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Electronic Supplementary Information

σ-hole activation and structural changes upon perfluorination of aryl halides: direct evidence from gas phase rotational spectroscopy

Dingding Lv,[a] Assimo Maris,[a] Luca Evangelisti,[a] Andrea Maggio,[a] Wentao Song,[a] Ashley A. Elliott,[b] Sean A. Peebles,[b] Justin L. Neill,[c] Matt T. Muckle,[c] Brooks H. Pate,[c] Rebecca A. Peebles,*[,b] and Sonia Melandri*[,a]

Abstract

Enhancement of the σ-hole on the halogen atom of aryl halides due to perfluorination of the ring is demonstrated by use of the Extended Townes−Dailey (ETD) model coupled to a Natural Atomic Orbital Bond analysis on two perfluorinated aryl halides (C_6F_5Cl and C_6F_5Br) and their hydrogenated counterparts. The ETD analysis, which quantifies the halogen *p*-orbitals populations, relies on the nuclear quadrupole coupling constants which in this work are accurately determined experimentally from the rotational spectra. The rotational spectra investigated by Fourier-transform microwave spectroscopy performed in supersonic expansion are reported for the parent species of C_6F_5Cl and C_6F_5Br and their ^{13}C, ^{37}Cl or ^{81}Br substituted isotopologues observed in natural abundance. The experimentally determined rotational constants combined with theoretical data at the MP2/aug-cc-pVTZ level provide precise structural information from which an elongation of the ring along its symmetry axis due to perfluorination is proved.

[a] *Dipartimento di Chimica "G. Ciamician",Università di Bologna, via F. Selmi 2, 40126, Bologna Italy*
E-mail: sonia.melandri@unibo.it
[b] *Department of Chemistry and Biochemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920, USA*
[c] *Department of Chemistry, University of Virginia, McCormick Rd., PO Box 411319, Charlottesville, VA 22904, USA*

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Table S1. Experimental (r_0 and r_s) and theoretical (r_e, MP2/aug-cc-pVTZ) principal axis system coordinates (Å) of C_6F_5Cl.

	r_0		$\|r_s\|$		r_e	
	a_0	b_0	a_s	b_s	a_e	b_e
C_1	1.116(7)	0	1.111 (6)	0.114*i (4)[a]	1.1222	0
C_2, C_6	0.412(2)	±1.198(5)	0.391 (2)	1.1942 (4)	0.4145	±1.1999
C_3, C_5	-0.973(4)	±1.204(2)	0.9682 (9)	1.1986 (4)	-0.9748	±1.2034
C_4	-1.672(4)	0	1.6696 (5)	0.134*i (4)	-1.6704	0
F_2, F_6	1.061(4)	±2.359(4)	-	-	1.0616	±2.3612
F_3, F_5	-1.639(4)	±2.355(5)	-	-	-1.6416	±2.3539
F_4	-3.002(4)	0	-	-	-2.9990	0
Cl	2.834(1)	0	2.83310(9)	0.027*i (4)	2.8323	0

[a] In a few cases the square of the coordinate has been determined to be small and negative leading to an imaginary value of the coordinate.

Table S2. Experimental (r_0 and r_s) and theoretical (r_e, MP2/aug-cc-pVTZ) principal axis system coordinates (Å) of C_6F_5Br.

	r_0		$\|r_s\|$		r_e	
	a_0	b_0	a_s	b_s	a_e	b_e
C_1	0.58(1)	0	-	-	0.5695	0
C_2, C_6	-0.141(2)	±1.192(4)	0.09*i (2)[a]	1.192 (2)	-0.1381	±1.1987
C_3, C_5	-1.529(2)	±1.203(6)	1.525(2)	1.199 (2)	-1.5273	±1.2033
C_4	-2.229(2)	0	-	-	-2.2222	0
F_2, F_6	0.489(4)	±2.363(9)	-	-	0.5044	±2.3628
F_3, F_5	-2.192(8)	±2.356(6)	-	-	-2.1959	±2.3531
F_4	-3.56(1)	0	-	-	-3.5510	0
Br	2.436(1)	0	2.43422 (2)	0	2.4271	0

[a] In a few cases the square of the coordinate has been determined to be small and negative leading to an imaginary value of the coordinate.

Table S3. Experimental (r_0 and r_s) and theoretical (r_e, MP2/aug-cc-pVTZ) principal axis system coordinates (Å) of C_6H_5Cl.

	r_0		$\|r_s\|$[a]		r_e	
	a_0	b_0	a_s	b_s	a_e	b_e
C_1	0.43(2)	0	0.43(5)	0	0.4295	0
C_2, C_6	-0.250(8)	±1.215(5)	0.23(4)	±1.215(3)	-0.2514	±1.2137
C_3, C_5	-1.645(3)	±1.209(4)	1.64(3)	±1.211(3)	-1.6450	±1.2057
C_4	-2.346(3)	0	2.344(2)	0	-2.3445	0
H_2, H_6	0.31(2)	±2.142(7)	-	-	0.3024	±2.1420
H_3, H_5	-2.181(8)	±2.150(7)	-	-	-2.1815	±2.1453
H_4	-3.436(3)	0	-	-	-3.4260	0
Cl	2.166(1)	0	2.165(3)	0	2.1658	0

[a] Rotational constants taken from ref. [33]

Table S4. Experimental (r_0 and r_s) and theoretical (r_e, MP2/aug-cc-pVTZ) principal axis system coordinates (Å) of C_6H_5Br.

	$\boldsymbol{r_0}$		$\lvert\boldsymbol{r_s}\rvert$[a]		$\boldsymbol{r_e}$	
	a_0	b_0	a_s	b_s	a_e	b_e
C_1	-0.25(3)	0	0.1888	0	-0.2545	0
C_2, C_6	-0.943(9)	±1.215(7)	0.9332	±1.2144	-0.9362	±1.2140
C_3, C_5	-2.336(4)	±1.209(6)	2.3340	±1.2064	-2.3299	±1.2055
C_4	-3.036(3)	0	3.0341	0	-3.0290	0
H_2, H_6	-0.40(3)	±2.15(1)	-	-	-0.3854	±2.1445
H_3, H_5	-2.87(1)	±2.15(1)	-	-	-2.8663	±2.1453
H_4	-4.126(3)	0	-	-	-4.1106	0
Br	1.632(1)	0	1.6326	0	1.6281	0

[a] Rotational constants taken from ref. [34]

Table S5. Measured transition frequencies of four isotopologues of C_6F_5Cl, in MHz.

