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THE RELATIONSHIPS BETWEEN IODINE COVALENT AND HALOGEN BONDS FEATURES

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Identification of the iodine molecule in the multicomponent organic compounds, in particular in co-crystals of sulfur-containing hydrocarbons is solved effectively by the Raman spectroscopy method [1]. This method is most informative with respect to the properties of iodine bonds and is sensitive to changes under the influence of noncovalent interactions. The aims of our research were to demonstrate the relationships between the strength of the I-I covalent and S…I halogen bonds and between the bond features (such as electron delocalization indices) and experimental and calculated Raman spectra for iodine- and sulfur-containing organic compounds. The objects of research were structures with CSD refcodes DAYBOU [2], DIJYUR [3], HAFLAC, HAFLEG [4], PEJKIY [5], TIJLUU [6], WURGEW [7].

Localization of the equilibrium geometry and the Raman spectra calculations were performed using Firefly 8.0.1 [8] (B3LYP/6-31G**) for isolated complexes and using CRYSTAL14 [9] (B3LYP/DZVP) for crystals. The calculations utilized the supercomputer resources of South Ural State University [10]. Local characteristics of the electron density $\rho(r_b)$ at the bond critical points for I-I and S…I interactions were obtained in the approximation for isolated complexes and using periodic boundary conditions for crystals. Programs AIMALL [11] and TOPOND14 [12] were used.

The weakening of the I-I covalent bond, fixed in the Raman spectra, is associated with strengthening of the S…I halogen bond, in which I_2 is involved. It is evidenced by the shift in the wave numbers of the valent vibration ν(I-I) to the region of lower values. Therefore, we believe that the shift of the bound iodine vibration band to lower wavenumbers, in comparison to crystalline iodine, indirectly characterizes the strength of the halogen bond. The electron density characteristics obtained by QTAIM at the bond critical points $\rho(r_b)$ illustrate the quantitative relationship between the weakening of I-I bonds and the strengthening of the halogen bonds S…I.

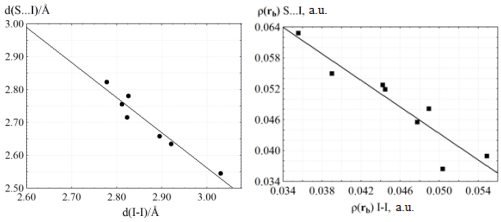

Figure 1. The relationships between: a) the experimentally observed bond lengths I-I and S…I in crystals; b) the calculated electron density characteristics for the I-I and S…I

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