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Supporting information for article:

The nature of π-hole interaction between iodide anion and quinoid ring in the crystalline state

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S1. Residual densities and other details on refinement

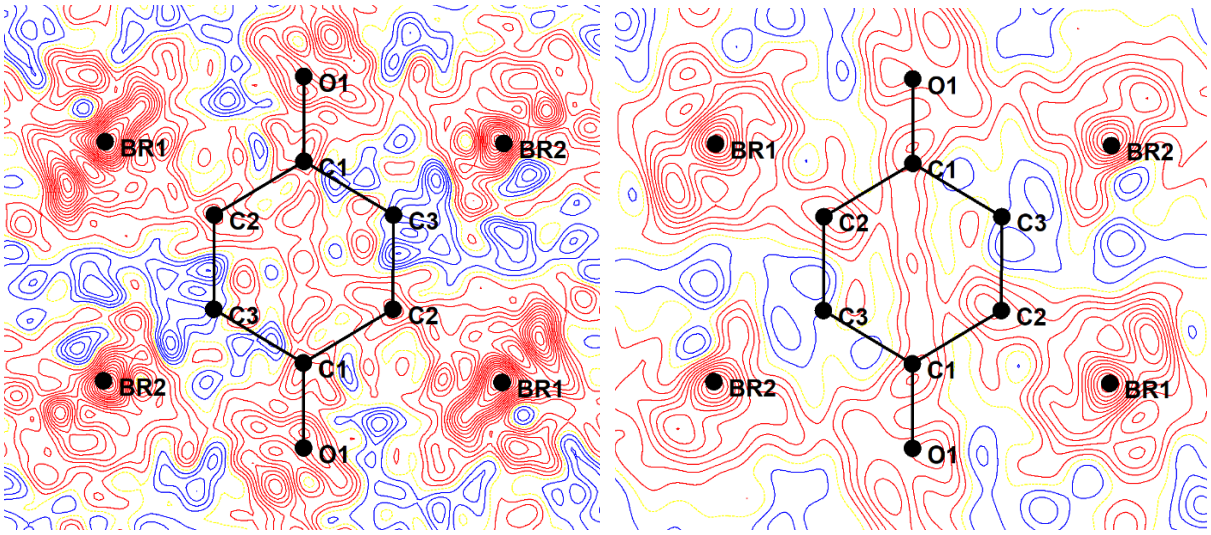

Figure S1 Residual density in the mean plane of Br_4Q with a) all reflections used and b) only low-angle reflections (sin θ / λ < 0.7 Å^{-1}) used. Positive density is shown in blue and negative in red; yellow dotted lines represent zero density. The spacing between contours is of 0.05 eÅ^{-3}.

