Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 58-61

Halogen *vs.* ionic bonding: an unusual isomorphism between the neutral $(C_5Me_5)_2Fe/C_2I_2$ cocrystal and ionic $[(C_5Me_5)_2Fe]Br_3$ crystal

Yury V. Torubaev, Ivan V. Skabitsky, Georgy A. Saratov and Petr Y. Barzilovich

Experimental details

Solvents were purified, dried and distilled under a nitrogen atmosphere prior to use. Commercial $(Me_5C_5)_2Fe$ was recrystallized before use; I_2, Br_2 and acetic acid used without additional purification. Iodoacetylene (C_2I_2) was prepared following reported procedure [1].

Preparation of the crystals of $(Me_5C_5)_2Fe/C_2I_2$ (**1**)

0.028g (~0.1mmol) of C_2I_2 and 0.033g (~0.1mmol) of $(Me_5C_5)_2Fe$ were dissolved in 0.3ml of hot heptane in a 5 mm test tube under moderate heating to assure complete dissolving of the starting materials. Orange reaction mixture was allowed to cool down to room temperature and evaporate slowly for 12 hours. Resulting yellow prismatic crystals where separated from mother liquor, washed quickly with cold pentane, dried in a stream of argon and used for single crystal XRD analysis.

Crystal structure determination

Bruker AXS Smart APEX CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (0.71070 Å) was used for the cell determination and intensity data collection for compound **1**. The data were collected by the standard 'phi-omega scan techniques and were scaled and reduced using SHELXL-97 software. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXL-97 and Olex2 software [2], [3]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model. Atomic coordinates and other structural parameters of **1** have been deposited with the Cambridge Crystallographic Data Center (CCDC 1528250).

Computational details

Intermolecular interaction energy calculation and subsequent, Hierfield surface and energy frameworks generation were performed using Crystal Explorer 17.5 (TONTO, B3LYP-DGDZVP) [4] for all unique molecular pairs in the first coordination sphere of a molecule (3.8Å), using experimental crystal geometries. For the cocrystals **1 - 2** the above procedure has been performed twice – separately for each co-former molecule in the asymmetric unit [5].

Electrical conductivity measurements

The conductivity was measured on a Z2000 impedance meter (LTD “Elins”) (operating frequencies were in the range from 2 MHz—1 Hz) and potentiostat-galvanostat P8 (LTD “Elins”) using Pt/solid electrolyte/Pt symmetrical cells. The amplitude of the external alternating signal was 80—100 mV depending on the impedance of the sample without direct current polarization. The frequency dependence of the resistance was analyzed by the graphical-analytical method [6]. The samples placed in the cells with nitrogen-atmosphere were prepared as pressed (~ 8 atm) pellets 1.1—1.3 mm thick and 5 mm in diameter. It should be noted that a substantial contribution of the electrode impedance to the cell resistance was observed in none of the cases. This conclusion was supported by the fact that the impedance was independent of the nature of the electrodes (carbon paper, platinum).

