Electronic Supplementary Information (ESI)

The properties of Substituted 3D-Aromatic Neutral Carboranes: The Potential for σ-Hole Bonding

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Table S1. Traceless quadrupole moments (D-Å) at B3LYP/def2-TZVPP optimized geometries.

	Q_{xx}	Q_{yy}	Q_{zz}
6_T-2Br^{C}H	1.240	-0.620	-0.620
6_T-2Br^{C}F	9.755	-6.362	-3.394
6_T-2I^{C}H	4.600	-2.300	-2.300
6_T-2I^{C}F	14.271	-8.398	-5.873
6_T-2Br^{B}H	-7.120	0.152	6.968
6_T-2Br^{B}F	3.140	-3.950	0.810
6_T-2I^{B}H	-5.261	-0.782	6.043
6_T-2I^{B}F	6.431	-5.615	-0.817

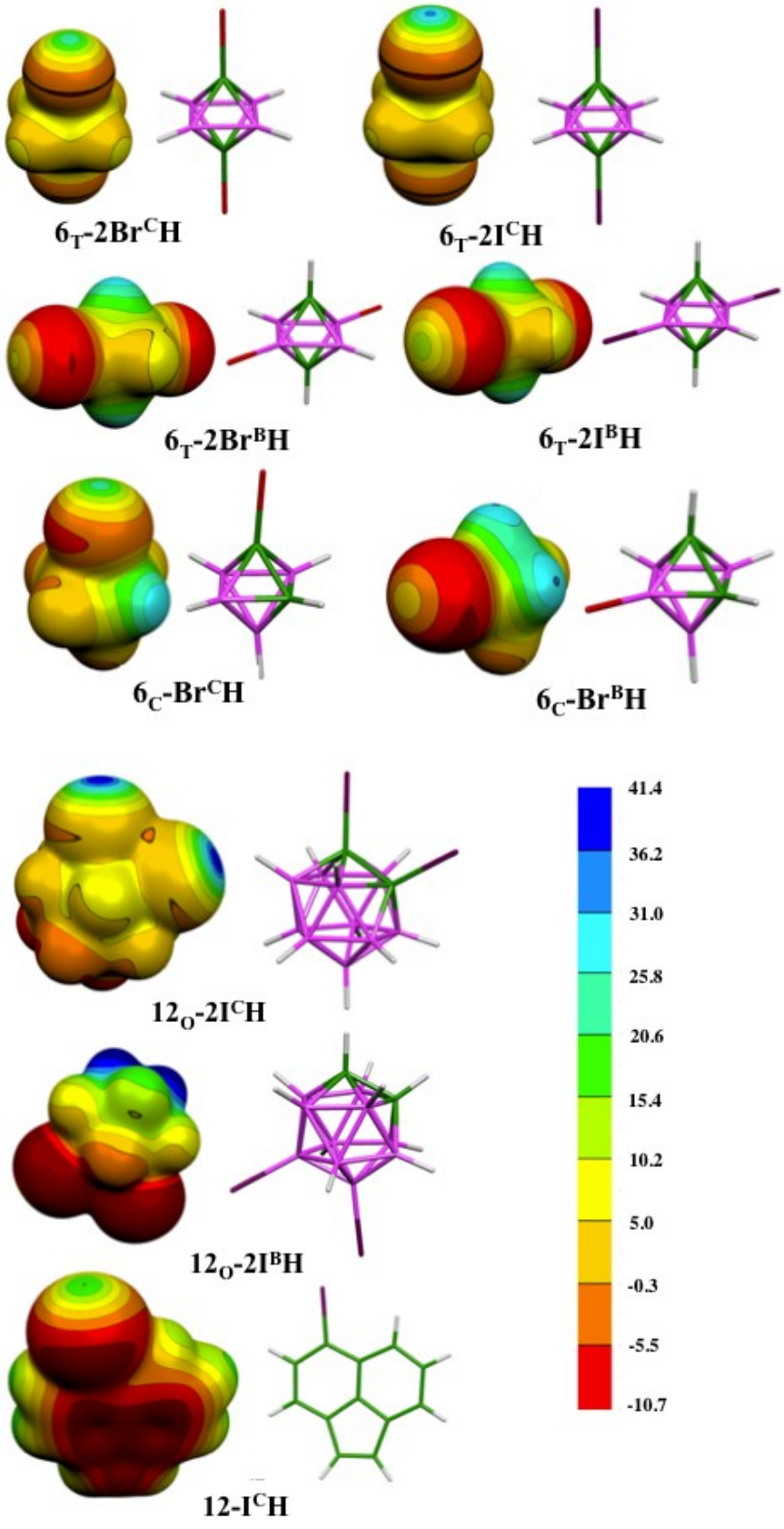
Table S2. Deviations of the geometries optimized at DFT-D3/B3LYP/def2-TZVPP and B3LYP/def2-TZVPP level of theory.