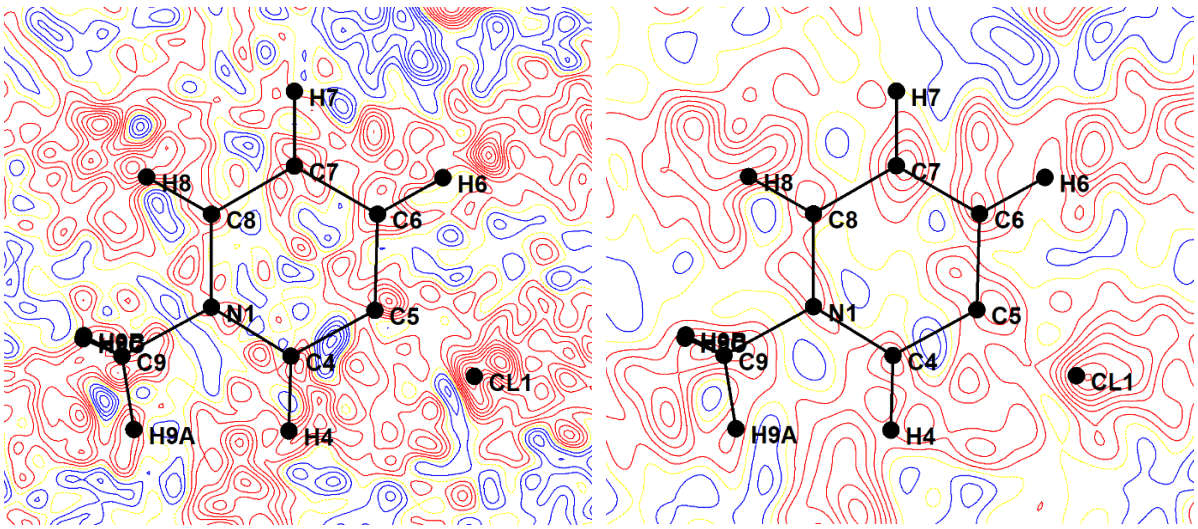

Figure S2 Residual density in the mean plane of 3-Cl-*N*-MePy cation with a) all reflections used and b) only low-angle reflections (s < 0.7 Å^{-1}) used. Positive density is shown in blue and negative in red; yellow dotted lines represent zero density. The spacing between contours is of 0.05 eÅ^{-3}.

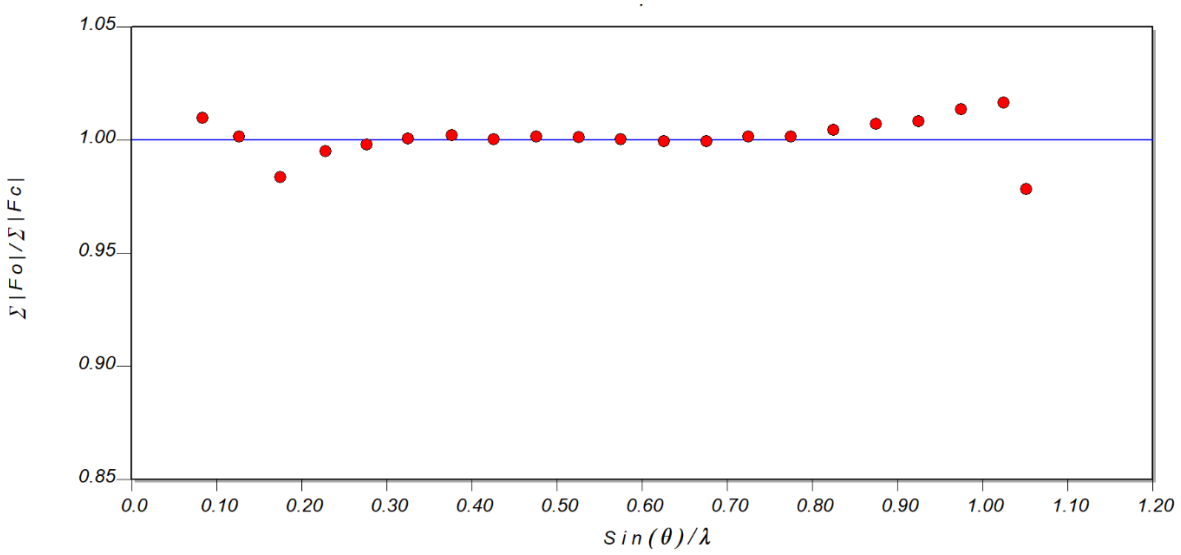

Figure S3 XDRK plot showing the fit of $<Y_{obs}>$ *vs.* $<Y_{calc}>$ as a function of resolution.

