Supporting Information

Characterization of the short O=C···O=C π-hole tetrel bond in the solid state

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S1. Synthesis and Crystallization

Both **FBQ** and **ClBQ** were purchased directly from Sigma-Aldrich and was used further as it is. Both compounds were crystallized in a saturated solution of toulene at 4°C.

S2. Data collection, structure refinement details and multipolar modelling of experimental data:

The high resolution X-ray charge density for **FBQ** and routine data for **ClBQ** was collected using MoKα (λ =0.71073) Apex II equipped with CCD Detector at 100(2) K (Oxford Cryosystem N_2 cooling system).In case of **FBQ**, the data collection strategy was chosen in such a way to yield high resolution data [$(\sin\theta/\lambda)_{max}$= 1.08 Å^{-1}] with high redundancy and completeness. Cell refinement, data integration and reduction were carried out using the APEX3[1] software package. Face indexing was performed for numerical absorption correction[2, 3]. SORTAV[4] program present in the WinGX[5]software package was utilized for sorting, scaling and merging of the data. The crystal structure was solved by direct methods[6,7] and refined on the basis of spherical-atom approximation based on F^2 using SHELXL2014[8,9].

Experimental multipolar modelling of electron density in FBQ: The multipolar charge density refinement was performed against F^2 using the Hansen-Coppens multipolar model[11] implemented in the MoPro/MoProviewer[12] package. The refinement was performed up to a resolution of $(\sin\theta/\lambda)_{max}$= 1.08 Å^{-1} for reflections with I > 0σ(I). In the first step of the refinement, the scale factor was refined against all these diffraction data. In the next step, the position and anisotropic displacement parameters for all the non-hydrogen atoms for sinθ/λ> 0.7Å^{-1} were refined. Then P_{val}, P_{lm}, κ andκ' were refined in a step wise manner with all data. Different set of κ and κ was used for each atom. The multipolar expansion was truncated up to octapole level (l_{max} = 3) for all atom. The default value given for the (nl, ζ) parameters of the

Slater type radial functions in the *MoPro* program was utilized. The topological analysis of the electron density was performed and visualized using MoPro/MoProViewer. All information concerning the data collection and the multipolar modelling are given in table S1. To judge and confirm the quality of the modelled electron density, variation of $|F_{obs}|/|F_{calc}|$ with sin $(\theta)/\lambda$ and of F_{obs} with F_{calc} are presented in figure S1. Fig. S2 represent the fractional dimensional plot [Fig. 2(a)-(c)], residual density plot [Fig. 2(d)-(f)], 2D deformation density [Fig. 2(g)-(i)] and Laplacian maps [Fig. 2(j)-(l)] in the molecular plane.

Table S1: Crystallographic Information Table

Compound name	**FBQ**	**ClBQ**
Compound composition	$C_6F_4O_2$	$C_6Cl_4O_2$
CCDC No.	1835904	1835905
Formula Weight	180.06	245.86
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$
***a* (Å)**	6.5213(2)	8.5371(7)
***b* (Å)**	5.35080(10)	5.6623(4)
***c* (Å)**	8.8186(2)	8.6712(7)
α (°)	90	90
β (°)	106.8960(10)	105.946(4)
γ (°)	90	90
Volume (Å^3), Z	294.435(13), 2	403.03(5), 2
ρ_{calc}(g/cm^3)	2.032	2.026
F(000)	176	240
μ(mm^{-1})	0.231	1.412
T(K)	100(2)	100(2)
λ(Å)	0.71073	0.71073
Total number of reflections	19646	4503
Unique reflections	3082	1219
Redundancy, completeness (%)	7.4, 99%	3.5, 99%
$R_{int(all)}$	0.0321	0.0304
Spherical Atom refinement		
R_{obs}, R_{all}	0.0395, 0.0463	0.0340, 0.0382
$wR2\_{obs}$, $wR2\_{all}$	0.1165, 0.1215	0.0891, 0.0919
Goodness-of-fit	1.085	1.057
$\Delta\rho_{min,max}$(e/ Å^3)	-0.32, 0.74	-0.29, 0.50
Multipole refinement		
$(Sin\theta/\lambda)_{max}$(Å^{-1})	1.08	
Reflns. used [I>0σ]	3082	
Goodness-of-fit	1.285	
$R(F^2)$, $wR_2(F^2)$	0.0359, 0.0690	
$\Delta\rho_{min,max}$(e/ Å^3)	-0.13, 0.17	

