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Supporting Information

for

Unraveling aromaticity: the dual worlds of pyrazole, pyrazoline, and 3D carborane

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Energy decomposition analysis of pyrazole^{CC} (fragments used, molecular orbitals overlaps, and fragment molecular orbitals), cartesian coordinates and energies of all compounds under analysis, and whole set of ring current density maps

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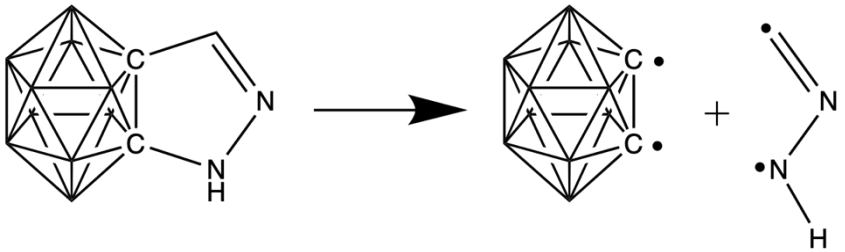


Figure S1: Model system used in the energy decomposition analysis of pyrazole^{CC}.

Table S1: Overlap matrix between the fragment molecular orbitals (FMOs) of the two fragments considered in the EDA analysis of pyrazole^{CC}. FMOs energies (in eV) also enclosed.

							carboryne$^{\alpha\alpha}$	
		-8.42	-8.27	-8.18	-8.18	-6.91	-5.59	-1.35
$N_2CH_2^{\beta\beta}$		HOMO-4	HOMO-3	HOMO-2	HOMO-1	SOMO	SOMO'	LUMO
-11.91	HOMO-4	0.002	0.004	0.001	0.011	0.107	0.156	0.013
-11.41	HOMO-3	0.001	0.001	0.005	0.009	0.187	0.085	0.008
-10.02	HOMO-2	0.004	0.003	0.003	0.042	0.039	0.082	0.006
-7.21	SOMO	0.027	0.015	0.007	0.002	0.072	0.331	0.062
-5.25	HOMO-1	0.022	0.028	0.000	0.001	0.019	0.215	0.097
-4.94	SOMO'	0.018	0.009	0.009	0.004	0.255	0.158	0.022
-1.71	LUMO	0.001	0.017	0.014	0.047	0.022	0.005	0.036