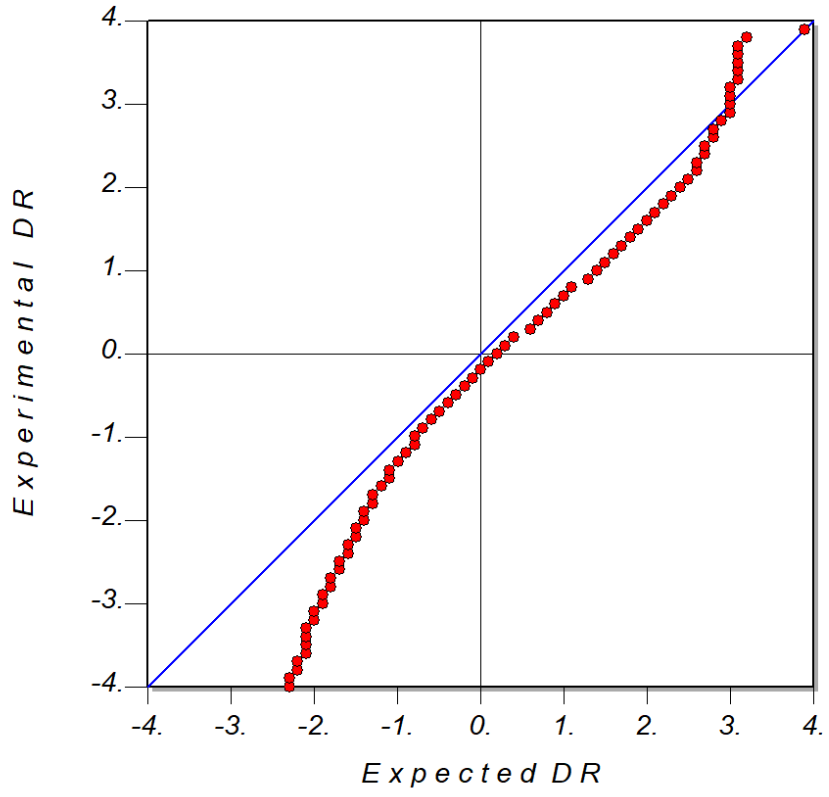

Figure S4 XDRK plot showing the expected and experimental $Y_{obs} - Y_{calc}$ data profile.

S2. ORTEPs, deformation densities, Laplacians and electrostatic potential

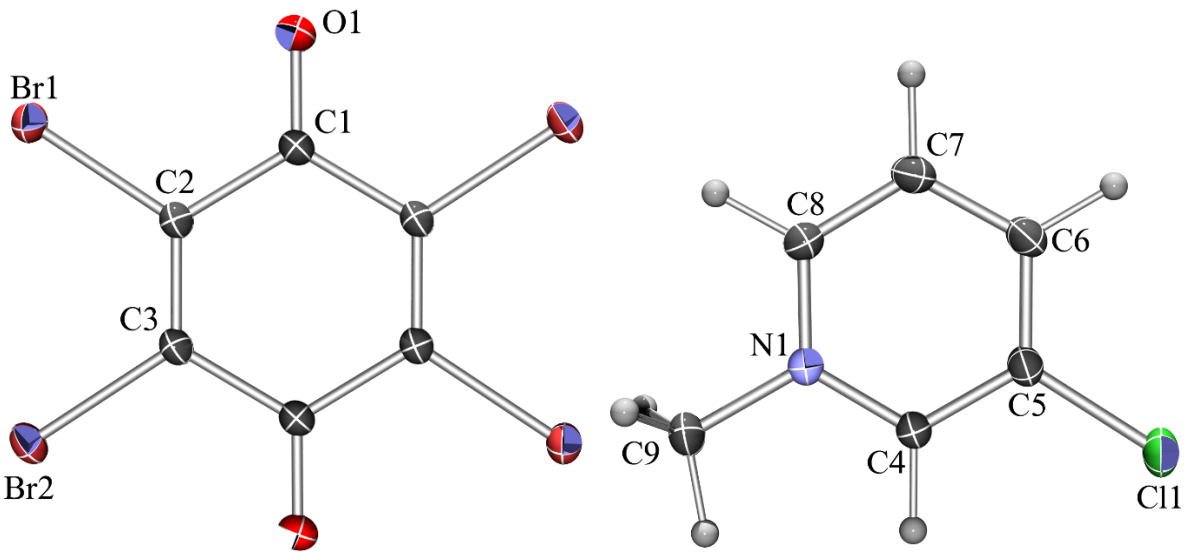

Figure S5 ORTEP-3 drawings of of a) Br_4Q and b) 3-Cl-*N*-MePy cation. Displacement ellipsoids are drawn for the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

