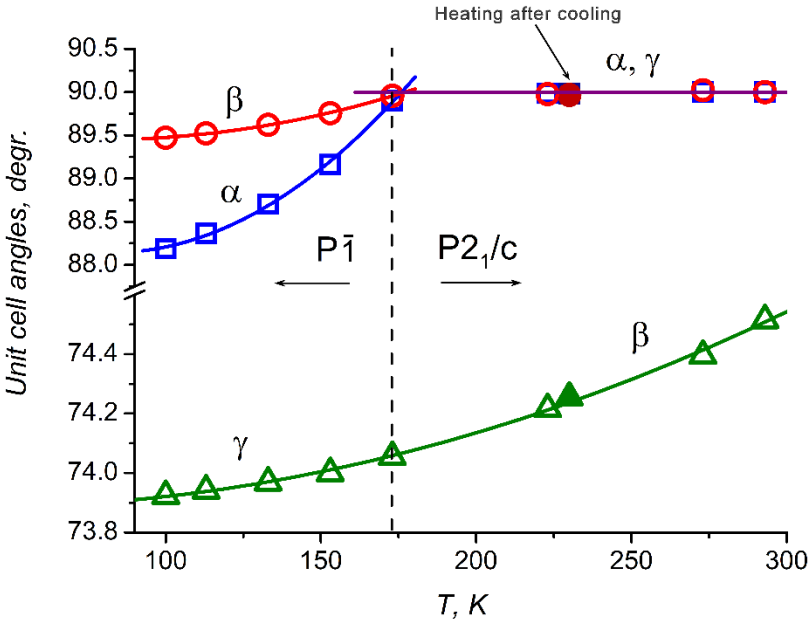
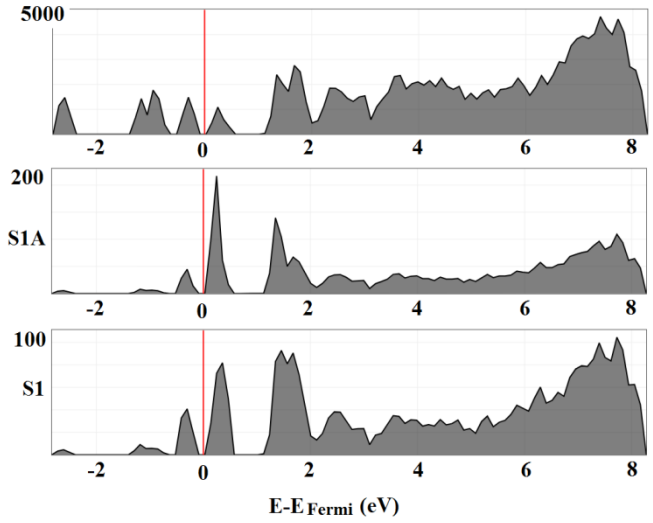
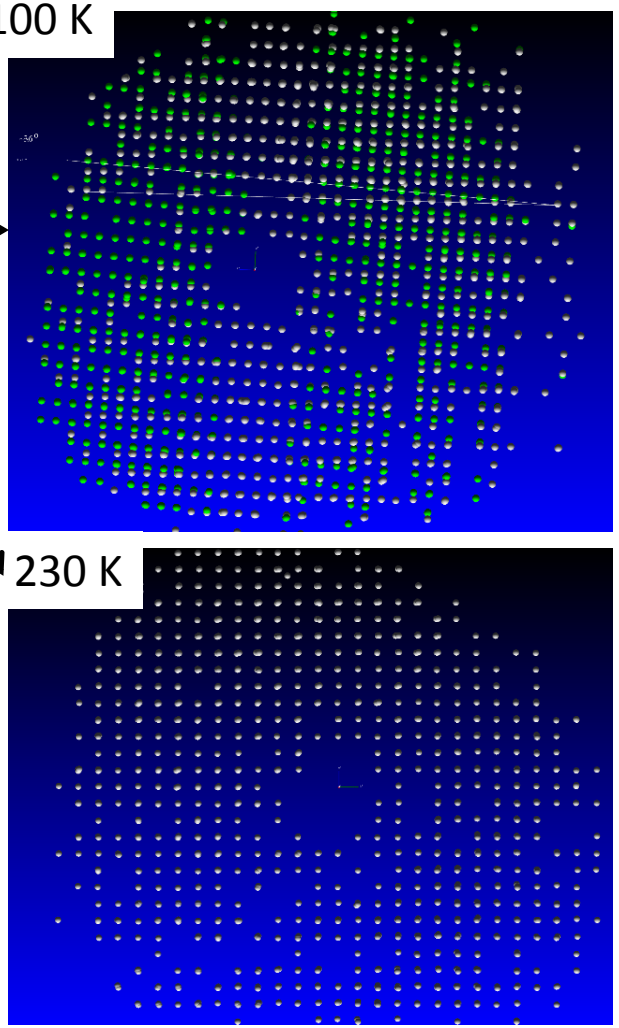
Results and Discussion II



Temperature dependency of cell angles in **TQ** iodide



DOS diagram of low-temperature **TQ** phase with non-equivalent sulfur atoms



Diffraction peaks in reverse space of different domain types within one single crystal of **TQ**

Methods

- DFT/WC1LYP/TZVP (DZVP for I) CRYSTAL17 program
- Huber 3 diffractometer with a 60° offset angle and Pilatus3X 1M (CdTe) in temperature range from 293 (1) to 100 (1) K using an Oxford Cryojet.

Conclusions

- Low temperature polymorphic transition of **TQ** iodide was observed at 173 K with the symmetry reduction from P21/c to P-1.
- Domain structure of single crystal is observed via X-ray diffraction under cooling.
- Theoretic band gap estimation is 2.463 eV (**TQ**) and 2.533 (**OQ**) eV. Non-equivalence of sulfur atoms is found in low-temperature **TQ** phase in values of DOS projections.

Acknowledgments

This work was supported by the Ministry of Science and High Education of the Russian Federation, FENU 2020-0019

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