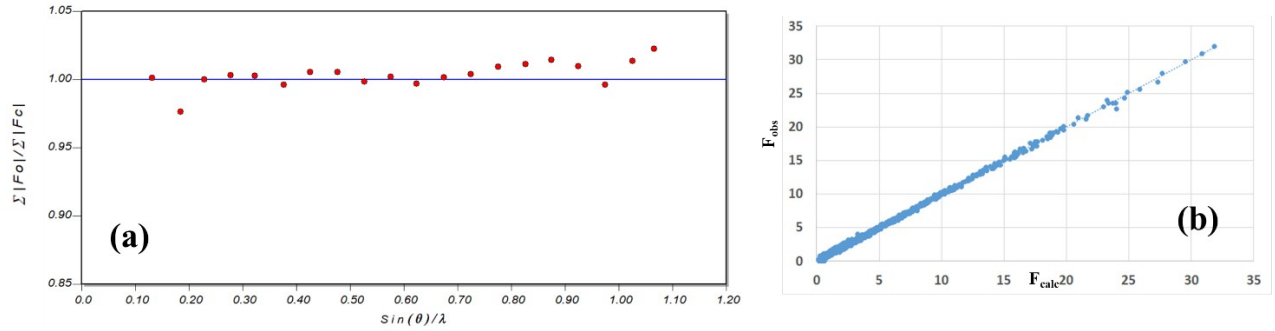

Figure S1: (a) Variation of $|F_{obs}|/|F_{calc}|$ with sin (θ)/λ in **FBQ** (b) Variation of F_{obs} with F_{calc} in **FBQ.**