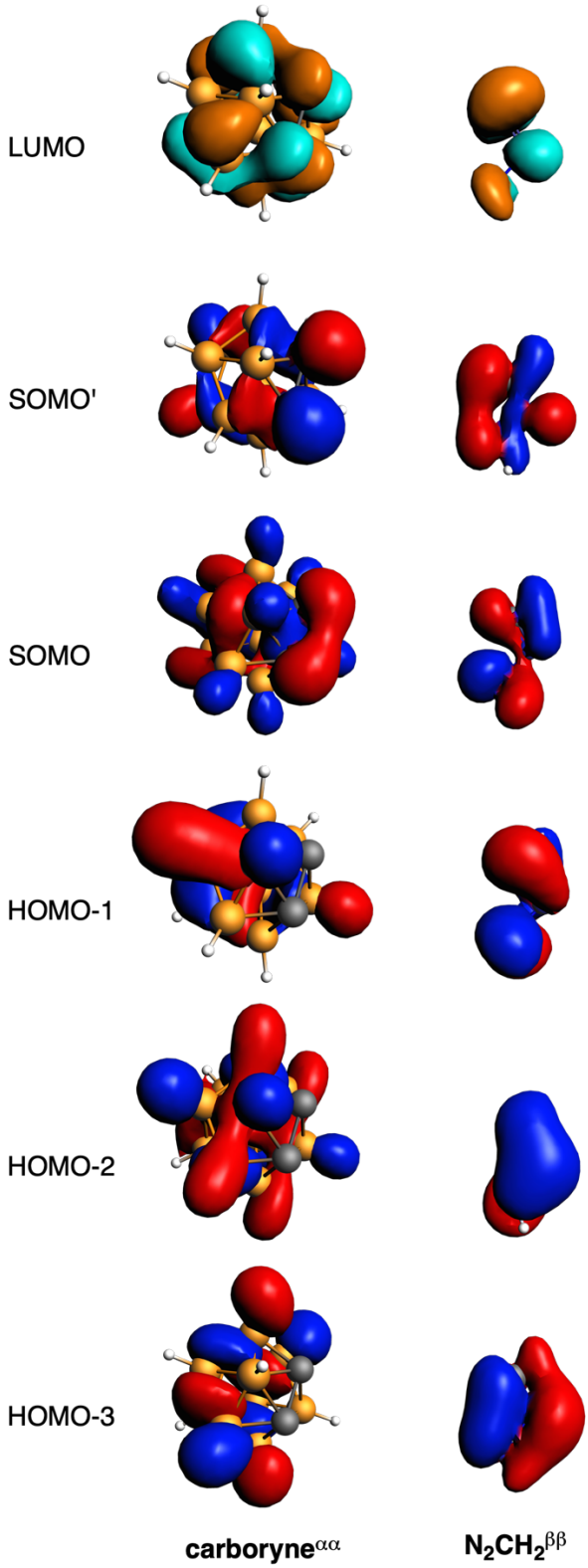


Figure S2: FMOs of each fragment considered in the EDA of pyrazole^{CC}.

Table S2: Cartesian coordinates (in Å) and electronic energies (in Hartrees) of all systems under analysis. Computed at B3LYP/6-311++G(d,p) level of theory.

Indazole (-379.9767278)

1	7	0	-2.264576	0.835361	0.000000
2	7	0	-1.099799	1.535108	0.000000
3	6	0	1.745971	-1.418451	0.000000
4	6	0	0.388873	-1.684127	0.000000
5	6	0	-0.505526	-0.600754	0.000000
6	6	0	0.000000	0.722724	0.000000
7	6	0	1.374234	0.996285	0.000000
8	1	0	-2.692626	-1.198629	0.000000
9	1	0	0.021871	-2.703609	0.000000
10	6	0	2.230422	-0.090891	0.000000
11	6	0	-1.925986	-0.438763	0.000000
12	1	0	2.455806	-2.236733	0.000000
13	1	0	1.753127	2.011119	0.000000
14	1	0	3.300815	0.078181	0.000000
15	1	0	-1.136295	2.540244	0.000000

Indazoline (-381.161345)

1	7	0	-2.398264	0.084525	0.126066
2	7	0	-1.490581	1.209274	-0.011420
3	6	0	2.218541	-0.712610	0.034381
4	6	0	1.011243	-1.419036	0.010931
5	6	0	-0.179294	-0.709648	-0.016715
6	6	0	-0.170547	0.686482	-0.016043
7	6	0	1.020474	1.401982	0.000613
8	1	0	-1.718404	1.713474	-0.862326
9	1	0	1.012399	-2.503481	0.004546
10	6	0	2.217887	0.682522	0.020820
11	6	0	-1.618724	-1.154809	-0.133804
12	1	0	3.158232	-1.250870	0.062241
13	1	0	1.019105	2.485332	0.009988
14	1	0	3.159506	1.218807	0.040562
15	1	0	-1.906276	-1.929273	0.580246
16	1	0	-1.829595	-1.531994	-1.142238
17	1	0	-2.670528	0.092114	1.103372

Pyrazole (-226.280132)

1	6	0	-0.745660	-0.892221	0.000000
2	6	0	0.664322	-0.997500	0.000000
3	6	0	1.111723	0.308120	0.000000
4	7	0	0.000000	1.087278	0.000000
5	7	0	-1.145889	0.376077	0.000000
6	1	0	1.265179	-1.891315	0.000000
7	1	0	-0.050690	2.092728	0.000000
8	1	0	-1.480068	-1.682961	0.000000
9	1	0	2.104488	0.727665	0.000000

Pyrazoline (-227.4485913)

1	6	0	1.008512	0.670997	0.044739
2	6	0	-0.206060	1.218056	0.055058
3	6	0	-1.226560	0.114542	-0.117672
4	7	0	-0.423396	-1.130778	0.030319
5	7	0	0.979341	-0.744811	0.005213
6	1	0	-0.433751	2.271038	0.123905
7	1	0	-0.568366	-1.494094	0.965865
8	1	0	1.970094	1.165186	0.078950
9	1	0	-1.703847	0.161981	-1.106605

