Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Does the occurrence of resonance (by the delocalization of radical/cationic/anionic charges) induce the existences of intra molecular halogen --- halogen contacts?

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Scheme S1: Substitution classification table.

Table S1: sigma hole values ($V_{s, max}$) for cation/anionic systems and radical system with substituted systems

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Table S3: C – C – C angle ***for cation/anionic systems and radical system with substituted systems***

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Table S8: ellipticity of BCP for cation/anionic systems and radical system with substituted systems

R_1	R_2	R_3		
H	H	H		(i)
NO_2	H	H	EWG only	(ii)
H	NO_2	H		
H	H	NO_2		
CH_3	H	H	EDG only	(iii)
H	CH_3	H		
H	H	CH_3		
NO_2	H	CH_3	Both EWG & EDG	(iv)
H	NO_2	CH_3		
CH_3	H	NO_2		
NO2	CH_3	H		
CH_3	NO_2	H		
H	CH_3	NO_2		

Scheme S1: Substitution classification table.

Table S1: sigma hole values ($V_{s,\,max}$) for cation/anionic systems and radical system with substituted systems

	Homo X---X interactions			Hetero X --- X interactions		
R_1, R_2, R_3	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
cH, H,H	0.4196	0.4582	0.4661	0.4290	0.4529	0.4592
aH, H,H	0.0251	0.0201	0.0254	0.0025	0.0076	0.0406
rH, H,H	0.1389	0.1169	0.1328	0.1195	0.1347	0.1203
NO_2, H, H	0.1952	0.1657	0.1860	0.1732	0.1736	0.1584
H, NO_2, H	0.1917	0.1641	0.1755	0.1657	0.1729	0.1626
H, H, NO_2	0.1952	0.1657	0.1860	0.1610	0.1748	0.1726
CH_3, H, H	0.1352	0.1151	0.1282	0.1125	0.1329	0.1173
H, CH_3, H	0.1351	0.1116	0.1287	0.1159	0.1309	0.1165
H, H, CH_3	0.1352	0.1151	0.1282	0.1150	0.1211	0.1181
NO_2, H, CH_3	0.1713	0.1559	0.1858	0.1658	0.1704	0.1557
H, NO_2, CH_3	0.1953	0.1547	0.1599	0.1589	0.1664	0.1491
CH_3, H, NO_2	0.1714	0.1559	0.1758	0.1502	0.1697	0.1605
NO_2, CH_3, H	0.1730	0.1612	0.1743	0.1651	0.1679	0.1526
CH_3, NO_2, H	0.1953	0.1547	0.1599	0.1532	0.1600	0.1506
H, CH_3, NO_2	0.1730	0.1612	0.1743	0.1502	0.1622	0.1611

c- cation structure. a - anion structure. r – radical structure.

Table S2: intra molecular halogen --- halogen bond length for cation/anionic systems and radical system with substituted systems

1,3 2	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
Σ_{VDW}	3.70	3.50	2.94	3.60	3.32	3.22
cH, H, H	3.36	3.17	2.61	3.26	2.97	2.88
aH, H, H	3.60	3.44	3.01	3.52	3.26	3.20
rH, H,H	3.46	3.27	2.76	3.36	3.08	3.00
NO2, H, H	3.44	3.24	2.73	3.32	3.06	2.97
H, NO2, H	3.42	3.23	2.70	3.33	3.03	2.95
H, H, NO2	3.44	3.24	2.73	3.34	3.06	2.98
CH3, H, H	3.42	3.23	2.72	3.33	3.04	2.96
H, CH3, H	3.40	3.21	2.69	3.30	3.02	2.93
H, H, CH3	3.42	3.23	2.72	3.33	3.05	2.96
NO2, H, CH3	3.40	3.21	2.68	3.30	3.01	2.93
H, NO2, CH3	3.39	3.19	2.64	3.29	2.99	2.91
CH3, H, NO2	3.40	3.21	2.68	3.34	3.02	2.93
NO2, CH3, H	3.35	3.13	2.55	3.23	2.90	2.81
CH3, NO2, H	3.39	3.19	2.64	3.29	2.99	2.83
H, CH3, NO2	3.35	3.13	2.55	3.24	3.02	2.83

c- cation structure. a - anion structure. r – radical structure.