J'	K_a'	K_c'	J''	K_a''	K_c''	F'+½	F''+½	ν-^{35}Cl	$\Delta\nu$	ν-^{37}Cl	$\Delta\nu$	ν-^{13}C1	$\Delta\nu$	ν-^{13}C2	$\Delta\nu$	ν-^{13}C3	$\Delta\nu$	ν-^{13}C4	$\Delta\nu$
5	2	3	4	2	2	5	4	6614.971	-0.001										
5	2	3	4	2	2	6	5	6615.506	0.001										
5	2	3	4	2	2	4	3	6615.901	0.008										
5	2	3	4	2	2	7	6	6616.449	0.003										
5	2	3	4	2	2	5	5	6619.064	-0.002										
3	3	0	2	1	1	5	4	6696.764	-0.008										
5	3	2	4	3	1	6	5	6747.722	0.005										
5	3	2	4	3	1	5	4	6750.643	0.005										
5	3	2	4	3	1	7	6	6757.623	0.005										
5	3	2	4	3	1	4	3	6760.460	0.004										
6	3	4	5	3	3	7	6	7200.119	0.001	7073.336	-0.004	7190.133	-0.007	7193.791	0.000				
6	3	4	5	3	3	6	5	7200.927	0.002	7073.999	0.003	7190.945	-0.006	7194.588	-0.006	7188.214	0.000		
6	3	4	5	3	3	6	6	7201.701	-0.008										
6	3	4	5	3	3	8	7	7204.064	0.002	7076.557	0.005			7197.719	0.004	7191.342	0.003		
6	3	4	5	3	3	5	4	7204.849	0.000	7077.209	0.001			7198.494	-0.002	7192.113	-0.008		
6	3	4	5	3	3	5	5	7207.897	-0.001										
9	1	8	9	1	9	8	8	7325.275	-0.006										
9	2	8	9	0	9	8	8	7325.515	-0.004										
9	1	8	9	1	9	11	11	7325.789	0.003										
9	2	8	9	0	9	11	11	7326.029	0.004										
9	1	8	9	1	9	9	9	7328.500	0.005										
9	2	8	9	0	9	9	9	7328.726	-0.010										
9	1	8	9	1	9	10	10	7329.041	-0.002										
9	2	8	9	0	9	10	10	7329.282	-0.003										
7	2	6	6	2	5	8	8	7370.818	-0.001										
7	2	6	6	2	5	7	6							7371.809	0.005			7363.864	0.005
7	2	6	6	2	5	8	7							7371.957	-0.002			7364.002	-0.006
7	2	6	6	2	5	6	5	7382.359	0.002	7281.253	0.002			7372.537	-0.002				
7	2	6	6	2	5	9	8	7382.632	0.001	7281.529	0.001			7372.818	0.011	7367.724	0.004	7364.860	-0.005
7	1	6	6	1	5	8	8	7385.294	-0.005										
7	1	6	6	1	5	7	6	7396.423	0.002	7300.652	-0.001	7388.931	0.002	7386.035	0.000	7381.176	0.001		
7	1	6	6	1	5	8	7	7396.697	0.001			7389.204	-0.002	7386.299	-0.007	7381.443	-0.005		
7	1	6	6	1	5	6	5	7396.903	0.000			7389.413	0.007	7386.523	-0.002				
7	1	6	6	1	5	9	8	7397.189	0.002	7301.211	-0.001	7389.695	0.002	7386.808	0.002				
7	1	6	6	1	5	7	7	7399.097	-0.006										

7	1	6	6	1	5	6	6	7408.427	0.005										
6	4	3	5	4	2	6	6	7532.052	-0.004										
6	4	3	5	4	2	7	6	7532.223	0.001	7367.341	-0.005	7519.003	-0.005	7529.575	-0.002	7521.154	-0.004		
6	4	3	5	4	2	5	5	7534.453	0.000										
6	4	3	5	4	2	6	5	7534.870	-0.002	7369.453	0.005	7521.661	-0.002			7523.803	0.000	7505.258	0.003
6	5	2	5	5	1	7	6	7540.144	-0.006	7362.784	-0.004								
6	4	3	5	4	2	8	7	7541.470	-0.002	7374.683	0.001			7538.811	0.002	7530.395	0.003	7511.856	-0.005
6	4	3	5	4	2	5	4	7544.082	-0.002	7376.763	0.000	7530.886	-0.008			7532.999	-0.002		
6	5	2	5	5	1	6	5	7545.114	-0.006										
6	5	2	5	5	1	8	7	7555.654	-0.003	7374.903	-0.008								
6	5	2	5	5	1	5	4	7560.686	-0.006										
6	2	4	5	2	3	7	7	7567.182	-0.001										
6	2	4	5	2	3	5	4	7577.580	-0.001	7480.899	0.001	7570.232	-0.006	7566.378	-0.003	7561.650	-0.004	7560.947	-0.006
6	2	4	5	2	3	8	7	7578.468	0.000	7481.566	0.002	7571.127	0.005			7562.546	0.002	7561.837	0.004
6	2	4	5	2	3	6	5	7578.889	0.000	7481.722	-0.001	7571.525	-0.001	7567.713	-0.004	7562.980	-0.001	7562.211	-0.006
6	2	4	5	2	3	7	6	7579.786	0.001	7482.394	0.000	7572.419	0.000	7568.618	0.001	7563.879	-0.001	7563.104	-0.001
6	5	1	5	5	0	7	6	7580.980	-0.007	7393.638	-0.009								
6	2	4	5	2	3	6	6	7582.448	-0.001										
6	5	1	5	5	0	6	5	7586.078	-0.007	7397.627	-0.003								
6	2	4	5	2	3	5	5	7590.251	-0.002										
3	3	1	2	1	2	5	4	7591.418	-0.001										
6	5	1	5	5	0	8	7	7597.038	-0.007	7406.099	-0.001								
6	5	1	5	5	0	5	4	7602.195	-0.007	7410.102	-0.007								
3	3	1	2	1	2	3	2	7606.575	0.003										
3	3	1	2	1	2	4	3	7624.308	-0.005										
6	4	2	5	4	1	7	6	7918.864	-0.003	7695.576	0.004	7900.691	-0.001	7922.246	0.003	7910.692	0.002	7878.252	-0.002
6	4	2	5	4	1	6	6	7919.704	-0.004										
6	4	2	5	4	1	6	5	7922.031	-0.003	7698.108	0.002			7925.395	-0.009	7913.853	0.001	7881.429	0.003
6	4	2	5	4	1	5	5	7925.719	-0.001										
6	4	2	5	4	1	7	7	7926.811	-0.004										
6	4	2	5	4	1	8	7	7930.420	-0.001	7704.607	0.001	7912.257	0.003	7933.804	0.006	7922.245	0.004	7889.787	-0.002
6	4	2	5	4	1	5	4	7933.422	-0.001	7706.927	0.002	7915.259	0.000	7936.790	-0.010	7925.241	-0.002	7892.790	0.004
4	3	1	3	1	2	3	2	8034.221	-0.003	7991.376	-0.007								
4	3	1	3	1	2	6	5	8041.006	0.001	7996.995	-0.005								
4	3	1	3	1	2	5	5	8042.481	-0.003										
4	3	1	3	1	2	3	3	8047.808	0.002										
4	3	1	3	1	2	4	3	8049.097	-0.004	8003.793	-0.006								
4	3	1	3	1	2	4	4	8055.437	-0.004										