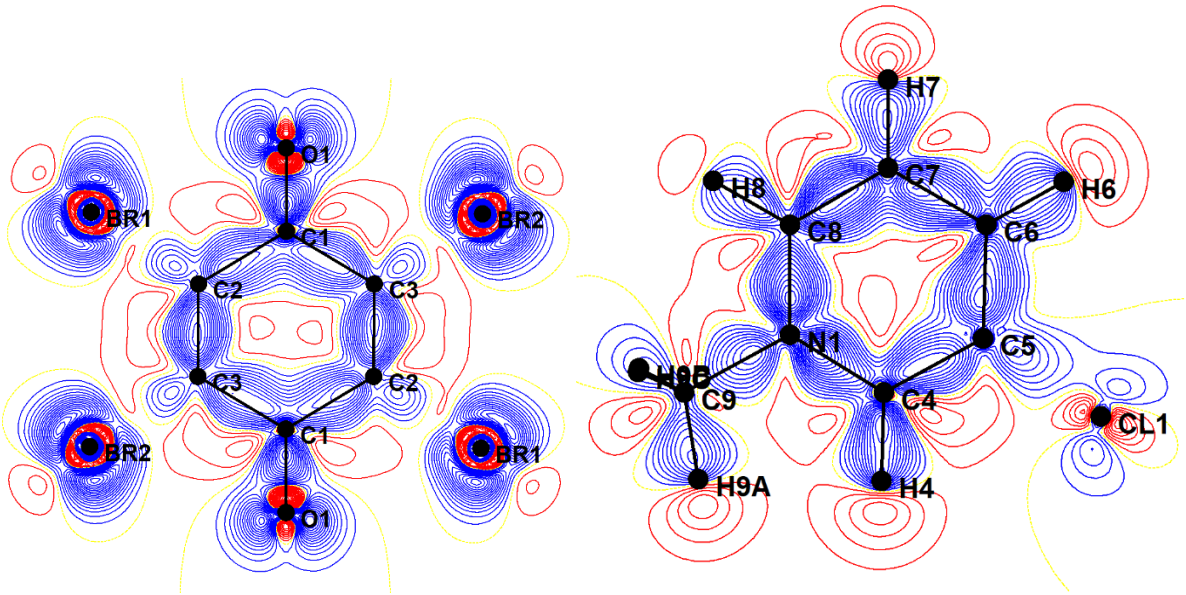

Figure S6 Deformation density maps in the mean planes of a) Br_4Q and b) 3-Cl-*N*-MePy cation. The spacing between contours is of 0.05 e $Å^{-3}$; the positive density is blue, the negative is red and the zero contour is drawn as a yellow dotted line.