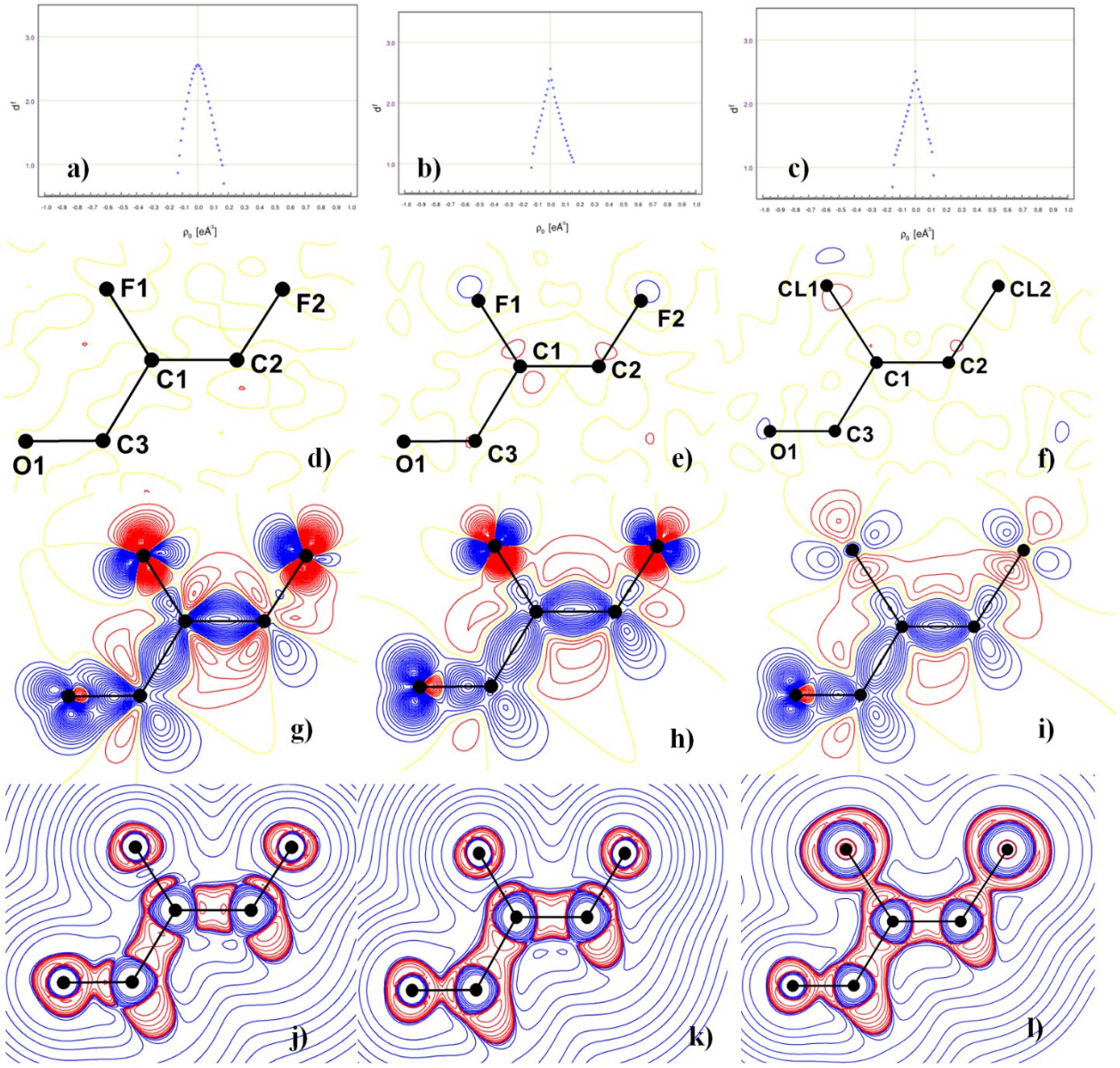

Figure S2: Fractal dimensional plot of FBQ from (a) experiment and (b) theory. (c) Fractal dimensional plot of ClBQ from theory. Residual density plot of FBQ from (d) experiment and (e) theory. (f) Residual density plot of ClBQ from theory at 0.1 e/Å^3 contour level. 2D deformation density of FBQ from (g) experiment and (h) theory at 0.05 e/Å^3 contour level. (i) 2D deformation density of ClBQ from theory. 2D Laplacian of FBQ from (j) experiment and (k) theory (l) 2D Laplacian of ClBQ from theory.

S3. Theoretical Calculations

Theoretical Modelling of electron density: Single point periodic quantum mechanical calculations were performed at the TZVP[13, 14]level using the CRYSTAL09[15] package for both **FBQ** and **ClBQ**. The positional parameters obtained from the experimental charge density was utilized for the calculations. The shrinking factors (IS1, IS2, and IS3) and the reciprocal lattice vectors were set to 4 (with 30 k-points in irreducible Brillouin zone). The bielectronic Coulomb and exchange series values for the truncation parameter were set as ITOL1_ITOL4 = 8 and ITOL5 = 17, respectively, for the calculations. The level shifter was set to 0.7 Hartree/cycle. An SCF convergence limit of the order of 10^{-7} Hartree was used. This convergence limit is well acceptable in the scientific community given that other charge density studies have used similar convergence limit for theoretical structure factor calculations[16]. For the theoretical charge density refinement, the atomic thermal displacement parameters for all the atoms were set to zero. During the refinement, the structure factor were assigned unit weight. The multipolar refinement of the theoretical data was carried up to the same level as those used for the experimental charge density refinement. For **FBQ**, The final R(F^2) and *w*R(F^2) was obtained to be 0.010 and 0.006, respectively while that for **ClBQ** was obtained to be 0.005 and 0.003, respectively which confirms the good quality of the multipolar model and of the core and valence wave functions used.

Electrostatic Potential Maps and Energy Framework

3D Molecular Electrostatic Potential Map (MESP) were plotted on Hirshfeld isosurface using CrystalExplorer17 software[17] at MP2/6-311G** level. The interaction energies were calculated using the same software via energy framework module at B3LYP/6-31G** level.

Natural Bond Orbital Analysis

The Natural Bond Orbital analysis[18,19] was performed at B3LYP/6-311G** level using NBO6.0[19]package integrated with Gaussian09[21] program. The ChemCraft[22] visualization software was utilized for plotting the bond orbitals between the interacting atoms.

