

Use of transferrable multipoles to extend the range of X-ray charge density study to variable-temperature and high pressure

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X-ray charge density is the most powerful experimental method to study interatomic and intermolecular interactions, such as two-electron multicentric (2e/mc) covalent bonding [1-3]. However, it is limited to high-quality crystals and good enough data can be collected only at low temperature and ambient pressure. In order to gain more information on behaviour of novel 2e/mc interactions, a broader range of conditions (temperatures and pressures) are required. These are normally limited to resolutions of 0.8 Å or lower and are thus unsuitable for multipolar refinement and study of charge density.

If good high-resolution diffraction data are not available, charge density can be obtained using transferrable multipoles from optimal data set [4]. Thus, multipoles obtained by multipolar refinement of high-resolution data can be transferred to lower-resolution variable-temperature (VT) and high pressure (HP) diffraction data, allowing us to study charge density at a broad range of conditions. We have tested this method in study of 2e/mc bonding in 4-cyano-*N*-methylpyridinium salt of 5,6-dichloro-2,3-dicyanosemiquinone radical anion ([4-CN-*N*-MePy]⁺[DDQ]⁻), which we have recently studied by VT and HP X-ray diffraction [5] and by X-ray charge density [6]. Multipolar parameters obtained by a multipolar refinement of high-resolution data measured at 100 K [6] were thus transferred to lower-resolution VT and HP data; the results and their validity are discussed. Since 2e/mc is an intermolecular interaction, which involves a non-localised electron pair, its electron density is low; so its study is less reliable than that of stronger intramolecular covalent bonding. Therefore, our transferred-multipole models must satisfy the following three criteria to be considered valid:

- (i) overall reduction of disagreement *R*-factors and residual density compared to regular spherical refinement;
- (ii) electron densities should follow a clearly defined trend;
- (iii) experimentally obtained electron densities should be in a good agreement with theoretical ones.

[1] Kertesz, M. (2018). *Chem. Eur. J.*, **25**, 400-416.

[2] Molčanov, K. & Kojić-Prodić, B. (2019). *IUCrJ*, **6**, 156-166.

[3] Molčanov, K.; Milašinović, V. & Kojić-Prodić, B. (2019). *Cryst. Growth Des.*, **19**, 5967-5980.

[4] Domagała, S.; B. Fournier, D. Liebschner, B. Guillot, Jelsch, C. (2012). *Acta Cryst. A.*, **A68**, 337-351.

[5] Bogdanov, N. E.; Milašinović, V.; Zahkarov, B.; Boldyreva, E. V.; Molčanov, K. (2020). *Acta Cryst. B.*, **B76**, manuscript XK5067, in print.

[6] Milašinović, V.; Krawczuk, A.; Kojić-Prodić, B.; Molčanov, K. (2020). Manuscript in preparation.

Keywords: charge density; high pressure; variable temperature; transferrable multipoles; two-electron multicentric bonding

This work was funded by the Croatian Science Foundation, grant no. IP-2019-04-4674.