4	3	1	3	1	2	5	4	8055.995	-0.003	8009.481	-0.006							
11	2	9	11	2	10	11	11	8127.923	-0.006									
11	2	9	11	2	10	12	12	8128.220	-0.009									
11	3	9	11	1	10	11	11	8128.412	0.004									
6	3	3	5	3	2	7	6	8160.084	0.000	7978.161	0.005	8145.766	0.000	8157.172	0.004			
6	3	3	5	3	2	6	5	8160.588	0.000	7978.644	0.003	8146.285	0.005	8157.661	0.005			
6	3	3	5	3	2	6	6	8162.953	0.002									
6	3	3	5	3	2	8	7	8163.790	0.000	7981.407	0.004	8149.510	-0.003	8160.820	0.001			8131.721	-0.002
6	3	3	5	3	2	5	4	8164.255	0.000	7981.863	0.001	8149.995	0.006	8161.275	0.005	8152.207	-0.005		
6	3	3	5	3	2	5	5	8172.773	-0.006									
7	3	5	6	3	4	8	8	8180.139	0.000									
7	3	5	6	3	4	8	7			8059.011	0.002	8176.997	0.001	8177.837	-0.006	8171.444	0.008	8164.478	-0.001
7	3	5	6	3	4	7	6			8059.152	-0.004	8177.167	0.003	8178.012	0.006			8164.654	0.006
7	3	5	6	3	4	9	8			8060.578	-0.002			8179.714	-0.001	8173.323	0.010	8166.380	-0.006
7	3	5	6	3	4	6	5			8060.708	0.008							8166.530	-0.002
8	2	7	7	2	6	9	9	8242.347	0.003										
8	2	7	7	2	6	8	7	8253.961	-0.002	8142.746	-0.001			8242.810	-0.002	8237.192	-0.005	8234.360	-0.006
8	2	7	7	2	6	9	8	8254.156	-0.001	8142.903	-0.004			8243.009	0.003	8237.382	-0.009	8234.559	-0.003
8	2	7	7	2	6	7	6	8254.562	-0.002					8243.416	0.001	8237.800	0.002	8234.960	-0.005
8	2	7	7	2	6	10	9	8254.741	0.000	8143.347	-0.004			8243.593	0.002	8237.978	0.004	8235.151	0.008
8	2	7	7	2	6	8	8	8256.361	-0.002										
8	1	7	7	1	6	8	7	8257.678	0.000	8148.137	-0.008			8246.349	-0.006	8240.811	0.001	8238.359	0.010
8	1	7	7	1	6	9	8	8257.877	-0.001	8148.312	-0.002	8249.324	0.001	8246.557	0.004	8241.015	0.007	8238.551	0.000
8	1	7	7	1	6	7	6	8258.191	-0.003	8148.516	-0.001	8249.643	0.007	8246.870	-0.004	8241.321	-0.006	8238.854	-0.003
8	1	7	7	1	6	10	9	8258.402	-0.001	8148.690	-0.002	8249.834	-0.011	8247.083	0.002			8239.071	0.003
8	1	7	7	1	6	8	8	8260.083	-0.003										
8	2	7	7	2	6	7	7	8266.456	-0.002										
8	1	7	7	1	6	7	7	8270.193	-0.002										
7	2	5	6	2	4	8	8	8372.954	-0.003										
7	2	5	6	2	4	6	5	8382.640	-0.001	8291.670	-0.002	8375.599	-0.007	8368.768	-0.006	8364.184	0.002	8366.726	0.010
7	2	5	6	2	4	9	8	8383.217	-0.001	8292.160	-0.001	8376.195	0.008	8369.344	-0.001	8364.754	-0.001	8367.299	-0.001
7	2	5	6	2	4	7	6	8383.655	-0.001	8292.548	-0.002			8369.777	0.003	8365.193	0.002	8367.751	0.000
7	2	5	6	2	4	8	7	8384.241	0.000	8293.042	-0.003	8377.220	-0.001	8370.351	-0.002	8365.773	-0.001	8368.346	0.002
7	2	5	6	2	4	7	7	8386.319	-0.002										
7	2	5	6	2	4	6	6	8394.004	-0.001										
4	2	2	3	0	3	3	2	8426.260	-0.004										
4	2	2	3	0	3	5	4	8432.015	-0.004										
7	4	4	6	4	3	8	7	8721.670	-0.003	8547.240	0.000	8707.882	0.007	8716.448	-0.002	8707.650	-0.003	8690.681	-0.003