Table S3: C – C – C angle ***for cation/anionic systems and radical system with substituted systems***

	Homo X---X interactions			Hetero X --- X interactions		
R_1, R_2, R_3	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
cH, H,H	2.514	2.500	2.430	2.506	2.468	2.462
aH, H,H	2.592	2.585	2.555	2.588	2.568	2.567
rH, H,H	2.520	2.511	2.464	2.515	2.487	2.485
NO_2, H, H	2.501	2.487	2.431	2.492	2.457	2.453
H, NO_2, H	2.526	2.518	2.478	2.523	2.498	2.496
H, H, NO_2	2.501	2.487	2.431	2.496	2.467	2.460
CH_3, H, H	2.533	2.522	2.469	2.526	2.493	2.490
H, CH_3, H	2.493	2.483	2.433	2.488	2.459	2.456
H, H, CH_3	2.533	2.522	2.469	2.528	2.500	2.495
NO_2, H, CH_3	2.516	2.500	2.437	2.507	2.471	2.466
H, NO_2, CH_3	2.545	2.536	2.484	2.541	2.516	2.512
CH_3, H, NO_2	2.516	2.500	2.437	2.503	2.474	2.467
NO_2, CH_3, H	2.463	2.449	2.386	2.454	2.412	2.410
CH_3, NO_2, H	2.545	2.536	2.484	2.538	2.506	2.497
H, CH_3, NO_2	2.463	2.449	2.386	2.458	2.430	2.421

c- cation structure. a - anion structure. r – radical structure.

Table S4: intra molecular halogen --- halogen bond angle for cation/anionic systems and radical system with substituted systems

		Homo X---X interactions			Hetero X --- X interactions			
c- cation a - anion r – structure.	R_1, R_2, R_3	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F	structure. structure. radical
	cH, H,H	76.36	78.32	85.99	80.31	93.45	91.27	
		76.36	78.32	85.99	74.48	69.87	73.49	
	aH, H,H	74.56	76.03	80.74	77.82	87.87	85.76	
		74.56	76.03	80.74	72.91	69.26	72.03	
	rH, H,H	75.36	77.16	83.57	79.10	90.88	88.65	
		75.36	77.16	83.57	73.58	69.56	72.87	
	NO_2, H, H	75.63	77.17	82.85	79.14	90.25	87.97	
		74.89	76.98	84.07	73.33	69.66	73.07	
	H, NO_2, H	75.85	77.88	85.22	79.80	92.50	90.33	
		75.85	77.88	85.22	74.02	70.10	73.67	
	H, H, NO_2	75.63	77.17	82.85	78.67	90.74	88.75	
		74.89	76.98	84.07	73.78	69.43	72.58	
	CH_3, H, H	77.53	79.32	85.59	81.24	93.15	90.90	
		74.75	76.71	83.48	73.07	69.25	72.58	
	H, CH_3, H	75.74	77.66	84.56	79.83	92.20	89.90	
		75.92	77.82	84.59	73.89	69.72	73.20	
	H, H, CH_3	77.53	79.32	85.59	78.53	90.58	88.42	
		74.75	76.71	83.48	75.67	71.38	74.73	
	NO_2, H, CH_3	75.16	76.77	83.03	78.72	90.06	87.91	
		77.05	79.08	86.29	75.42	71.61	75.05	
	H, NO_2, CH_3	74.43	76.51	84.42	78.36	98.05	88.92	
		79.06	81.09	88.74	77.24	73.08	76.70	
	CH_3, H, NO_2	75.16	76.77	83.03	81.69	93.08	91.09	
		77.05	79.08	86.29	71.18	69.21	72.43	
	NO_2, CH_3, H	76.51	79.00	87.49	80.99	95.85	93.37	
		75.43	77.33	85.35	73.39	69.27	73.01	
	CH_3, NO_2, H	74.43	76.51	84.42	83.04	96.12	96.46	
		79.06	81.09	88.74	72.74	69.11	72.67	
	H, CH_3, NO_2	76.51	79.00	87.49	79.48	92.96	90.31	
		75.43	77.33	85.35	74.68	68.15	74.87	

Table S5: electron density for cation/anionic systems and radical system with substituted systems

1,3 2	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
cH, H,H	0.0146	0.0142	0.0112	0.0144	0.0128	0.0126
aH, H,H	0.0094	0.0082	----	0.0087	0.0079	0.0067
rH, H,H	0.0120	0.0114	0.0088	0.0117	0.0112	0.0102
NO_2, H, H	0.0127	0.0119	0.0093	0.0124	0.0113	0.0108
H, NO_2, H	0.0128	0.0122	0.0101	0.0124	0.0119	0.0115
H, H, NO_2	0.0127	0.0119	0.0093	0.0124	0.0113	0.0108
CH_3, H, H	0.0128	0.0123	0.0096	0.0125	0.0117	0.0112
H, CH_3, H	0.0132	0.0128	0.0105	0.0130	0.0123	0.0118
H, H, CH_3	0.0128	0.0123	0.0096	0.0125	0.0117	0.0112
NO_2, H, CH_3	0.0134	0.0128	0.0104	0.0131	0.0129	0.0118
H, NO_2, CH_3	0.0136	0.0131	0.0115	0.0134	0.0131	0.0126
CH_3, H, NO_2	0.0134	0.0128	0.0104	0.0121	0.0129	0.0118
NO_2, CH_3, H	0.0147	0.0147	0.0140	0.0148	0.0155	0.0152
CH_3, NO_2, H	0.0136	0.0131	0.0115	0.0134	0.0136	0.0146
H, CH_3, NO_2	0.0147	0.0147	0.0140	0.0146	0.0123	0.0147

c-cation system, r-radical system, a- anionic system

Table S6: laplacian electron density of BCP for cation/anionic systems and radical system with substituted systems