S4. Intermolecular interactions

Table S2: Possible intermolecular interactions in **motif II** of FBQ and ClBQ with geometrical parameters and interaction energies

Molecule	Interaction (A-B···X-Y)	B···X (Å)	∠A-B···X (°)	∠Y-X···B (°)	Symmetry	$E_{Electrostatic}$ (kJ/mol)	$E_{Dispersion}$ (kJ/mol)	$E_{Repulsion}$ (kJ/mol)	E_{Total} (kJ/mol)
FBQ	O1=C3···O1=C3	2.8576(7)	98.1	145.1	1-x, -0.5+y, 0.5-z	-11.78	-13.41	9.39	-15.8
	F2-C2···O1=C3	2.9906(6)	99.5	152.3	x, 1.5-y, 0.5+z				
	C2-F2···F1-C1	3.2142(4)	132.4	91.3	x, 2.5-y, 0.5+z				
ClBQ	O1=C3···O1=C3	2.7719(2)	99.6	160.7	1-x, 0.5+y, 0.5-z	-16.34	-21.25	16.19	-21.4
	C2-Cl2···Cl1-C1	3.7675(7)	121.1	84.4	x, 1.5-y, 0.5+z				

S5. Topological Analysis

Table S3: Topological parameters of **FBQ** for intramolecular bonds from experiment and theory (Crystal09, *in italics)*

Bond	**R_{ij} (Å)**	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**λ_1**	**λ_2**	**λ_3**	**ε**
C1-F1	1.3250 *1.3187*	2.02 *1.98*	-11.84 *-13.30*	-16.68 *-14.99*	-15.29 *-14.87*	20.14 *16.56*	0.09 *0.01*
C2-F2	1.3246 *1.3220*	1.89 *1.97*	-16.01 *-13.00*	-14.24 *-14.99*	-13.95 *-14.62*	12.18 *16.61*	0.02 *0.03*
C3-O1	1.2133 *1.2140*	2.96 *2.74*	-32.74 *-22.29*	-29.78 *-22.27*	-25.61 *-20.74*	22.66 *20.72*	0.16 *0.07*
C1-C2	1.3372 *1.3378*	2.48 *2.37*	-26.82 *-23.10*	-22.32 *-19.57*	-14.95 *-14.26*	10.45 *10.73*	0.49 *0.37*
C1-C3	1.4789 *1.4777*	1.87 *1.80*	-15.64 *-12.63*	-14.88 *-13.00*	-11.82 *-11.36*	11.06 *11.73*	0.26 *0.14*
C2-C3	1.4835 *1.4769*	1.80 *1.81*	-15.08 *-12.30*	-14.05 *-13.11*	-11.00 *-11.27*	9.97 *12.08*	0.28 *0.16*

Table S4: Topological parameters of **ClBQ** for intramolecular bonds from theory (Crystal09, *in italics)*

Bond	**R_{ij} (Å)**	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**λ_1**	**λ_2**	**λ_3**	**ε**
C1-Cl1	*1.7025*	*1.30*	*-1.31*	*-6.82*	*-6.34*	*12.03*	*0.07*
C2-Cl2	*1.7004*	*1.33*	*-1.86*	*-7.12*	*-6.33*	*11.59*	*0.12*
C3-O1	*1.2099*	*2.81*	*-22.98*	*-24.77*	*-22.38*	*24.17*	*0.11*
C1-C2	*1.3399*	*2.34*	*-22.76*	*-18.23*	*-14.45*	*9.92*	*0.26*

C1-C3	*1.4885*	*1.77*	*-12.39*	*-12.51*	*-11.23*	*11.36*	*0.11*
C2-C3	*1.4886*	*1.77*	*-12.42*	*-12.60*	*-11.13*	*11.31*	*0.13*

Table S5: Topological parameters for O=C···O=C π-hole tetrel bond from experiment and theory (in *italics*)

Intermolecular Interaction	**R_{ij} (Å)**	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**ε**	**G (kJmol^{-1} bohr^{-3})**	**V (kJmol^{-1} bohr^{-3})**	**|V|/G**
FBQ	2.8995 *2.9370*	0.06 *0.05*	0.84 *0.84*	0.58 *0.14*	17.99 *17.45*	-13.03 *-11.92*	0.72 *0.92*
ClBQ	2.8185	0.06	1.02	1.04	21.3	-14.85	0.69

Note: It has been observed in other studies also that the values of ellipticity obtained from experimental and theoretical method for the same interaction can have significant difference in case of intermolecular interactions not involving hydrogens. Similarly, literature reports shows that the magnitude of ellipticity can be large for some non-hydrogen bonds[23].

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