7	4	4	6	4	3	8	8	8722.226	-0.002									
7	4	4	6	4	3	7	6	8722.721	-0.003	8548.087	-0.002	8708.933	0.003	8717.508	0.012	8708.699	-0.001		
7	4	4	6	4	3	9	8	8726.694	-0.003	8551.312	0.001	8712.918	-0.001	8721.452	0.001	8712.662	0.003	8695.745	0.011
7	4	4	6	4	3	6	6	8727.298	-0.007										
7	4	4	6	4	3	6	5	8727.720	-0.004	8552.155	0.000					8713.681	-0.003	8696.763	-0.006
7	6	2	6	6	1	8	7	8794.215	-0.009	8585.193	-0.006								
7	6	2	6	6	1	7	6	8798.053	-0.010	8588.200	-0.009								
7	6	1	6	6	0	8	7	8806.731	-0.013	8594.001	-0.010								
7	6	2	6	6	1	9	8	8808.255	-0.010	8596.149	-0.007								
7	6	1	6	6	0	7	6	8810.600	-0.017	8597.047	0.004								
7	6	2	6	6	1	6	5	8812.150	-0.009	8599.192	-0.008								
7	6	1	6	6	0	9	8	8820.939	-0.011	8605.052	-0.009								
7	6	1	6	6	0	6	5	8824.865	-0.014	8608.111	-0.008								
7	5	3	6	5	2	7	7	8861.162	-0.011										
7	5	3	6	5	2	8	7	8861.989	-0.007	8654.882	-0.003			8860.502	0.005				
7	5	3	6	5	2	7	6	8864.384	-0.007	8656.772	-0.004			8862.879	-0.010				
7	5	3	6	5	2	9	8	8871.547	-0.004	8662.402	-0.006								
7	5	3	6	5	2	6	5	8873.919	-0.007	8664.285	-0.002								
7	5	2	6	5	1	8	7	9044.314	0.003	8797.006	-0.001								
7	5	2	6	5	1	7	6	9047.002	0.009	8799.077	-0.001								
7	5	2	6	5	1	9	8	9055.370	0.008	8805.467	-0.003								
7	5	2	6	5	1	6	5	9058.018	0.000	8807.523	-0.001								
9	2	8	8	2	7	9	8	9123.075	0.002										
9	2	8	8	2	7	10	9	9123.237	0.002										
9	2	8	8	2	7	8	7	9123.555	0.003										
9	2	8	8	2	7	11	10	9123.725	0.006										
9	1	8	8	1	7	9	8	9123.933	-0.002										
9	1	8	8	1	7	10	9	9124.100	0.002										
9	1	8	8	1	7	8	7	9124.391	-0.006										
9	1	8	8	1	7	11	10	9124.572	0.003										
8	2	6	7	2	5	7	6	9181.347	-0.011	9073.633	0.015								
8	2	6	7	2	5	8	7	9181.480	0.019										
8	2	6	7	2	5	10	9	9181.627	-0.005										
8	2	6	7	2	5	9	8	9181.753	0.018	9074.095	0.010								
7	3	4	6	3	3	7	6	9345.126	0.003										
7	3	4	6	3	3	6	5	9345.318	0.005	9185.778	0.008								
7	3	4	6	3	3	8	7	9345.488	0.008										
7	3	4	6	3	3	9	8	9345.685	0.007	9185.992	0.009								

7	4	3	6	4	2	8	7	9494.367	0.005	9239.097	0.007
7	4	3	6	4	2	7	6	9495.562	0.014	9240.088	-0.001
7	4	3	6	4	2	9	8	9500.754	0.009	9244.371	0.011
7	4	3	6	4	2	6	5	9501.925	0.009	9245.362	0.011
8	4	5	7	4	4	9	8	9810.078	0.006	9636.371	0.003
8	4	5	7	4	4	8	7	9810.448	0.009	9636.689	0.007
8	4	5	7	4	4	10	9	9812.701	0.003	9638.569	0.002
8	4	5	7	4	4	7	6	9813.052	0.008	9638.850	-0.008
5	3	2	4	1	3	4	3	9904.347	0.000		
5	3	2	4	1	3	7	6	9906.287	-0.005		
5	3	2	4	1	3	5	4	9908.177	-0.001		
5	3	2	4	1	3	6	5	9910.131	0.007		
8	7	2	7	7	1	10	9	10053.754	-0.005		
8	6	3	7	6	2	9	8	10139.693	-0.006		
8	6	3	7	6	2	8	7	10141.802	0.004		
8	5	4	7	5	3	9	8	10143.132	-0.001		
8	6	3	7	6	2	7	6	10151.217	-0.005		
8	6	2	7	6	1	9	8	10209.634	-0.013		
8	6	2	7	6	1	8	7	10211.863	0.007		
8	6	2	7	6	1	10	9	10219.733	0.011		
8	6	2	7	6	1	7	6	10221.927	0.005		
8	3	5	7	3	4	7	6	10267.883	0.009		
8	3	5	7	3	4	10	9	10268.422	-0.006		
8	3	5	7	3	4	8	7	10269.271	0.005	10146.542	0.009
8	3	5	7	3	4	9	8	10269.815	-0.010	10146.955	0.010
5	4	1	4	2	2	4	3	10448.027	0.007		
5	4	1	4	2	2	7	6	10454.284	-0.001		
5	4	1	4	2	2	5	4	10467.470	-0.006		
5	4	1	4	2	2	6	5	10473.886	-0.008		
8	5	3	7	5	2	8	7	10645.053	0.015		
8	5	3	7	5	2	10	9	10651.513	0.002		
8	5	3	7	5	2	7	6	10652.973	0.011		
8	4	4	7	4	3	9	8	10917.750	-0.003		
8	4	4	7	4	3	8	7	10917.969	0.020	10674.131	0.005
8	4	4	7	4	3	10	9	10920.196	0.002		
8	4	4	7	4	3	7	6	10920.386	0.013		
9	3	6	8	3	5	8	7	11039.503	-0.003		
9	3	6	8	3	5	11	10	11039.898	0.009	10927.575	-0.005

9	3	6	8	3	5	9	8	11040.586	0.007
9	3	6	8	3	5	10	9	11040.968	0.001
9	5	5	8	5	4	10	9	11341.146	-0.011
9	5	5	8	5	4	9	8	11341.697	0.019
9	5	5	8	5	4	11	10	11344.624	0.003
9	5	5	8	5	4	8	7	11345.137	0.015
9	7	3	8	7	2	10	9	11391.805	-0.018
9	7	3	8	7	2	11	10	11400.908	0.018
9	7	2	8	7	1	11	10	11424.596	-0.017
9	6	4	8	6	3	10	9	11479.539	-0.005
9	6	4	8	6	3	9	8	11480.707	-0.001
9	6	4	8	6	3	11	10	11485.964	0.007
9	6	4	8	6	3	8	7	11487.113	0.001
9	6	3	8	6	2	10	9	11731.823	0.011
9	6	3	8	6	2	11	10	11739.734	0.009
5	4	2	4	2	3	7	6	11758.968	0.016
6	4	2	5	2	3	5	4	11765.558	0.007
6	4	2	5	2	3	8	7	11768.274	0.015
6	4	2	5	2	3	6	5	11774.535	-0.001
6	4	2	5	2	3	7	6	11777.271	0.016
9	5	4	8	5	3	10	9	12256.240	0.004
9	5	4	8	5	3	9	8	12256.895	0.002
10	6	5	9	6	4	11	10	12771.618	-0.004
10	6	5	9	6	4	10	9	12772.243	-0.006
10	6	5	9	6	4	9	8	12776.462	0.014
10	4	6	9	4	5	9	8	12959.677	-0.002
10	4	6	9	4	5	12	11	12960.067	-0.008
10	4	6	9	4	5	10	9	12961.108	-0.007
10	4	6	9	4	5	11	10	12961.517	0.002
10	6	4	9	6	3	11	10	13387.732	-0.003
10	6	4	9	6	3	10	9	13388.601	-0.003
10	6	4	9	6	3	12	11	13393.878	0.009
11	4	7	10	4	6	10	9	13698.956	-0.005
11	4	7	10	4	6	13	12	13699.241	-0.002
11	4	7	10	4	6	12	11	13700.339	-0.004
11	6	6	10	6	5	12	11	13974.277	-0.014
11	6	6	10	6	5	13	12	13976.865	-0.001
12	4	8	11	4	7	14	13	14457.323	0.005

11	5	6	10	5	5	13	12	14812.237	-0.001
11	5	6	10	5	5	11	10	14812.492	-0.003
11	5	6	10	5	5	12	11	14812.710	-0.011

Table S6. Measured transition frequencies of four isotopologues of C_6F_5Br, in MHz.