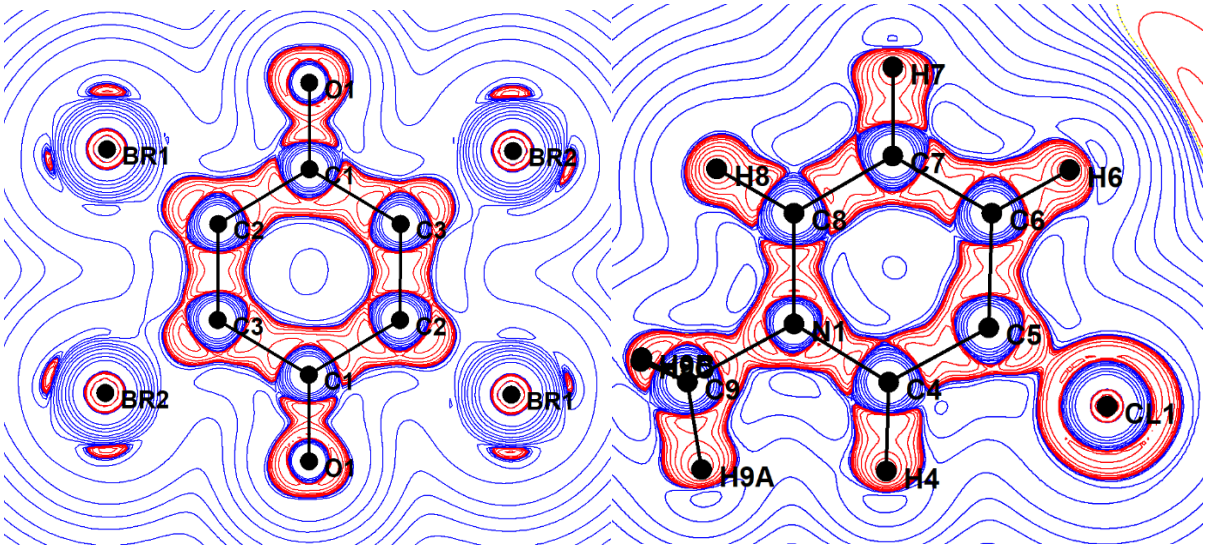

Figure S7 Laplacian of electron density plotted in the mean planes of a) Br_4Q and b) 3-Cl-*N*-MePy cation. The contours are drawn for 2, 4, $8\cdot10^n$ e Å^{-5}, n = –3…2; positive Laplacian is blue and negative is red.

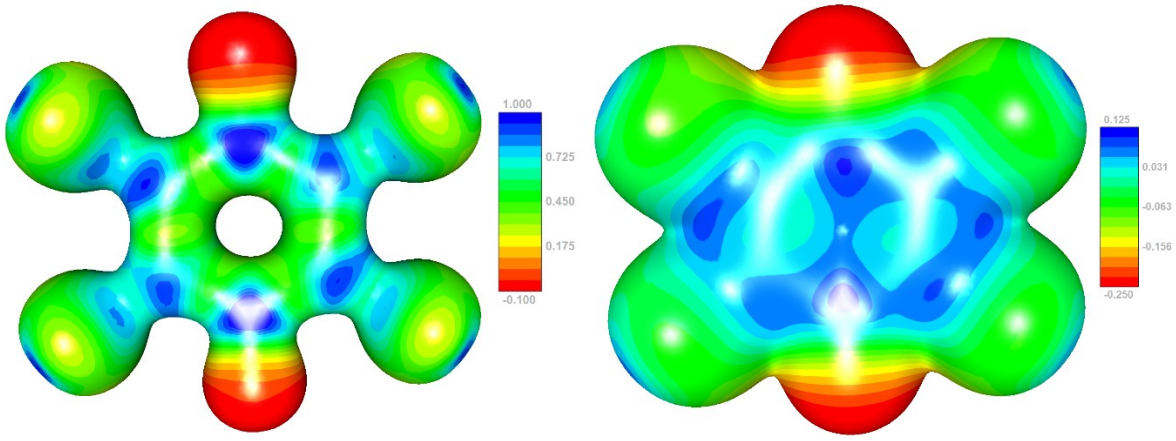

Figure S8 Electrostatic potential of Br4Q molecule plotted onto an electron density isosurface of a) 0.5 e Å^{-3} and b) 0.05 e Å^{-3}.

S3. Other geometric data

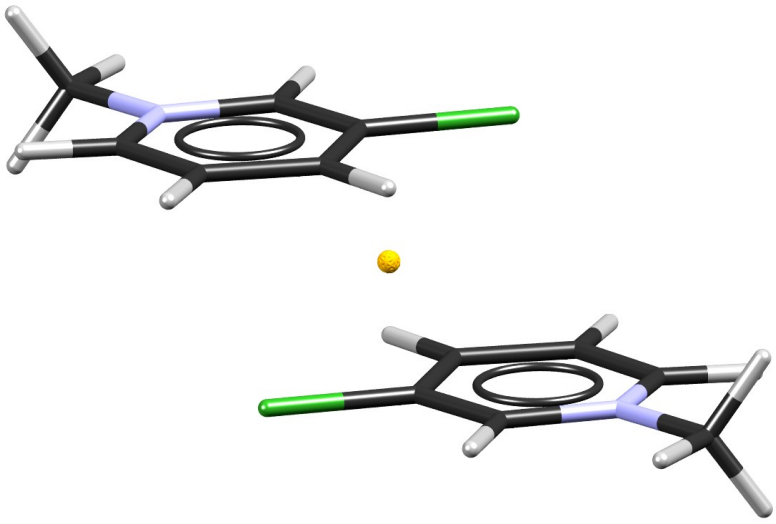

Figure S9 A pair of antiparallel stacked 3-chloro-*N*-methylpyridinium cations related by an inversion centre (shown as a yellow sphere).