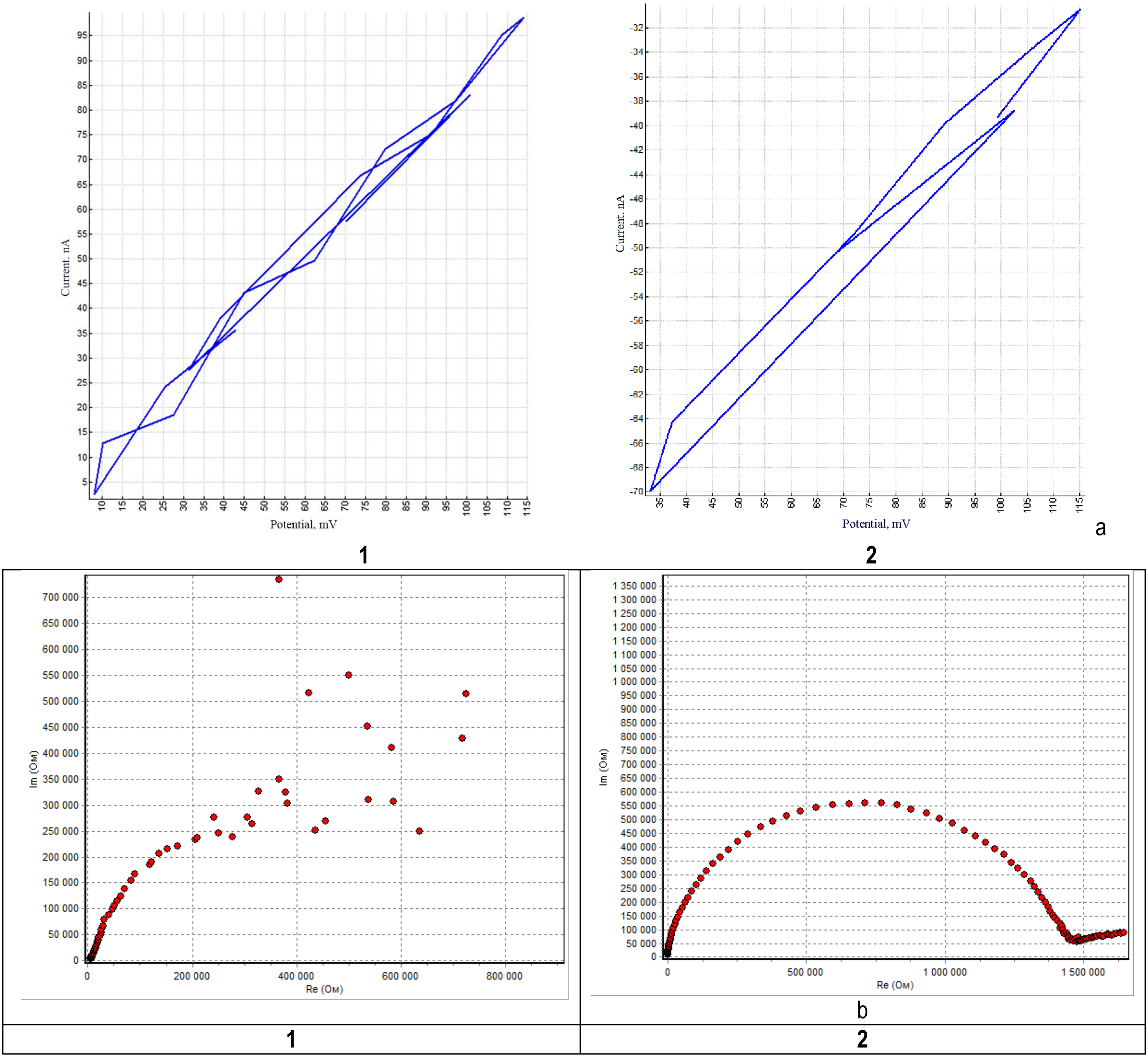


Figure S1 Electric conductivity measurements of **1** and **2**. a– CVA (50 mV/s), current *vs* potential for **1** and **2**, b – the impedance spectrum Im(Om) *vs* Re(Om) for **1** and **2.**

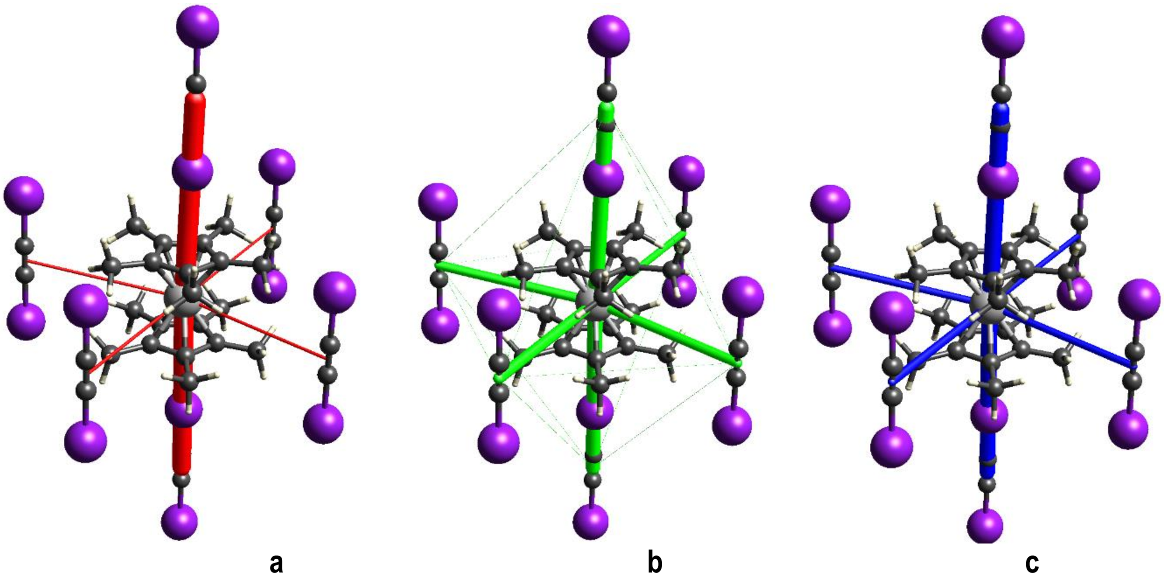


Figure S2 Graphic presentation of electrostatic (red) and dispersion (green) contribution into the total energy of intermolecular interactions (blue) in **1** (a-c)**.** See **Table S1** below for energy values.