10	1	0	1.413205	-1.122254	-0.833436
11	1	0	-2.024302	0.125693	0.629854

Pyrazonline2 (-227.4692596)

1	6	0	1.187559	-0.199182	-0.080545
2	6	0	0.492284	1.131843	0.108132
3	6	0	-0.962229	0.698607	-0.140396
4	7	0	-0.900494	-0.736728	0.212624
5	7	0	0.393912	-1.200405	-0.033077
6	1	0	0.637703	1.491638	1.134533
7	1	0	-1.574103	-1.335855	-0.246228
8	1	0	2.254099	-0.351786	-0.181897
9	1	0	-1.228729	0.839037	-1.197319
10	1	0	-1.688091	1.219205	0.483481
11	1	0	0.839505	1.910082	-0.572545

Pyrazole^{CC} (-479.8371731)

1	5	0	1.553756	0.011744	1.458400
2	1	0	2.131376	0.025900	2.487100
3	5	0	2.078353	0.922695	0.017105
4	1	0	3.056569	1.582171	0.030554
5	5	0	0.622595	1.437498	0.896889
6	1	0	0.432704	2.449640	1.470542
7	6	0	-0.646572	0.776310	-0.017432
8	7	0	-2.038532	1.077644	-0.084428
9	5	0	2.116155	-0.874559	0.020892
10	1	0	3.121325	-1.491946	0.033177
11	5	0	0.701190	-1.445641	-0.891480
12	1	0	0.565754	-2.461825	-1.471421
13	5	0	1.592084	0.008309	-1.431992
14	1	0	2.196837	0.015908	-2.444866
15	5	0	0.651799	1.436892	-0.902498
16	1	0	0.477270	2.448510	-1.479471
17	5	0	0.686432	-1.447385	0.901043
18	1	0	0.537898	-2.464764	1.475996
19	5	0	-0.177729	-0.023447	1.475647
20	1	0	-0.994542	-0.032423	2.319937
21	5	0	-0.142835	-0.019799	-1.492623
22	1	0	-0.939525	-0.028385	-2.354614
23	6	0	-0.622675	-0.828470	-0.014900
24	1	0	-2.404016	1.877775	0.411069
25	1	0	-2.517583	-2.100224	0.008885
26	6	0	-2.081036	-1.113409	-0.006165
27	7	0	-2.814520	-0.057424	0.011166

Pyrazole^{CB} (-479.8456006)

1	5	0	1.580787	0.043351	-1.434532
2	1	0	2.119793	-0.100947	-2.471607
3	5	0	2.047150	-0.952921	-0.037616
4	1	0	2.916651	-1.740215	-0.139505
5	6	0	0.604957	-1.239815	-0.863189
6	1	0	0.437964	-2.144629	-1.427932
7	6	0	-0.671310	-0.687400	0.019358
8	7	0	-2.017121	-1.091669	-0.119374
9	5	0	2.170651	0.831308	0.033038
10	1	0	3.225285	1.360016	0.036535
11	5	0	0.775345	1.446445	0.955072
12	1	0	0.825251	2.424578	1.613613
13	5	0	1.584730	-0.083921	1.446628
14	1	0	2.207372	-0.200809	2.441724

15	5	0	0.588700	-1.437919	0.862178
16	1	0	0.409037	-2.520132	1.288187
17	5	0	0.758554	1.508571	-0.838631
18	1	0	0.789362	2.517519	-1.449591
19	5	0	-0.169677	0.151368	-1.439098
20	1	0	-0.884747	0.036122	-2.362536
21	5	0	-0.159856	0.045319	1.477933
22	1	0	-0.897984	-0.056761	2.389969
23	5	0	-0.696652	0.986032	0.050453
24	1	0	-2.338832	-1.885416	0.417338
25	1	0	-2.878585	2.020432	0.064838
26	6	0	-2.261593	1.130310	0.031999
27	7	0	-2.891671	0.003599	-0.010220

