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Multicentric two-electron covalent bonding (pancake bonding) between semiquinone radicals determines bulk properties

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Fine details of stacking interactions in three different types of π-stacked tetrachlorosemiquinone radical anions (Cl_4Q) were studied by a combination of X-ray charge density, quantum chemical computation and atoms-in-molecules (AIM) analysis: 1) stacks of pancake-bonded radical dimers in triclinic polymorph of *N*-MePy·Cl_4Q (*N*-MePy = *N*-methylpyridinium cation), 2) stacks of trimers of partially charged semiquinones in $[4\text{-damp}])_2[Cl_4Q]_3$ (4-damp = 4-dimethylamino-*N*-methylpyridinium) and 3) stacks of equidistant radicals in orthorhombic polymorph of *N*-MePy·Cl_4Q. For the first time, we provide experimental evidence (based on X-ray charge density) of two-electron multicentric covalent bonding (pancake bonding) between the radicals.

Typical pancake-bonded radical dimers in 1) are characterised by short interplanar distance (2.86 Å) and multiple bonding (3,-1) critical points between the rings with maximum electron density exceeding 0.095 e $Å^{-3}$; in addition, a (3,+3) critical point (local minimum of electron density) was also found, indicating a cage-like electronic structure. The covalent contribution to total interaction in a dimer was calculated to be -9.4 kcal mol^{-1}. Between the dimers, interplanar separation is 3.60 Å and only negligible electron density is found.

In trimers there are two electrons shared between three closely interacting rings (interplanar separations are *ca*. 2.84 Å), and (3,-1) bonding critical points are found with maximum electron density of 0.077 e $Å^{-3}$; there are also two (3,+3) local minima [1]. The calculated covalent contribution is -6.8 kcal mol^{-1}

Maximum electron density between the rings in a stack of equidistant radicals (interplanar separation of 3.17 Å) is much lower, 0.050 e $Å^{-3}$, and there is no local minimum of electron density. However, the HOMO orbitals extend between the rings, and the calculated covalent contribution is -2.9 kcal mol^{-1}. This compound is a 1D semiconductor [2,3], and its semiconductivity is explained by pancake bonding extending along the stack.

References:

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