Table S1 Interaction Energies CE-B3LYP/DGDZVP (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor Table S1a below)

	R	E_ele	E_pol	E_dis	E_rep	E_tot
apical	7.42	-33.3	-4.0	-31.7	58.9	-29.4
equatorial	8.42	-2.9	-0.3	-23.8	12.6	-16.2
	6.22	-5.2	-0.2	-20.0	16.2	-13.0
	6.05	-5.3	-0.2	-22.6	16.7	-15.1
	6.22	-5.2	-0.2	-20.0	16.2	-13.0

Table S1a Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017) [7]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP	1.057	0.740	0.871	0.618

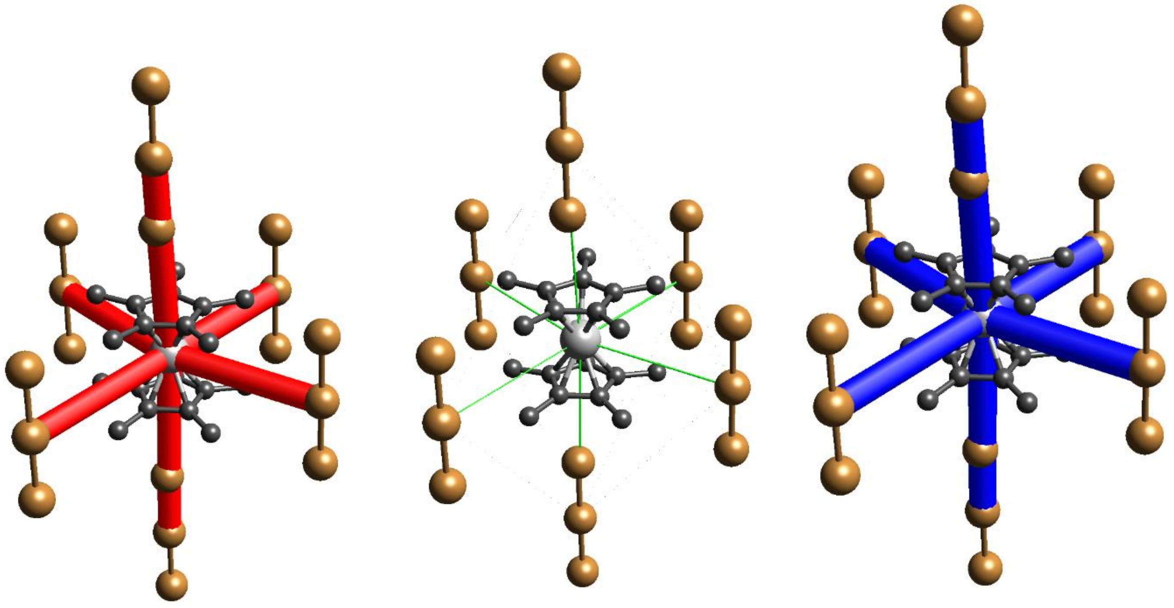


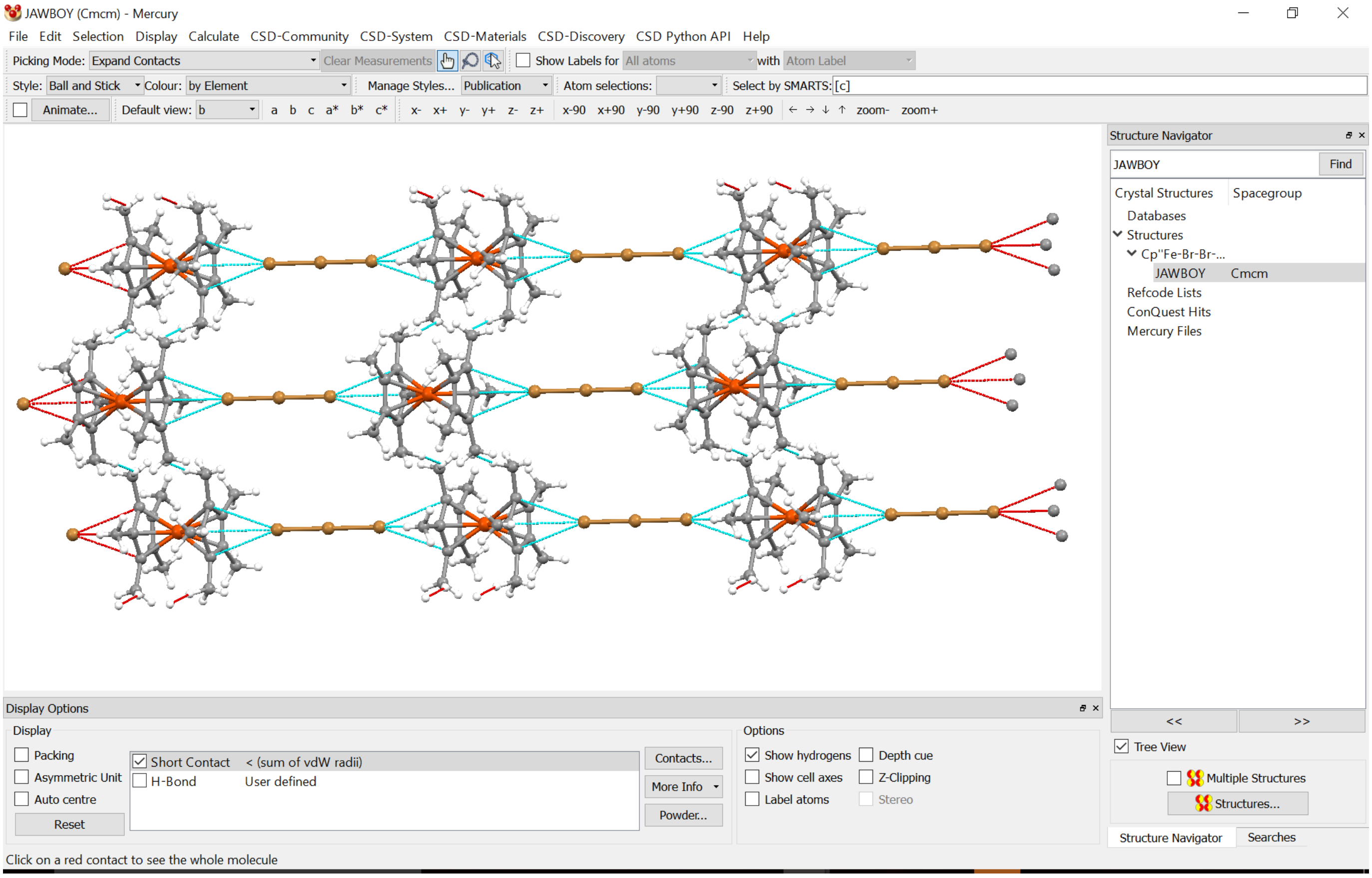
Figure S3 Graphic presentation of electrostatic (red) and dispersion (green) contribution into the total energy of intermolecular interactions (blue) in **2**(a-c). See **Table S2** below for energy values

Table S2 Interaction Energies CE-B3LYP/DGDZVP (kJ/mol)
R is the distance between molecular centroids (mean atomic position) in Å.
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor **Table S2a** below)

	R	E_ele	E_pol	E_dis	E_rep	E_tot
apical	7.59	-208.1	-32.3	-20.9	31.7	-242.6
equatorial	6.04	-216.5	-33.0	-19.5	19.5	-258.3
	6.55	-203.6	-26.4	-13.6	9.3	-240.8
	5.81	-227.9	-37.8	-24.3	25.5	-274.3

Table S2a Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017) [7]

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-B3LYP ... B3LYP/DGDZVP	1.057	0.740	0.871	0.618


JAWBOY (Cmcm) - Mercury

Picking Mode: Expand Contacts