Pyrazole[BB] (-479.8762496)

1	5	0	1.558536	0.009623	1.451045
2	1	0	2.353079	0.030217	2.317513
3	6	0	1.940649	0.849211	-0.000705
4	1	0	2.900953	1.339886	-0.001092
5	5	0	0.639060	1.442229	0.902650
6	1	0	0.790528	2.453469	1.488197
7	5	0	-0.770952	0.844623	0.000427
8	7	0	-2.210453	1.089577	-0.000192
9	6	0	1.983007	-0.796985	-0.000210
10	1	0	2.966004	-1.240425	-0.000326
11	5	0	0.701889	-1.454799	-0.898714
12	1	0	0.899743	-2.458233	-1.483454
13	5	0	1.557729	0.008711	-1.451630
14	1	0	2.351510	0.028654	-2.318811
15	5	0	0.638562	1.441638	-0.903422
16	1	0	0.789013	2.452838	-1.489299
17	5	0	0.702455	-1.454351	0.899399
18	1	0	0.900838	-2.457290	1.484806
19	5	0	-0.170958	-0.028169	1.463305
20	1	0	-0.801428	-0.034516	2.459516
21	5	0	-0.171757	-0.028997	-1.462617
22	1	0	-0.803350	-0.036056	-2.458102
23	5	0	-0.737987	-0.915126	0.000785
24	1	0	-2.741779	1.941945	0.000209
25	1	0	-2.856455	-2.066835	0.000440
26	6	0	-2.282080	-1.147908	0.000435
27	7	0	-2.979691	-0.047643	-0.000216

Pyrazolyne[CC] (-481.0461566)

1	5	0	1.526498	0.042035	1.517302
2	1	0	2.043976	0.077901	2.577260
3	5	0	2.146954	0.902951	0.082655
4	1	0	3.132713	1.550154	0.129051
5	5	0	0.653820	1.462091	0.858386
6	1	0	0.442788	2.490103	1.396109
7	6	0	-0.580682	0.792166	-0.110666
8	7	0	-1.966796	1.158442	-0.296254
9	5	0	2.161206	-0.889482	0.139128
10	1	0	3.154486	-1.520279	0.228104
11	5	0	0.789492	-1.471132	-0.832884
12	1	0	0.669924	-2.501563	-1.392097
13	5	0	1.728569	-0.046655	-1.367216
14	1	0	2.394423	-0.073986	-2.340854
15	5	0	0.774559	1.408831	-0.928288
16	1	0	0.651800	2.402967	-1.547388

17	5	0	0.668628	-1.417536	0.945080
18	1	0	0.464650	-2.412434	1.543183
19	5	0	-0.204043	0.031105	1.413179
20	1	0	-1.043001	0.053513	2.238626
21	5	0	0.000502	-0.057918	-1.515987
22	1	0	-0.736504	-0.079421	-2.428470
23	6	0	-0.576145	-0.808350	-0.058098
24	1	0	-2.218165	2.012698	0.187306
25	7	0	-2.799533	0.066281	0.186866
26	6	0	-2.068629	-1.164577	-0.156435
27	1	0	-2.346994	-1.954925	0.538342
28	1	0	-2.304402	-1.471597	-1.174519
29	1	0	-2.819583	0.116927	1.205478

Pyrazolyne^{CB} (-481.0603202)

