

MS31 Unconventional interactions or symmetries for optimized and new properties, including chirality

MS31-04

π - π^* charge transfer between an iodide anion and a quinoid ring

K. Močanov ¹, V. Milašinović ¹, V. Vuković ², A. Krawczuk ³, C. Hennig ⁴, M. Bodensteiner ²

¹Rudjer Bošković Institute - Zagreb (Croatia), ²Universität Regensburg - Regensburg (Germany), ³Universität Goettingen - Goettingen (Germany), ⁴ESRF - Grenoble (France)

Abstract

π -hole interaction between an iodide anion and a quinoid ring in a co crystal of 3-chloro-*N*-methylpyridinium iodide with tetrabromoquinone (**3-Cl-N-MePy-I-Br₄Q**) involves a sandwich-like I⁻⋯quinone⋯I⁻ moiety with close contacts between the iodide anion and carbon skeleton of the quinoid ring (Fig 1). Distance between the iodide and the ring mean plane is 3.73 Å, which is slightly shorter than the sum of van der Waals radii for C and I. This close contact forms because the quinoid ring with four electron-withdrawing substituents is severely electron-depleted, resulting in a large π -hole at the carbonyl C atom [1,2]. In the studied case there is also a partial electron transfer between the iodide and the quinone which is noted by a change of colour: the neutral quinone is yellow, while the co-crystals and the semiquinone crystals are black.

This unusual interaction is studied by quantum crystallography, combining X-ray charge density with quantum chemical modelling; a study under a wide range of conditions involves variable-temperature crystallography (80 - 400 K) and high-pressure crystallography.

The interaction involves an π - π^* charge transfer, so the quinoid ring has a partial negative charge (estimated to 0.08 - 0.11 e) and a partial radical character. The X-ray charge density study revealed two symmetry-independent bonding critical points between the iodide and carbon atoms of the ring with maximum electron density of 0.065 e Å⁻³, which were reproduced by quantum chemical modelling. Energy of the interaction is estimated to -13 kcal mol⁻¹, which is comparable to hydrogen bonding; it is dominantly of electrostatic nature, with a considerable dispersion component.

References

[1] K. Močanov, G. Mali, J. Grdadolnik, J. Stare, V. Stilinovič, B. Kojić-Prodč (2018). *Cryst. Growth Des.*, **18**, 5182-5193.

[2] V. Milašinović, K. Močanov (2021). *CrystEngComm*, **21**, 2304-2315.

A sandwich-like IBr₄Q-unit.