	RMSD (Å)
6_T-2I^{C}H	0.002
6_T-2I^{C}F	0.002
6_T-OH^{C}H	0.001
6_T-OH^{C}F	0.003
6_T-2I^{B}H	0.0007
6_T-2I^{B}F	0.000
6-Br^{C}H	0.0004
6-Br^{C}F	0.002
6^S-Br^{C}H	0.012
6^S-Br^{C}F	0.008
6^S-I^{C}H	0.011
6^S-I^{C}F	0.006

Table S3. Various physical–chemical properties (dipole moment, μ in D; $V_{s,max}$ in kcal/mol; polarisability α in a.u.; LUMO energy in a.u.; solvation free energy, ΔG_{solv} in kcal/mol) are given as ranges.

	μ	**$V_{s,max}$**	**α**	**LUMO**	**ΔG_{solv}**

6^{S}-Br^{C}H	2.4	-2.1	88.6	-0.0107	-1.4
6^{S}-I^{C}H	2.4	5.2	101.0	-0.0388	



Computed electrostatic potentials on 0.001 au molecular surfaces of selected systems. Color of the ESP ranges in kcal/mol. Atom Color Coding - [C: green; H: white; B: pink; Br:dark-red; I: magenta]

B3LYP/def2-TZVPP optimized Cartesian coordinates of isolated systems, including electronic energies in gas phase and the energy differences between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) ($\Delta E_{HOMO-LUMO}$) (All energies are given in a.u).

6_T-Br^{C}H

E= -2752.87944

$\Delta E_{HOMO-LUMO}$ = 0.2696

B	-1.467961	0.042586	0.075115
B	-0.492315	0.657437	-1.193256
B	0.580006	1.334876	-0.040032
C	0.126757	-0.215704	0.018007
B	-0.395421	0.719882	1.228322
C	-1.018730	1.599463	0.017051
Br	-2.025818	3.195595	0.016156
H	-2.464505	-0.573900	0.131267
H	-0.354395	0.758901	2.400119
H	-0.544824	0.636295	-2.365054
H	1.565271	1.969232	-0.096214
H	0.700936	-1.125662	0.018517

6_C-Br^{C}H

E= -2752.86415

$\Delta E_{HOMO-LUMO}$ = 0.2541

B	-1.471848	0.036789	0.081712
C	-0.478801	0.649269	-1.043568
B	0.587443	1.336177	-0.034247
B	0.208796	-0.344070	0.036686
B	-0.373345	0.687629	1.258378
C	-1.007318	1.585178	0.059570
Br	-2.016315	3.167045	-0.136265
H	-2.534717	-0.455720	0.003973
H	-0.399980	0.833659	2.424252
H	-0.608643	0.760348	-2.105241
H	1.478580	2.077023	-0.222195
H	0.825148	-1.334328	-0.113054

6-Br^{C}H

E= -2805.91941

$\Delta E_{HOMO-LUMO}$ =0.2232

C	-0.498765	0.109249	1.482424
C	0.418191	0.371468	2.491358
C	-0.032168	0.467049	3.803853
C	-1.380519	0.302295	4.099885
C	-2.284412	0.040245	3.076610
C	-1.848876	-0.058135	1.759317
Br	0.110091	-0.024038	-0.324949
H	-2.548045	-0.261634	0.961310
H	1.465093	0.498838	2.257099
H	0.677864	0.671244	4.594335
H	-1.724985	0.377700	5.122333
H	-3.335469	-0.089284	3.298425

6^S-Br^{C}H

E= -2809.55516

$\Delta E_{HOMO-LUMO}$ = 0.2611

C	1.103791	0.166650	-0.988274
C	-0.367730	0.249806	-1.401215
C	-1.289272	0.664007	-0.260582
C	-1.062907	-0.156396	1.003364
C	0.409427	-0.239070	1.413489
C	1.291616	-0.711114	0.253275
Br	-1.060379	2.624332	0.136751
H	1.477607	1.172978	-0.784914
H	1.692274	-0.223130	-1.821365
H	-0.706898	-0.742650	-1.724030
H	-0.498959	0.916609	-2.253335
H	-2.329875	0.625217	-0.567978
H	-1.676003	0.228853	1.818011
H	-1.431767	-1.166201	0.783249
H	0.744394	0.744567	1.751193
H	0.510552	-0.913607	2.266165
H	1.038393	-1.747843	0.004931
H	2.340737	-0.713007	0.556264