1	5	0	1.557394	0.040643	-1.488313
2	1	0	2.040871	-0.097494	-2.553363
3	5	0	2.133110	-0.913851	-0.105408
4	1	0	3.017614	-1.679528	-0.239313
5	6	0	0.658956	-1.253135	-0.847765
6	1	0	0.472985	-2.167485	-1.390108
7	6	0	-0.598096	-0.707059	0.085677
8	7	0	-1.921157	-1.236222	0.048565
9	5	0	2.208865	0.868151	-0.065721
10	1	0	3.247784	1.424408	-0.125253
11	5	0	0.850740	1.462232	0.919787
12	1	0	0.911255	2.447322	1.567868
13	5	0	1.718719	-0.043245	1.390654
14	1	0	2.396722	-0.134443	2.351852
15	5	0	0.725633	-1.425245	0.863159
16	1	0	0.592004	-2.502683	1.316129
17	5	0	0.732697	1.499538	-0.865280
18	1	0	0.710888	2.497649	-1.494927
19	5	0	-0.194908	0.107461	-1.384297
20	1	0	-0.943169	-0.031335	-2.280374
21	5	0	-0.026114	0.047179	1.497947
22	1	0	-0.717443	-0.063554	2.447196
23	5	0	-0.660120	0.967276	0.109662
24	1	0	-2.142254	-1.664892	0.940449
25	1	0	-3.065869	-0.168275	-1.154950
26	6	0	-2.244529	1.186392	0.170002
27	7	0	-2.857296	-0.146683	-0.163730
28	1	0	-2.621809	1.914487	-0.549887
29	1	0	-2.578470	1.498270	1.162402

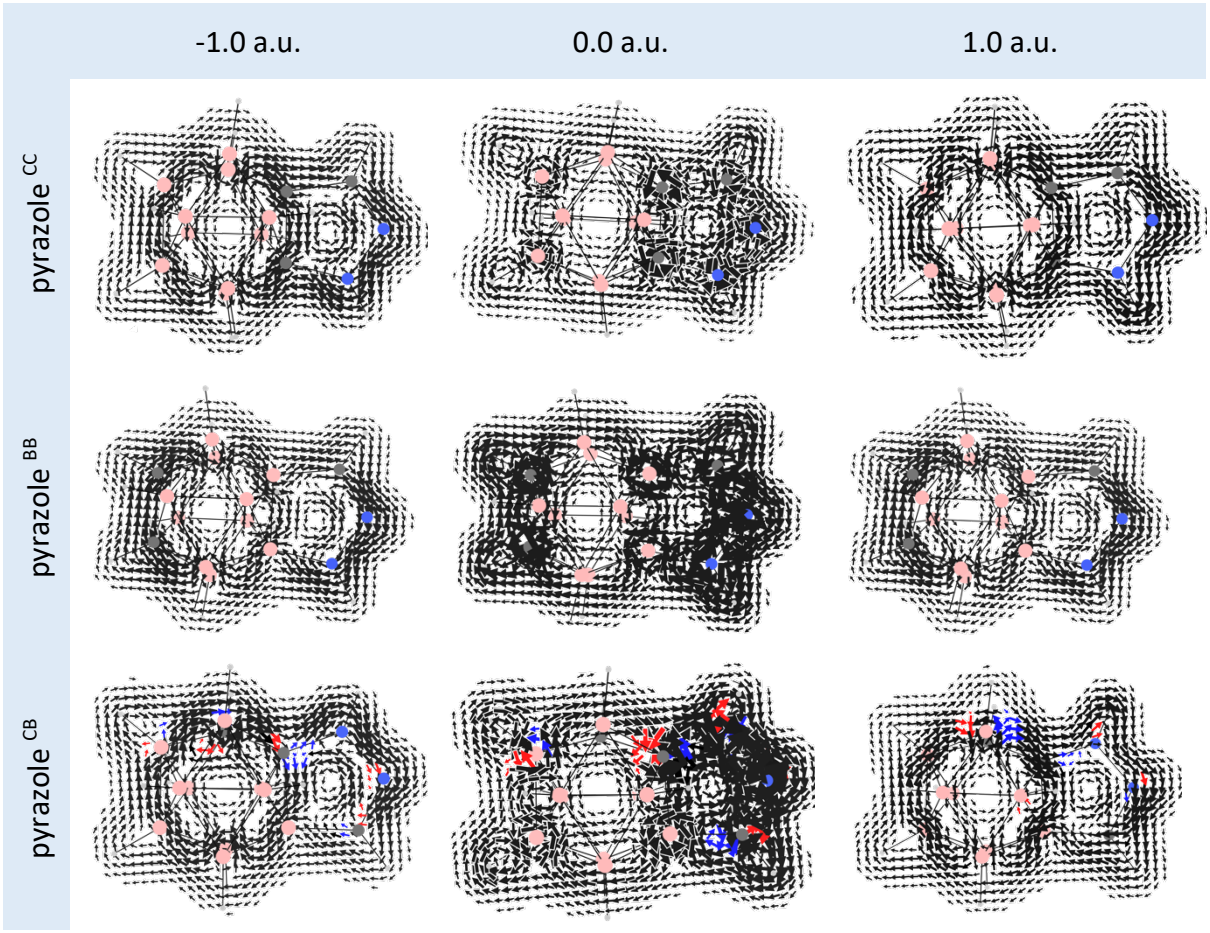
Pyrazolyne^{BB} (-481.0796582)

