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BOOK OF ABSTRACTS

HALOGEN BONDING IN DIPHENYLIODONIUM DICHROMATE

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Halogen bonding (XB) — together with other types of noncovalent interactions — has exponentially emerged as an important concept in polymer science, supramolecular design, and crystal engineering. Modern XB-based crystal engineering mainly utilizes monovalent halogen organic compounds, exhibiting one σ-hole per one halogen(I) site. In the vast majority of cases, these atoms form two-center XBs. A suitable alternative to the polyhalogenated compounds is a diaryliodonium salt bearing I(III) site as a double σ-hole donor. A suitable XB-accepting synthon for these species should provide a number of nucleophilic sites. In this work, we chose the dichromate anion as such XB-accepting building block.

Complex $[Ph_2I]_2[Cr_2O_7]$ (Ph = C_6H_5) was obtained by ion exchange reaction between water solutions of potassium dichromate and diphenyliodonium triflate. Single crystals of the complex suitable for X-ray diffraction (XRD) were released from the water by slow evaporation of the solvent at room temperature in air. Inspection of the XRD data of the obtained crystals revealed the presence of interionic C–I···O XBs between iodine atoms of the cations and nucleophilic oxygen atoms of $[Cr_2O_7]^{2-}$ anion, where the latter acts as XB-accepting synthon forming XBs by two O-centers (Fig. 1a). The distances between the iodine and oxygen atoms are shorter than the appropriate sum of the van der Waals radii, and the angles ∠(C–I···O) around I centers fulfill to the IUPAC criteria for XBs. Other noncovalent interactions are presented by C–I···C XBs between the iodine centers and C^{Ar} atoms of the cations. The observed contacts together form 2D chains in the crystal structure of $[Ph_2I]_2[Cr_2O_7]$ (Fig. 1b).

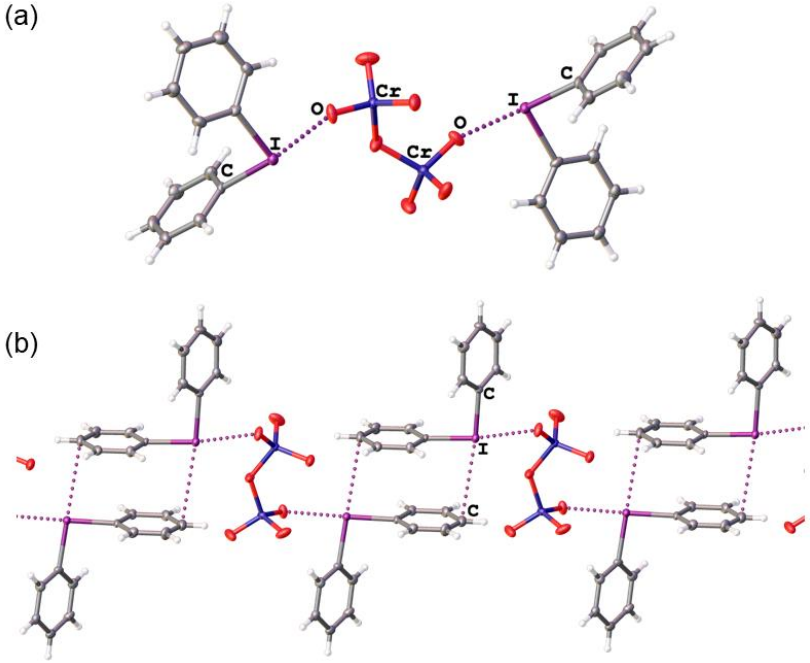

Figure 1. The C–I···O XBs (a) and 2D chains (b) in the crystal structure of $[Ph_2I]_2[Cr_2O_7]$. The XBs are given by dotted lines and thermal ellipsoids are shown with the 50% probability.

We examined the geometric and energetic features of the detected contacts using the combined experimental and theoretical approaches. The noncovalent nature of the interactions was confirmed theoretically by the DFT calculations via several computational tools (QTAIM, DFT energies, NCI and EDD plots, MEP surfaces, ELF analysis). In this work, we found the first example of the XB that involves oxygen atoms of the dichromate anion acting as XB acceptor toward iodine(III) centers of the diphenyliodonium cations behave as σ-hole donors.