1,3 2	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
H, H,H	0.0446	0.0549	0.0736	0.0496	0.0576	0.0634
H, H,H	0.0283	0.0319	----	0.0305	0.0299	0.0305
H, H,H	0.0374	0.0446	0.0482	0.0400	0.0438	0.0469
NO_2, H, H	0.0378	0.0473	0.0531	0.0425	0.0472	0.0502
H, NO_2, H	0.0384	0.0485	0.0557	0.0441	0.0494	0.0534
H, H, NO_2	0.0378	0.0473	0.0531	0.0424	0.0472	0.0502
CH_3, H, H	0.0395	0.0480	0.0523	0.0438	0.0476	0.0510
H, CH_3, H	0.0482	0.0504	0.0577	0.0458	0.0509	0.0550
H, H, CH_3	0.0395	0.0480	0.0523	0.0438	0.0478	0.0513
NO_2, H, CH_3	0.0419	0.0507	0.0591	0.0465	0.0496	0.0557
H, NO_2, CH_3	0.0413	0.0521	0.0649	0.0474	0.0546	0.0593
CH_3, H, NO_2	0.0419	0.0507	0.0591	0.0428	0.0492	0.0552
NO_2, CH_3, H	0.0458	0.0591	0.0843	0.0529	0.0673	0.0742
CH_3, NO_2, H	0.0413	0.0521	0.0649	0.0472	0.0524	0.0697
H, CH_3, NO_2	0.0458	0.0591	0.0843	0.0520	0.0512	0.0715

c-cation system, r-radical system, a- anionic system

Table S7: energy of BCP for cation/anionic systems and radical system with substituted systems

1,3 2	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
H, H,H	0.0195	0.0215	0.0251	0.0205	0.0217	0.0228
H, H,H	0.0098	0.0109	----	0.0110	0.0101	0.0108
H, H,H	0.0157	0.0165	0.0173	0.0154	0.0170	0.0171
NO_2, H, H	0.0167	0.0175	0.0184	0.0163	0.0181	0.0181
H, NO_2, H	0.0177	0.0182	0.0197	0.0176	0.0192	0.0195
H, H, NO_2	0.0167	0.0175	0.0184	0.0164	0.0182	0.0181
CH_3, H, H	0.0169	0.0181	0.0188	0.0176	0.0188	0.0189
H, CH_3, H	0.0177	0.0192	0.0205	0.0186	0.0199	0.0203
H, H, CH_3	0.0169	0.0181	0.0188	0.0176	0.0187	0.0189
NO_2, H, CH_3	0.0180	0.0191	0.0206	0.0187	0.0199	0.0202
H, NO_2, CH_3	0.0195	0.0199	0.0229	0.0193	0.0214	0.0218
CH_3, H, NO_2	0.0180	0.0191	0.0206	0.0169	0.0194	0.0202
NO_2, CH_3, H	0.0210	0.0231	0.0289	0.0219	0.0265	0.0276
CH_3, NO_2, H	0.0195	0.0199	0.0229	0.0208	0.0215	0.0262
H, CH_3, NO_2	0.0210	0.0231	0.0289	0.0215	0.0199	0.0265

c-cation system, r-radical system, a- anionic system

Table S8: ellipticity of BCP for cation/anionic systems and radical system with substituted systems

1,3 2	Br---Br	Cl---Cl	F---F	Br---Cl	Br---F	Cl---F
H, H,H	0.0555	0.0071	1.1770	0.0328	0.1227	0.1706
H, H,H	0.0306	0.0678	----	0.0307	0.4082	0.5341
H, H,H	0.0940	0.0959	1.3672	0.0497	0.1170	0.0617
NO_2, H, H	0.0433	0.0865	1.7219	0.0271	0.0563	0.0869
H, NO_2, H	0.0389	0.0886	0.4968	0.0842	0.0268	0.0335
H, H, NO_2	0.0433	0.0865	1.7219	0.0381	0.0345	0.0842
CH_3, H, H	0.1028	0.1100	0.6385	0.0998	0.0199	0.0296
H, CH_3, H	0.0933	0.1010	0.4723	0.0951	0.0203	0.0258
H, H, CH_3	0.1028	0.1100	0.6385	0.1118	0.0004	0.0198
NO_2, H, CH_3	0.1111	0.1049	0.6597	0.1070	0.0806	0.0368
H, NO_2, CH_3	0.0473	00995	0.2957	0.1048	0.0158	0.0012
CH_3, H, NO_2	0.1111	0.1049	0.6597	0.0795	0.0932	0.0417
NO_2, CH_3, H	0.0893	0.0919	0.2309	0.0794	0.0287	0.0131
CH_3, NO_2, H	0.0473	00995	0.2957	0.0838	0.1007	0.0081
H, CH_3, NO_2	0.0893	0.0919	0.2309	0.0988	0.0488	0.0019

c-cation system, r-radical system, a- anionic system