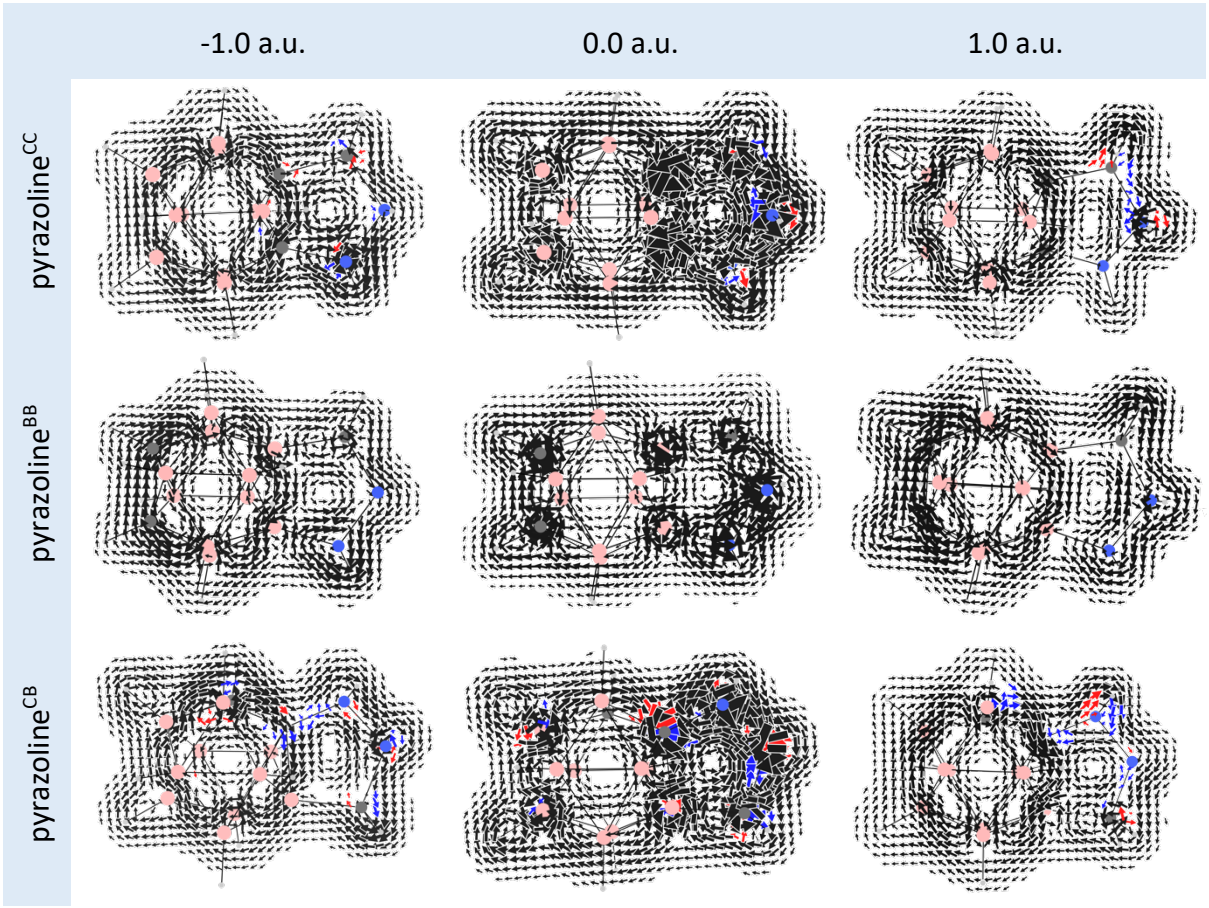
1	5	0	1.552997	-0.022693	1.494265
2	1	0	2.303613	-0.031212	2.399306
3	6	0	2.015839	0.821748	0.077585
4	1	0	2.983107	1.297060	0.122501
5	5	0	0.685418	1.431364	0.922138
6	1	0	0.824139	2.430203	1.530528
7	5	0	-0.706942	0.866897	-0.050415
8	7	0	-2.126818	1.257768	-0.062647
9	6	0	2.032343	-0.815506	0.055151
10	1	0	3.007053	-1.275609	0.094658
11	5	0	0.788188	-1.443434	-0.906181
12	1	0	0.995169	-2.442721	-1.495839
13	5	0	1.684380	0.015026	-1.407776
14	1	0	2.523070	0.037719	-2.231836