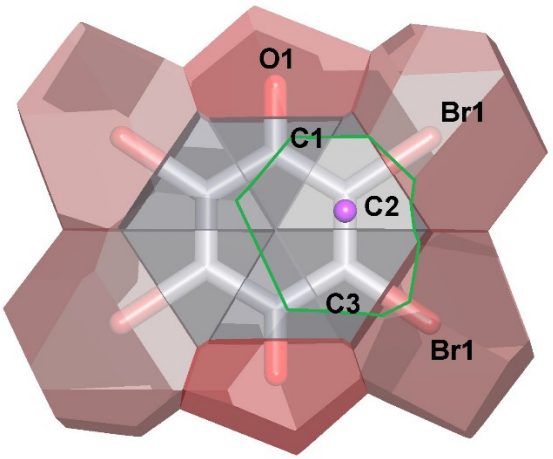

Figure S10 Surface of a Br_4Q molecule comprised of VDPs. Area corresponding to the contact with the iodide (shown as a purple sphere near C2) is highlighted in green.

S4. Topology of electron density

Table S1 Topology of electron density in Br_4Q, derived from electron-density after multipole refinement and periodic calculations (in italic).

Bond	Length (Å)	Electron Density (eÅ^{-3}) ρ_{cp}	Laplacian (eÅ^{-3})	Ellipticity	Bond order n_{topo}
C1−O1	1.2130(13)	2.874 *2.675*	−29.4 *−2.410*	0.17	1.50
C1−C2	1.4909(10)	1.790 *1.769*	−12.3 *−14.459*	0.10	0.86
C2−C3	1.3462(9)	2.307 *2.201*	−22.5 *−19.038*	0.27	1.65
C3−C1	1.4898(10)	1.840 *1.773*	−13.1 *−14.459*	0.09	0.90
C2−Br1	1.8778(7)	1.001 *1.131*	1.7 *−4.097*	0.26	
C3−Br2	1.8767(6)	0.990 *1.134*	1.7 *−4.097*	0.13	

Table S2 Topology of electron density in 3-Cl-*N*-MePy cation, derived from electron-density after multipole refinement and periodic calculations (in italic).

Bond	Length (Å)	Electron Density (eÅ^{-3}) ρ_{cp}	Laplacian (eÅ^{-3})	Ellipticity	Bond order n_{topo}
N1−C4	1.3497(9)	2.256 *2.124*	−21.7 *−15.905*	0.16	1.30
N1−C8	1.3469(10)	2.356 *2.132*	−26.0 *−15.423*	0.21	1.29
N1−C9	1.4745(11)	1.749	−10.6	0.04	1.04

		1.603	*−10.603*		
C4−C5	1.3833(10)	2.049 *2.103*	−18.5 *−18.315*	0.15	1.29
C5−C6	1.3924(11)	2.121 *2.054*	−17.0 *−17.592*	0.18	1.47
C6−C7	1.3889(12)	2.119 *2.041*	−19.9 *−17.110*	0.19	1.29
C7−C8	1.3865(12)	2.272 *2.083*	−21.1 *−18.074*	0.17	1.50
C5−Cl1	1.7262(7)	1.401 *1.346*	−1.3 *−6.266*	0.08	
C4−H4	1.08	1.820 *1.892*	−19.2 *−22.412*	0.09	0.90
C6−H6	1.08	1.701 *1.869*	−16.9 *−21.201*	0.03	0.99
C7−H7	1.08	1.681 *1.864*	−19.8 *−21.063*	0.09	0.80
C8−H8	1.08	1.550 *1.890*	−13.6 *−21.914*	0.12	0.82
C9−H9A	1.08(15)	1.725 *1.892*	−16.8 *−20.966*	0.14	0.96
C9−H9B	1.08(11)	1.443 *1.879*	−7.8 *−20.484*	0.16	0.92
C9−H9C	1.08(19)	1.692 *1.885*	−16.8 *−20.868*	0.15	0.93