12_O-Br^{C}H

E= -2905.76795

$\Delta E_{HOMO-LUMO}$ = 0.2426

C	-0.428965	-0.000189	0.076056
B	0.398024	-0.891362	1.264526
B	0.397636	0.894098	1.262486
B	1.878283	1.449159	0.450543
B	1.829593	0.888137	-1.233562
C	0.393228	-0.001650	-1.339499
B	1.830009	-0.890545	-1.231501
B	2.799689	0.000387	-0.044250
B	1.913143	0.001974	1.495472
B	1.878908	-1.447641	0.453892
B	0.354432	-1.454323	-0.421720
B	0.353793	1.453154	-0.425051
H	-0.245760	-1.475165	2.058530
Br	-2.347136	-0.000733	-0.019426
H	-0.217914	-0.002808	-2.226868
H	2.183538	-1.483020	-2.186980
H	2.384417	-2.472554	0.749572
H	2.446351	0.003267	2.549286
H	-0.246443	1.479418	2.055134
H	-0.325844	2.328918	-0.814015
H	2.182857	1.478589	-2.190391
H	3.978847	0.000548	-0.104393
H	2.383305	2.475000	0.743830
H	-0.324812	-2.331315	-0.808598

12_M-Br^{C}H

E= -2905.79421
$\Delta E_{HOMO-LUMO}$ = 0.2478

C	-0.450823	0.006302	0.068079
B	0.393540	-0.858635	1.260540
B	0.390258	0.908286	1.263133
B	1.866051	1.458208	0.443988
B	1.799921	0.901621	-1.253976
B	1.795845	-0.871779	-1.249380
B	1.901936	0.024197	1.489356
B	0.327809	-1.414396	-0.439171
B	0.326914	1.448980	-0.434272
H	-0.131358	-1.539917	2.060224
Br	-2.376397	-0.032347	0.154982
H	2.299781	-1.592781	-2.032976
H	-0.335428	2.381137	-0.713874
H	2.283156	1.511415	-2.141401
H	2.396315	2.463095	0.763011
H	-0.236679	-2.423811	-0.643365
B	0.283485	0.008972	-1.484342
H	-0.399111	-0.017795	-2.442489
H	-0.222534	1.467452	2.097600
H	2.475719	-0.106051	2.509982
B	2.770993	0.020690	-0.061664
C	1.784073	-1.291389	0.406195
H	3.941837	-0.112319	-0.062756
H	2.258698	-2.217136	0.690575

12_P-Br^{C}H

E= -2905.79940
$\Delta E_{HOMO-LUMO}$ = 0.2497

C	-0.451474	-0.000478	0.069777
B	0.384803	-0.891105	1.268118
B	0.385032	0.894337	1.265720
B	1.845456	1.440334	0.445973
B	1.779329	0.888165	-1.244311
B	1.779158	-0.890633	-1.242119
B	1.887149	0.002059	1.492773
B	1.845807	-1.438514	0.449462
B	0.318607	-1.445033	-0.428420
B	0.318174	1.443578	-0.431938
H	-0.210969	-1.474533	2.097666
Br	-2.379447	-0.001508	0.145893
H	2.367041	-1.479742	-2.075315
H	2.477088	-2.390540	0.735635
H	2.545183	0.003652	2.469367
H	-0.211145	1.479427	2.093829
H	-0.321590	2.389125	-0.715123
H	2.366795	1.475922	-2.078738
H	2.475837	2.393572	0.730042
H	-0.320281	-2.391713	-0.709477
C	2.605432	0.000672	-0.049802
H	3.682898	0.001048	-0.092696
B	0.276156	-0.001725	-1.478861
H	-0.390039	-0.003369	-2.448456

12-Br^{C}H

E= -3035.83427
$\Delta E_{HOMO-LUMO}$ = 0.1385

C	3.735041	5.289526	0.497878
C	4.453981	4.137559	0.088330
C	3.813775	2.993102	-0.334727
C	2.393175	2.914499	-0.380223
C	1.735292	4.073013	0.032531
C	2.361057	5.259822	0.470805
C	0.331089	4.225797	0.070247
C	-0.448328	3.164725	-0.324808
C	0.192320	1.971400	-0.750083
C	1.563489	1.834127	-0.782865
C	1.277468	6.195601	0.796663
C	0.085454	5.588711	0.561716
Br	4.872417	1.494277	-0.866179
H	4.287260	6.162620	0.821500
H	5.534028	4.158980	0.108862
H	-1.529805	3.216037	-0.319911
H	-0.422964	1.137226	-1.060573
H	2.008042	0.906533	-1.114240
H	-0.889295	6.028172	0.708812
H	1.415504	7.201272	1.163268