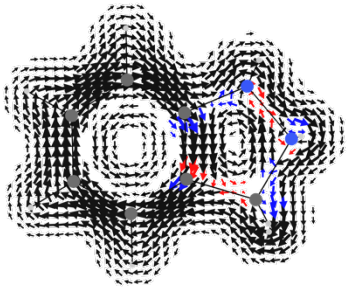
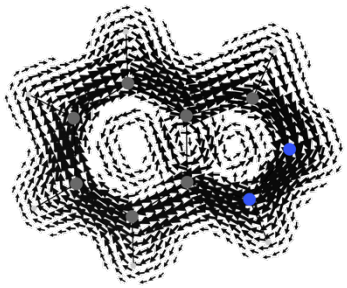
15	5	0	0.756835	1.452865	-0.868119
16	1	0	0.950700	2.464338	-1.441112
17	5	0	0.691487	-1.464085	0.880686
18	1	0	0.843128	-2.473719	1.469129
19	5	0	-0.183736	-0.025113	1.415814
20	1	0	-0.855747	-0.040969	2.386669
21	5	0	-0.047160	-0.002405	-1.487442
22	1	0	-0.631717	0.011137	-2.513531
23	5	0	-0.684534	-0.892004	-0.074629
24	1	0	-2.450538	1.725747	-0.899009
25	7	0	-2.964735	0.080040	0.143335
26	6	0	-2.249488	-1.210039	-0.153824
27	1	0	-2.598456	-1.954177	0.566246
28	1	0	-2.540445	-1.560225	-1.149266
29	1	0	-3.189038	0.088464	1.131571

Figure S3. Current density maps (all-electron contributions) for a perpendicular magnetic field over a plane 1 a.u. above the molecular plane of *o*-carboranes-fused pyrazole systems and reference systems. Red/blue arrows when the component parallel/antiparallel to **B** is greater than 30% of the vector modulus (top). Bond current strengths for a magnetic field perpendicular to the molecular plane (bottom). Values aside each arrow represent the percentage relationship with respect to a reference current Diatropic/paratropic circulations are clockwise / anticlockwise.