J'	K_a'	K_c'	J''	K_a''	K_c''	F'+½	F''+½	ν-^{79}Br	$\Delta\nu$	ν-^{81}Br	$\Delta\nu$	ν-^{13}C2	$\Delta\nu$	ν-^{13}C3	$\Delta\nu$
6	4	2	5	2	3	6	5	11754.946	0.011	11777.598	-0.010				
6	4	2	5	2	3	7	6	11723.677	0.012	11750.885	-0.006				
9	1	8	8	1	7	8	7			7025.211	0.003				
9	1	8	8	1	7	9	8			7024.177	0.006				
9	1	8	8	1	7	10	9			7021.957	0.008				
9	1	8	8	1	7	11	10			7023.191	0.004				
9	2	8	8	2	7	9	8	6991.226	0.007						
9	2	8	8	2	7	10	9	6989.267	0.008						
9	2	7	8	2	6	8	7			7808.907	0.005				
9	2	7	8	2	6	9	8			7807.756	0.009				
9	2	7	8	2	6	10	9			7805.242	0.007				
9	2	7	8	2	6	11	10			7806.911	0.008				
9	3	7	8	3	6	9	8	7478.613	0.009						
9	3	7	8	3	6	10	9	7477.675	0.010						
9	3	7	8	3	6	11	10	7468.702	0.008						
9	3	6	8	3	5	8	7	8164.867	0.011						
9	3	6	8	3	5	9	8	8176.853	0.012						
9	3	6	8	3	5	10	9	8174.984	0.013						
9	3	6	8	3	5	11	10	8165.671	0.012						
9	4	6	8	4	5	8	7	7656.742	0.004	7579.388	0.008				
9	4	6	8	4	5	9	8	7678.909	0.008	7597.822	0.004				
9	4	6	8	4	5	10	9	7680.147	0.008	7598.994	0.007				
9	4	6	8	4	5	11	10	7659.972	0.005	7581.972	0.008				
9	4	5	8	4	4	8	7			7787.334	0.009				
9	4	5	8	4	4	9	8			7809.308	0.009				
9	4	5	8	4	4	10	9			7811.013	0.005				
9	4	5	8	4	4	11	10			7790.379	0.013				
9	5	5	8	5	4	9	8	7676.318	0.005	7592.261	0.002				
9	5	5	8	5	4	10	9	7682.609	0.006	7597.392	0.003				
9	5	5	8	5	4	11	10	7647.448	0.004						
9	5	4	8	5	3	11	10	7672.531	0.002	7590.161	0.007				
9	6	3	8	6	2	8	7	7591.992	-0.007						
9	6	3	8	6	2	11	10	7601.890	-0.002	7524.163	0.000				
10	0	10	9	0	9	9	8	7018.764	0.008	6964.771	0.005				
10	0	10	9	0	9	10	9	7019.401	0.005	6965.273	0.007				
10	0	10	9	0	9	11	10	7017.505	0.005	6963.661	0.007				
10	0	10	9	0	9	12	11	7017.105	0.006	6963.327	0.006				
10	1	10	9	1	9	9	8	7017.138	0.007	6962.931	0.005				
10	1	10	9	1	9	10	9	7017.773	0.006	6963.448	0.007				
10	1	10	9	1	9	11	10	7015.955	0.007	6961.899	0.009				
10	1	10	9	1	9	12	11	7015.390	0.008	6961.425	0.007				
10	1	9	9	1	8	9	8	7720.312	0.007	7663.306	0.002	7712.448	-0.007		
10	1	9	9	1	8	10	9	7720.355	0.006	7663.211	0.006	7712.534	0.004		
10	1	9	9	1	8	11	10	7718.333	0.005	7661.506	0.006	7710.511	0.000	7699.056	-0.002
10	1	9	9	1	8	12	11	7718.616	0.007	7661.823	0.007	7710.765	0.000	7699.339	0.003
10	2	9	9	2	8	9	8	7673.325	0.008	7612.677	0.005	7666.530	0.007		
10	2	9	9	2	8	10	9	7675.463	0.006	7614.462	0.007			7656.513	-0.003
10	2	9	9	2	8	11	10	7673.859	0.006	7613.107	0.008				
10	2	9	9	2	8	12	11	7671.932	0.007	7611.487	0.007	7665.147	0.004	7652.989	0.003
10	2	8	9	2	7	9	8	8548.132	0.004	8484.798	0.001				
10	2	8	9	2	7	10	9	8544.731	0.004	8482.087	0.005				

