

MS22-P07 | QUINOID DIANION FORMING A LONE-PAIR PI-HOLE CONTACT

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Lone pair (lp)··· π interactions are quite rare and little studied type of π -hole interactions. They consist of a close contact which occurs between a lone pair and a π -hole of a planar ring. So far, the only studied examples involved aromatic rings, usually electron-depleted. Our study of lithium 2,5-dihydroxyquinonate DMSO solvate ($\text{Li}_2\text{DHQ}\cdot\text{DMSO}$) is thus the first instance of a lp··· π contact with (a) a non-aromatic and (b) an anionic ring. Distances between the sulphur atom and the ring centroid is 3.46 Å, and the closest S···C distance is only 3.25 Å, significantly shorter than the sum of van der Waals radii (3.66 Å).

This unprecedented interaction has been studied by X-ray charge density, to gain more insight into its nature. Topology of electron density revealed a bond critical point (3,-1) between the sulphur and a carbon atom of the ring (S1···C2) with maximum electron density of 0.066(2) e Å⁻³. These results are reproduced well by theoretical computations (periodic DFT in Crystal14, B3LYP/6-31G(d,p)); the same critical point is found with almost the same electron density value (0.063 e Å⁻³).

These results point out to an attractive interaction between the lone pair of the non-planar sulphur atom and the π -system of quinoid dianion.