Current density maps




-1.0 a.u.
0.0 a.u.
1.0 a.u.
pyrazoline^CC
pyrazoline^BB
pyrazoline^CB

indazoline	indazole
	
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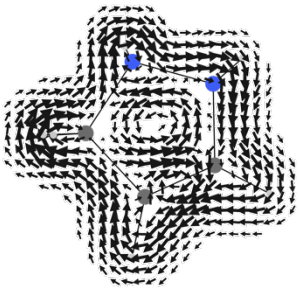
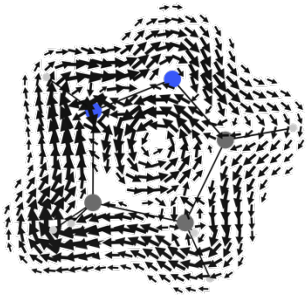
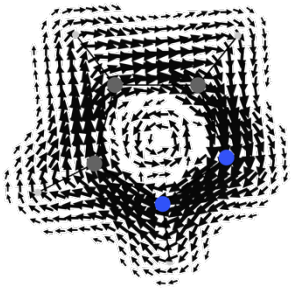
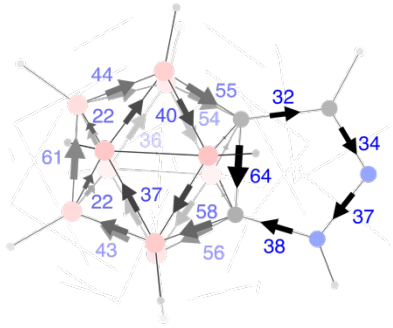
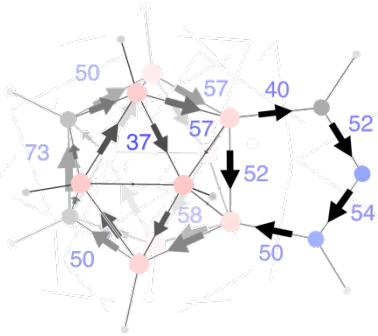
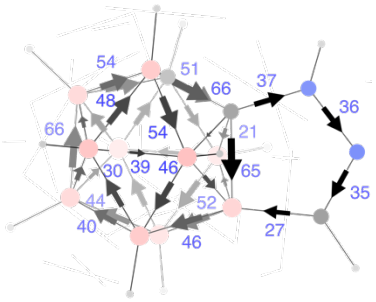
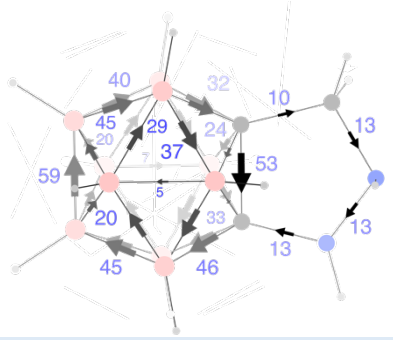
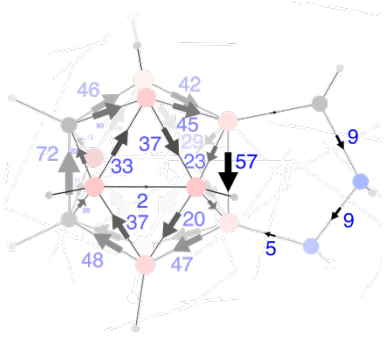
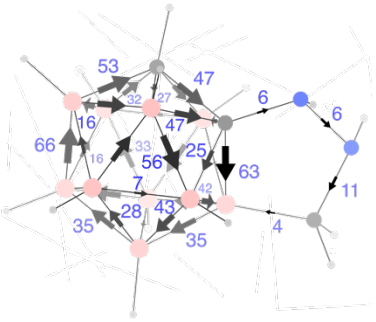
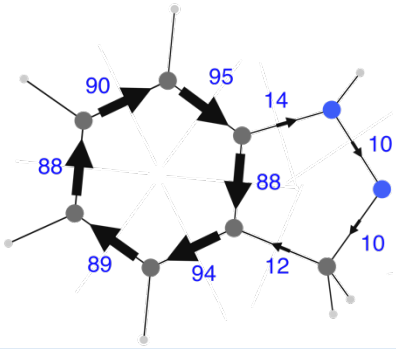
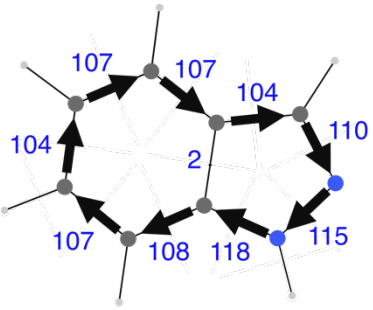
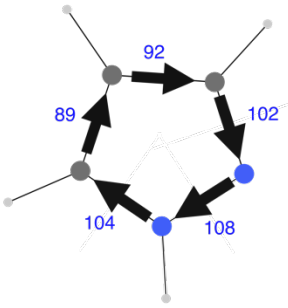
	
pyrazole	
	

Bond current strengths

pyrazole^{CC}	pyrazole^{BB}	pyrazole^{CB}
		
pyrazoline^{CC}	pyrazoline^{BB}	pyrazoline^{CB}
		
indazoline	indazole	pyrazole
		
3-pyrazoline	2-pyrazoline