10	2	8	9	2	7	11	10	8542.272	0.003	8480.012	0.005	8533.383	0.000		
10	2	8	9	2	7	12	11	8545.761	0.005	8482.805	0.002	8536.907	0.001	8524.389	-0.001
10	3	8	9	3	7	9	8	8223.031	0.005	8151.147	0.004				
10	3	8	9	3	7	10	9	8229.524	0.006	8156.594	0.006				
10	3	8	9	3	7	11	10	8228.347	0.008	8155.666	0.005				
10	3	8	9	3	7	12	11	8222.760	0.007	8150.857	0.008				
10	3	7	9	3	6	9	8	9071.037	0.008	8977.014	0.006				
10	3	7	9	3	6	10	9	9074.416	0.008	8980.404	0.008				
10	3	7	9	3	6	11	10	9074.728	0.008	8980.308	0.006				
10	3	7	9	3	6	12	11	9068.142	0.008	8974.883	0.008				
10	4	7	9	4	6	9	8	8503.875	0.004	8419.337	0.003				
10	4	7	9	4	6	10	9	8519.160	0.005	8432.101	0.004				
10	4	7	9	4	6	11	10	8519.370	0.007	8432.370	0.004				
10	4	7	9	4	6	12	11	8505.464	0.007	8420.584	0.007				
10	4	6	9	4	5	9	8	8899.012	0.004	8789.546	0.008				
10	4	6	9	4	5	10	9	8919.055	0.010	8806.200	0.011				
10	4	6	9	4	5	11	10	8919.807	0.011	8806.913	0.001				
10	4	6	9	4	5	12	11	8901.141	0.010	8791.233	0.011				
10	5	6	9	5	5	9	8	8530.049	0.000	8440.759	0.002				
10	5	6	9	5	5	10	9	8556.540	0.003	8462.812	-0.002				
10	5	6	9	5	5	11	10	8558.262	0.003	8464.288	0.001				
10	5	6	9	5	5	12	11	8534.293	0.004	8444.214	0.002				
10	5	5	9	5	4	9	8			8494.752	0.001				
10	5	5	9	5	4	10	9	8618.143	0.004	8517.679	-0.001				
10	5	5	9	5	4	11	10	8620.471	0.005	8519.755	0.002				
10	5	5	9	5	4	12	11	8594.592	0.002	8498.156	0.002				
10	6	5	9	6	4	9	8	8474.810	-0.010	8387.411	-0.005				
10	6	5	9	6	4	10	9	8511.920	-0.002	8418.179	-0.005				
10	6	5	9	6	4	11	10	8516.360	-0.002	8422.083	-0.004				
10	6	5	9	6	4	12	11	8481.384	-0.004	8392.718	-0.004				
10	6	4	9	6	3	10	9	8515.851	-0.002	8421.636	-0.007				
10	6	4	9	6	3	11	10	8520.499	-0.002	8425.250	-0.008				
10	6	4	9	6	3	12	11	8485.175	-0.006	8396.123	-0.004				
11	0	11	10	0	10	10	9	7686.165	0.004	7626.985	0.006				
11	0	11	10	0	10	11	10	7686.748	0.007	7627.439	0.006	7679.555	0.001		
11	0	11	10	0	10	12	11	7685.171	0.006	7626.106	0.007	7677.979	0.000		
11	0	11	10	0	10	13	12	7684.792	0.008	7625.788	0.007	7677.594	-0.001	7665.729	0.000
11	1	11	10	1	10	10	9	7685.495	0.005	7626.213	0.005				
11	1	11	10	1	10	11	10	7686.053	0.007	7626.660	0.006				
11	1	11	10	1	10	12	11	7684.528	0.007	7625.363	0.008			7665.025	0.003
11	1	11	10	1	10	13	12	7684.077	0.007	7624.985	0.007			7665.474	0.001
11	1	10	10	1	9	10	9	8373.573	0.006	8310.690	0.005				
11	1	10	10	1	9	11	10	8374.175	0.001	8311.098	0.005				
11	1	10	10	1	9	12	11	8372.606	0.004	8309.775	0.006				
11	1	10	10	1	9	13	12	8372.298	0.004	8309.572	0.005				
11	2	10	10	2	9	10	9	8350.349	0.005	8285.192	0.003	8342.746	0.000		
11	2	10	10	2	9	11	10	8351.839	0.005	8286.426	0.007	8344.237	-0.001		
11	2	10	10	2	9	12	11	8350.504	0.006	8285.291	0.007	8342.905	0.001		
11	2	10	10	2	9	13	12	8349.089	0.006	8284.115	0.005	8341.489	0.002		
11	2	9	10	2	8	10	9	9178.525	0.002	9113.925	-0.003				
11	2	9	10	2	8	11	10	9175.462	0.000	9111.765	0.000				
11	2	9	10	2	8	12	11	9173.482	0.001	9110.044	0.002				
11	2	9	10	2	8	13	12	9176.574	0.002	9112.663	0.000				
11	3	9	10	3	8	10	9	8951.668	0.003	8876.289	0.002				
11	3	9	10	3	8	12	11	8954.574	0.004	8878.781	0.005				

11	3	9	10	3	8	13	12	8951.092	0.004	8875.766	0.006				
11	3	8	10	3	7	11	10	9898.991	0.004	9807.133	0.001				
11	3	8	10	3	7	12	11	9897.111	0.002	9805.545	0.004				
11	3	8	10	3	7	13	12	9896.596	0.004	9804.819	0.004				
11	4	8	10	4	7	10	9	9326.981	0.000	9236.974	-0.001				
11	4	8	10	4	7	11	10	9337.513	0.005	9245.806	-0.001				
11	4	8	10	4	7	12	11	9337.174	0.002	9245.601	0.002				
11	4	8	10	4	7	13	12	9327.651	0.003	9237.472	0.001				
11	4	7	10	4	6	10	9			9801.580	0.004				
11	4	7	10	4	6	11	10			9813.599	0.005				
11	4	7	10	4	6	12	11			9813.587	0.003				
11	4	7	10	4	6	13	12			9802.416	0.006				
11	5	7	10	5	6	10	9	9414.325	-0.006	9315.398	-0.002				
11	5	7	10	5	6	11	10	9433.682	-0.001						
11	5	7	10	5	6	12	11	9434.651	0.002	9332.406	-0.002				
11	5	7	10	5	6	13	12	9416.751	0.000	9317.345	0.001				
11	5	6	10	5	5	10	9	9549.837	-0.003	9437.593	-0.002				
11	5	6	10	5	5	11	10	9572.059	0.001	9455.889	-0.002				
11	5	6	10	5	5	12	11	9573.430	0.004	9457.099	-0.001				
11	5	6	10	5	5	13	12	9552.597	-0.001	9439.793	0.000				
11	6	6	10	6	5	10	9	9363.660	-0.012						
11	6	6	10	6	5	11	10	9388.644	-0.007	9298.026	0.001				
11	6	6	10	6	5	12	11	9394.288	-0.004	9290.424	-0.010				
11	6	6	10	6	5	13	12	9366.092	-0.007	9265.044	-0.005				
11	6	5	10	6	4	10	9	9375.758	-0.014						
11	6	5	10	6	4	11	10	9404.258	-0.003	9299.079	-0.010				
11	6	5	10	6	4	12	11	9406.872	-0.007	9301.390	-0.007				
11	6	5	10	6	4	13	12	9380.049	-0.008	9278.938	-0.007				
12	0	12	11	0	11	11	10	8353.947	0.004	8289.599	0.003				
12	0	12	11	0	11	12	11	8354.453	0.004	8290.002	0.007				
12	0	12	11	0	11	13	12	8353.134	0.003	8288.882	0.004	8344.981	0.000	8332.078	0.002
12	0	12	11	0	11	14	13	8352.792	0.007	8288.593	0.005				
12	1	12	11	1	11	11	10	8353.674	0.003	8289.280	0.003				
12	1	12	11	1	11	12	11	8354.168	0.004	8289.673	0.003				
12	1	12	11	1	11	13	12	8352.873	0.004	8288.574	0.004	8345.076	-0.001	8332.160	-0.003
12	1	12	11	1	11	14	13	8352.499	0.005	8288.260	0.005	8344.701	0.001	8331.784	-0.004
12	1	11	11	1	10	11	10	9033.483	0.001	8964.897	0.001				
12	1	11	11	1	10	12	11	9034.315	0.001	8965.521	0.004				
12	1	11	11	1	10	13	12	9033.020	0.001	8964.434	0.007				
12	1	11	11	1	10	14	13	9032.454	0.002	8963.993	0.003				
12	2	11	11	2	10	11	10	9022.529	0.002	8952.654	0.000				
12	2	11	11	2	10	12	11	9023.705	0.002	8953.614	0.004				
12	2	11	11	2	10	13	12	9022.548	0.003	8952.636	0.005				
12	2	11	11	2	10	14	13	9021.456	0.004	8951.731	0.004				
12	2	10	11	2	9	11	10	9798.596	-0.001	9730.465	-0.001				
12	2	10	11	2	9	12	11	9796.750	-0.003	9728.355	-0.001				
12	2	10	11	2	9	13	12	9795.240	-0.003	9727.101	0.001				
12	2	10	11	2	9	14	13	9797.159	-0.001	9728.816	-0.002				
12	3	10	11	3	9	11	10	9658.718	-0.001						
12	3	10	11	3	9	12	11	9661.277	0.001	9582.125	-0.001				
12	3	10	11	3	9	13	12	9660.237	-0.002	9581.259	0.002				
12	3	10	11	3	9	14	13	9657.958	0.001	9579.304	0.000				
12	4	9	11	4	8	11	10	10121.918	-0.004	10027.946	-0.002				
12	4	9	11	4	8	12	11	10129.101	-0.001	10033.997	-0.002				
12	4	9	11	4	8	13	12	10128.460	-0.003	10033.529	-0.001				