☐ Show Labels for All atoms with Atom Label

Style: Ball and Stick

Colour: by Element

Manage Styles... Publication

Select by SMARTS: [c]

☐ Animate...

Default view: b

Structure Navigator: JAWBOY

Crystal Structures Spacegroup
Databases
Structures
Cp''Fe-Br-Br-...
JAWBOY Cmcm
Refcode Lists
ConQuest Hits
Mercury Files

Display Options

Display: ☐ Packing ☐ Asymmetric Unit ☐ Auto centre

☑ Short Contact < (sum of vdW radii)
☐ H-Bond User defined

Options: ☑ Show hydrogens ☐ Depth cue ☐ Show cell axes ☐ Z-Clipping ☐ Label atoms ☐ Stereo

☑ Tree View

☐ Multiple Structures

Click on a red contact to see the whole molecule

Figure S4 Short contacts in the fragment of the solid-state structure of **2**. Notice the distinct chained structure.

References

1. A. Webb, J. E. Klijn, P. A. Hill, J. L. Bennett and N. S. Goroff, *J. Org. Chem.*, 2004, **69**, 660–664.

2. G.M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.

3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

4. M. J. Turner, S. P. Thomas, M. W. Shi, D. Jayatilaka and M. A. Spackman, *Chem. Commun.*, 2015, **51**, 3691–3928.

5. http://130.95.176.70/wiki/index.php?title=Intermolecular_Interaction_Energies.

6. E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy: Theory, Experiment, and Applications*, 3rd Edn, John Wiley & Sons, 2018.

7. C. F. Mackenzie, P. R. Spackman, D. Jayatilaka and M. A. Spackman, *IUCrJ*, 2017, **4,** 575–587.