Poster

The role of multicentric pancake bond in 2D arrays of TCNQ radicals in crystals

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Multicentric covalent bond (*pancake bond*), which is common in crystals of planar organic radicals, is a type of π-interaction that involves spin pairing and formation of covalent bond between radical rings. Energy of such interaction is comparable to the energy of strong hydrogen bond and it can be as high as −20 kcal mol-1.[1] Study of these interactions involves exploring the nature of the chemical bond as well as developing the design of organic magnets and conductive materials since pronounced π-stacking motifs contribute to properties of the material, like electric conductivity and magnetism. [2]

7,7,8,8-tetracyanoquinodimethane (TCNQ) is one of the most stable planar organic radicals which is stabilized by four electron-withdrawing cyano groups. [3] It is a strong electron acceptor and therefore very suitable for the formation of salts. Hence, crystals of salts with stacks of planar organic radicals which involve pancake bond are of great interest in supramolecular chemistry as the foundation of new materials. [2]

In this work, we present a study of strong π–interactions, pancake bonds, in four different compounds: TCNQ radical anion salts with 1,4-dimethyl-DABCO (1), *N,N*-dipyridylmethanium (2), 4-benzoyl-N-methylpyridinium (3) [3] and *N,N'*-dimethyl-4,4'-bipyridinium (4) [3]. Prepared compounds were thoroughly investigated by quantum crystallographic methods which reveal fine details of crystal and electronic structure. [4] TCNQ radical anions form complex patterns of dimers in 1, trimers in 4 and tetramers in 2 and 3. Structures with trimers and tetramers involve 2D arrays of TCNQ radicals. Trimers and tetramers form layers by stacking in brick wall pattern. Such patterns and short distances between rings enable extending the *pancake bond* and long-range interactions which is the core of the properties of materials. [3] Electron density refinement reveals bond critical points between rings of radicals in all structures which is one of the confirmations of the presence of *pancake bond*.

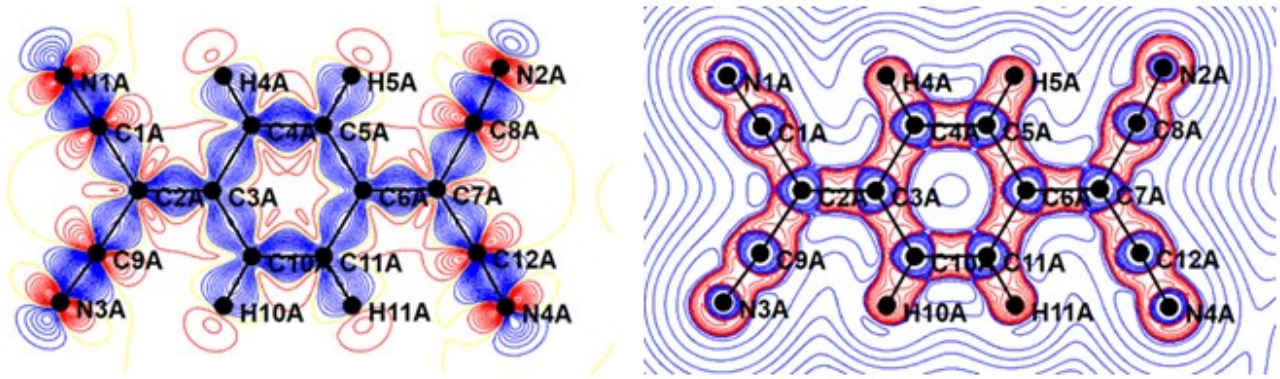

Figure 1. Deformation density maps in the mean plane of one TCNQ moiety in the crystal structure of 2 (left) and Laplacian of electron density in the mean plane of corresponding TCNQ moiety (right).

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[2] Ratera, I. & Veciana, J. (2012). Chem. Soc. Rev. 41, 303–349.

[3] Molčanov K., Milašinović V., Kojić-Prodić B., Maltar-Strmečki N., You J., Šantić A., Kanižaj L., Stilinović V. & Fotović L. (2022) IUCrJ. 9, 449–467.

[4] Milašinović, V., Molčanov, K., Krawczuk, A., Bogdanov, N.E., Zakharov, B.A., Boldyreva, E. V., Jelsch, C. & Kojić-Prodić, B. (2021). IUCrJ. 8, 644–654.

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