12	4	9	11	4	8	14	13	10122.082	-0.001	10028.027	-0.001
12	5	8	11	5	7	11	10	10289.166	-0.007		
12	5	8	11	5	7	14	13	10290.570	-0.003		
12	6	7	11	6	6	12	11	10281.250	-0.009		
12	6	7	11	6	6	13	12	10280.656	-0.007		
13	0	13	12	0	12	12	11	9021.912	0.003	8952.410	0.002
13	0	13	12	0	12	13	12	9022.356	0.003	8952.761	0.001
13	0	13	12	0	12	14	13	9021.236	0.004	8951.813	0.005
13	0	13	12	0	12	15	14	9020.927	0.003	8951.554	0.004
13	1	13	12	1	12	12	11	9021.801	-0.001	8952.282	0.003
13	1	13	12	1	12	13	12	9022.239	0.000	8952.630	0.003
13	1	13	12	1	12	14	13	9021.127	0.000	8951.687	0.005
13	1	13	12	1	12	15	14	9020.810	0.003	8951.417	0.004
13	1	12	12	1	11	12	11	9697.220	0.001	9623.133	0.001
13	1	12	12	1	11	13	12	9698.100	-0.001	9623.814	0.002
13	1	12	12	1	11	14	13	9697.008	0.000	9622.896	0.002
13	1	12	12	1	11	15	14	9696.359	0.002	9622.373	0.001
13	2	12	12	2	11	12	11	9692.228	0.002	9617.458	0.000
13	2	12	12	2	11	13	12	9693.236	-0.001	9618.271	0.000
13	2	12	12	2	11	14	13	9692.217	0.002	9617.410	0.001
13	2	12	12	2	11	15	14	9691.324	0.000	9616.677	0.002
13	4	9	12	4	8	12	11	11831.098	-0.008	11718.969	0.002
13	4	9	12	4	8	13	12	11837.568	-0.005	11712.443	-0.008
13	4	9	12	4	8	14	13	11835.836	-0.007	11709.147	-0.005
13	4	9	12	4	8	15	14	11832.746	-0.006	11708.152	-0.005
13	5	8	12	5	7	12	11	11595.315	-0.005		
13	5	8	12	5	7	13	12	11610.380	-0.005	11042.675	-0.009
13	5	8	12	5	7	14	13	11610.762	-0.005	11042.695	-0.011
13	5	8	12	5	7	15	14	11596.471	-0.004		
13	6	8	12	6	7	12	11			11033.564	-0.018
13	6	8	12	6	7	15	14			11035.120	-0.013
13	6	7	12	6	6	12	11			11100.206	-0.016
13	6	7	12	6	6	13	12			11115.713	-0.019
13	6	7	12	6	6	14	13			11116.490	-0.016
13	6	7	12	6	6	15	14			11101.939	-0.016
14	0	14	13	0	13	13	12	9689.972	0.002	9615.319	0.000
14	0	14	13	0	13	14	13	9690.364	0.002	9615.633	0.002
14	0	14	13	0	13	15	14	9689.394	-0.001	9614.811	0.002
14	0	14	13	0	13	16	15	9689.121	0.001	9614.580	0.001
14	1	14	13	1	13	13	12	9689.928	0.001	9615.269	0.002
14	1	14	13	1	13	14	13	9690.320	0.003	9615.580	0.003
14	1	14	13	1	13	15	14	9689.355	0.002	9614.761	0.003
14	1	14	13	1	13	16	15	9689.075	0.002	9614.526	0.003
14	1	13	13	1	12	14	13			10284.218	-0.002
14	1	13	13	1	12	15	14			10283.429	-0.002
14	1	13	13	1	12	16	15			10282.897	-0.002
14	2	13	13	2	12	13	12			10280.986	-0.004
14	2	13	13	2	12	14	13			10281.711	-0.001
14	2	13	13	2	12	15	14			10280.948	-0.001
14	2	13	13	2	12	16	15			10280.324	0.000
14	2	12	13	2	11	13	12	11070.671	-0.009	10989.164	-0.009
14	2	12	13	2	11	14	13	11070.700	-0.008	10989.082	-0.006
14	2	12	13	2	11	15	14	11069.736	-0.005	10988.259	-0.006
14	2	12	13	2	11	16	15	11069.836	-0.007	10988.429	-0.008
14	3	12	13	3	11	13	12	11029.627	-0.002	10943.291	-0.010

14	3	12	13	3	11	14	13	11030.740	-0.005	10944.241	-0.004
14	3	12	13	3	11	15	14	11030.043	-0.006	10943.628	-0.006
14	3	12	13	3	11	16	15	11028.790	-0.006	10942.601	-0.004
14	3	11	13	3	10	14	13			11846.290	-0.014
14	3	11	13	3	10	15	14			11845.218	-0.013
14	4	11	13	4	10	13	12	11624.715	-0.012		
14	4	11	13	4	10	14	13	11627.932	-0.012		
14	4	11	13	4	10	15	14	11627.014	-0.015		
14	4	11	13	4	10	16	15	11624.481	-0.009		
14	8	7	13	8	6	13	12			11777.097	0.004
14	8	7	13	8	6	14	13			11796.934	0.002
14	8	7	13	8	6	15	14			11798.592	0.002
14	8	7	13	8	6	16	15			11779.450	0.004
14	8	6	13	8	5	13	12			11777.943	0.004
14	8	6	13	8	5	14	13			11797.792	0.002
14	8	6	13	8	5	15	14			11799.453	0.002
14	8	6	13	8	5	16	15			11780.274	0.004
14	9	6	13	9	5	13	12			11725.663	0.004
14	9	6	13	9	5	14	13			11750.318	0.001
14	9	6	13	9	5	15	14			11752.848	0.001
14	9	6	13	9	5	16	15			11728.740	0.004
14	9	5	13	9	4	13	12			11725.696	0.004
14	9	5	13	9	4	14	13			11750.351	0.001
14	9	5	13	9	4	15	14			11752.882	0.001
14	9	5	13	9	4	16	15			11728.773	0.004
15	0	15	14	0	14	14	13			10278.280	-0.002
15	0	15	14	0	14	15	14			10278.557	-0.003
15	1	15	14	1	14	14	13			10278.259	-0.003
15	1	15	14	1	14	15	14			10278.537	-0.002
15	1	14	14	1	13	14	13	11029.809	-0.004	10945.100	-0.007
15	1	14	14	1	13	15	14	11030.608	-0.008	10945.736	-0.005
15	1	14	14	1	13	16	15	11029.792	-0.001	10945.050	-0.002
15	1	14	14	1	13	17	16	11029.167	-0.002		
15	2	14	14	2	13	14	13	11028.841	-0.008	10943.974	-0.003
15	2	14	14	2	13	15	14	11029.667	-0.003	10944.626	-0.005
15	2	14	14	2	13	16	15	11028.858	-0.005	10943.950	-0.004
15	2	14	14	2	13	17	16	11028.190	-0.004	10943.400	-0.004
15	2	13	14	2	12	14	13	11723.507	0.006	11635.628	-0.012
15	2	13	14	2	12	15	14	11723.910	-0.012	11635.900	-0.012
15	2	13	14	2	12	16	15	11723.102	-0.012	11635.215	-0.011
15	2	13	14	2	12	17	16	11722.810	-0.010	11635.034	-0.007
15	3	13	14	3	12	14	13	11703.036	0.006	11612.346	-0.011
15	3	13	14	3	12	15	14	11703.929	-0.011		
15	3	13	14	3	12	16	15	11703.276	-0.012	11612.532	-0.011
15	3	13	14	3	12	17	16	11702.315	0.006	11611.736	-0.007
16	0	16	15	0	15	15	14	11026.217	-0.004	10941.274	-0.002
16	0	16	15	0	15	16	15	11026.533	-0.001	10941.525	-0.001
16	0	16	15	0	15	17	16	11025.787	-0.004	10940.888	-0.006
16	0	16	15	0	15	18	17	11025.571	0.000	10940.707	-0.002
16	1	16	15	1	15	15	14	11026.210	-0.005	10941.261	-0.008
16	1	16	15	1	15	16	15	11026.521	-0.006	10941.525	0.008
16	1	16	15	1	15	17	16	11025.777	-0.006	10940.881	-0.005
16	1	16	15	1	15	18	17	11025.561	-0.003	10940.697	-0.004
16	1	15	15	1	14	15	14	11697.133	-0.005	11607.268	-0.008
16	1	15	15	1	14	16	15	11697.920	-0.009	11607.844	-0.007

16	1	15	15	1	14	17	16	11697.183	-0.010		
16	1	15	15	1	14	18	17	11696.617	0.006	11606.763	0.002
16	2	15	15	2	14	15	14	11696.756	-0.009	11606.770	0.002
16	2	15	15	2	14	16	15	11697.507	-0.007	11607.356	-0.009
16	2	15	15	2	14	17	16	11696.800	0.005	11606.763	0.001
16	2	15	15	2	14	18	17	11696.185	-0.010	11606.260	-0.008
17	0	17	16	0	16	16	15	11694.373	-0.008	11604.281	-0.009
17	0	17	16	0	16	17	16	11694.655	-0.008	11604.505	-0.009
17	0	17	16	0	16	18	17	11693.995	-0.008	11603.945	-0.008
17	0	17	16	0	16	19	18	11693.797	-0.008	11603.778	-0.009
17	1	17	16	1	16	16	15	11694.373	-0.006	11604.281	-0.006
17	1	17	16	1	16	17	16	11694.655	-0.005	11604.505	-0.006
17	1	17	16	1	16	18	17	11693.995	-0.005	11603.945	-0.005
17	1	17	16	1	16	19	18	11693.797	-0.005	11603.778	-0.006

Table S7. Fitted structural parameters by STRFIT program[55] for the C_6F_5Cl, C_6F_5Br, C_6H_5Cl, C_6H_5Br.

	C_6F_5Cl	C_6F_5Br	C_6H_5Cl	C_6H_5Br
C1X(Å)	1.718(6)	1.857(9)	1.74(2)	1.88(3)
C1C2(Å)	1.390(5)	1.393(7)	1.39(1)	1.40(2)
C2C3(Å)	1.386(5)	1.387(6)	1.40(1)	1.39(1)
C1C4(Å)	2.788(8)	[2.8079]	2.77(2)	2.79(3)
∠C2C1X(°)	120.5(2)	121.1(2)	119.1(9)	120(1)
∠C3C2C1(°)	120.7(4)	121.6(2)	119(1)	120(1)

Table S8. Orbital population and VPPA of the *p*-orbitals of the halogen atom in C_6H_5X and C_6F_5X (X= Cl, Br) calculated with the ETD model and the natural bond order NAO analysis.

ETD	p/s	P_{zz}	P_{yy}	P_{xx}	sum	P_{ave}	ΔP_{zz}	ΔP_{yy}	ΔP_{xx}
C_6F_5Cl	-	1.250	2	1.955	5.205	1.735	-0.485	0.265	0.220
C_6F_5Br	-	1.150	2	1.954	5.104	1.701	-0.551	0.299	0.253
C_6H_5Cl	-	1.335	2	1.965	5.300	1.767	-0.432	0.233	0.198
C_6H_5Br	-	1.265	2	1.975	5.240	1.747	-0.482	0.253	0.228
NAO (MP2/aug-cc-pVTZ)									
C_6F_5Cl	0.20	1.175	1.913	1.881	4.969	1.656	-0.481	0.257	0.225
C_6F_5Br	0.15	1.071	1.918	1.888	4.877	1.626	-0.555	0.293	0.262
C_6H_5Cl	0.21	1.234	1.923	1.89	5.047	1.682	-0.448	0.241	0.207
C_6H_5Br	0.17	1.134	1.924	1.892	4.95	1.65	-0.516	0.274	0.242

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