The Glidewell-Lloyd rule explains the local aromaticity and the relative stability of Benzoborepin isomers

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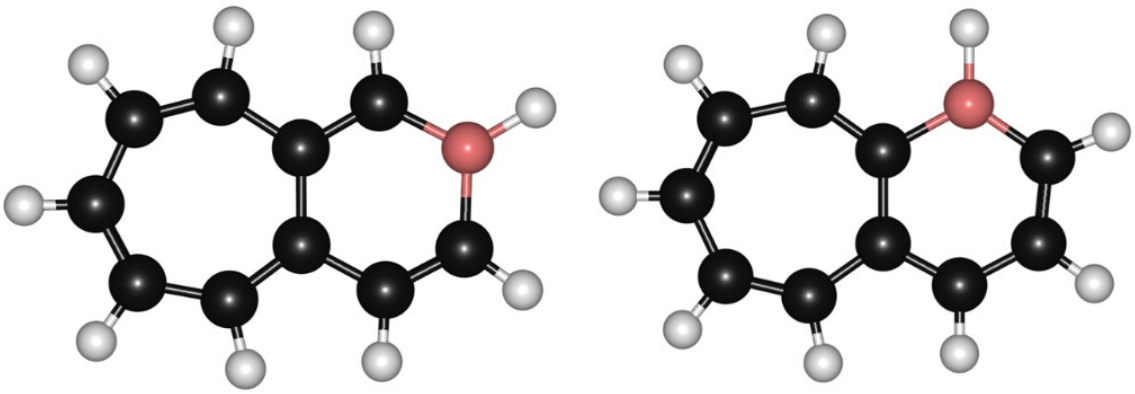
SUPPORTING INFORMATION

Figure S1. Relative stabilities (in kcal.mol^{-1}) of isomers containing the boron atom in the six-membered ring at the ωB97XD/def2-TZVP (Black) and CCSD(T)/def2-TZVP//ωB97XD/def2-TZVP (blue) levels.



20.1
(20.1)

20.4
(19.1)

Table S1. Natural population analysis for benzoborepines and benzotropylium cation at the ωB97X-D/def2-TZVP level.

Benzoborepin-1		Benzoborepin-2		Benzoborepin-3		Benzoborepin-4		Benzotropylium Cation	
C 1	-0.0326	C 1	-0.0580	C 1	-0.2760	C 1	-0.0448	C 1	-0.0273
C 2	-0.3343	C 2	-0.0580	B 2	0.4796	C 2	-0.0278	C 2	-0.0273
B 3	0.4814	C 3	-0.1015	C 3	-0.3781	C 3	-0.3787	C 3	-0.0367
C 4	-0.4967	C 4	-0.4888	C 4	-0.1864	B 4	0.3029	C 4	-0.1937
C 5	-0.1267	B 5	0.4468	C 5	-0.1567	C 5	-0.3967	C 5	-0.0548
C 6	-0.2226	C 6	-0.4888	C 6	-0.2100	C 6	-0.1797	C 6	-0.1938
C 7	-0.1361	C 7	-0.1015	C 7	-0.1002	C 7	-0.1347	C 7	-0.0367
H 8	-0.0677	H 8	0.1929	H 8	0.2058	H 8	0.2009	H 8	0.2350
H 9	0.2118	H 9	0.2113	H 9	0.2016	H 9	-0.0495	H 9	0.2474
H 10	0.1990	H 10	-0.0628	H 10	0.2075	H 10	0.2076	H 10	0.2436
H 11	0.2080	H 11	0.2113	H 11	0.2094	H 11	0.2018	H 11	0.2474
H 12	0.2015	H 12	0.1929	H 12	0.1952	H 12	0.2010	H 12	0.2351
C 13	-0.1873	C 13	-0.2013	C 13	-0.2012	C 13	-0.2053	C 13	-0.1395
C 14	-0.2124	C 14	-0.2013	C 14	-0.1741	C 14	-0.1993	C 14	-0.1396
C 15	-0.1480	C 15	-0.1739	C 15	-0.4437	C 15	-0.1791	C 15	-0.1616
H 16	0.2145	H 16	0.2170	H 16	0.2081	H 16	0.2170	H 16	0.2461
H 17	0.2148	H 17	0.2170	H 17	0.2008	H 17	0.2169	H 17	0.2461
H 18	0.2167	H 18	0.2102	H 18	0.2058	H 18	0.2123	H 18	0.2360
C 19	-0.1910	C 19	-0.1739	C 19	-0.1850	C 19	-0.1743	C 19	-0.1617
H 20	0.2077	H 20	0.2102	H 20	0.1976	H 20	0.2095	H 20	0.2360

Figure S2. Values and direction of the computed dipole moments for benzoborepines, benzotropylium cation and azulene at the ωB97x-D/def2-TZVP level.

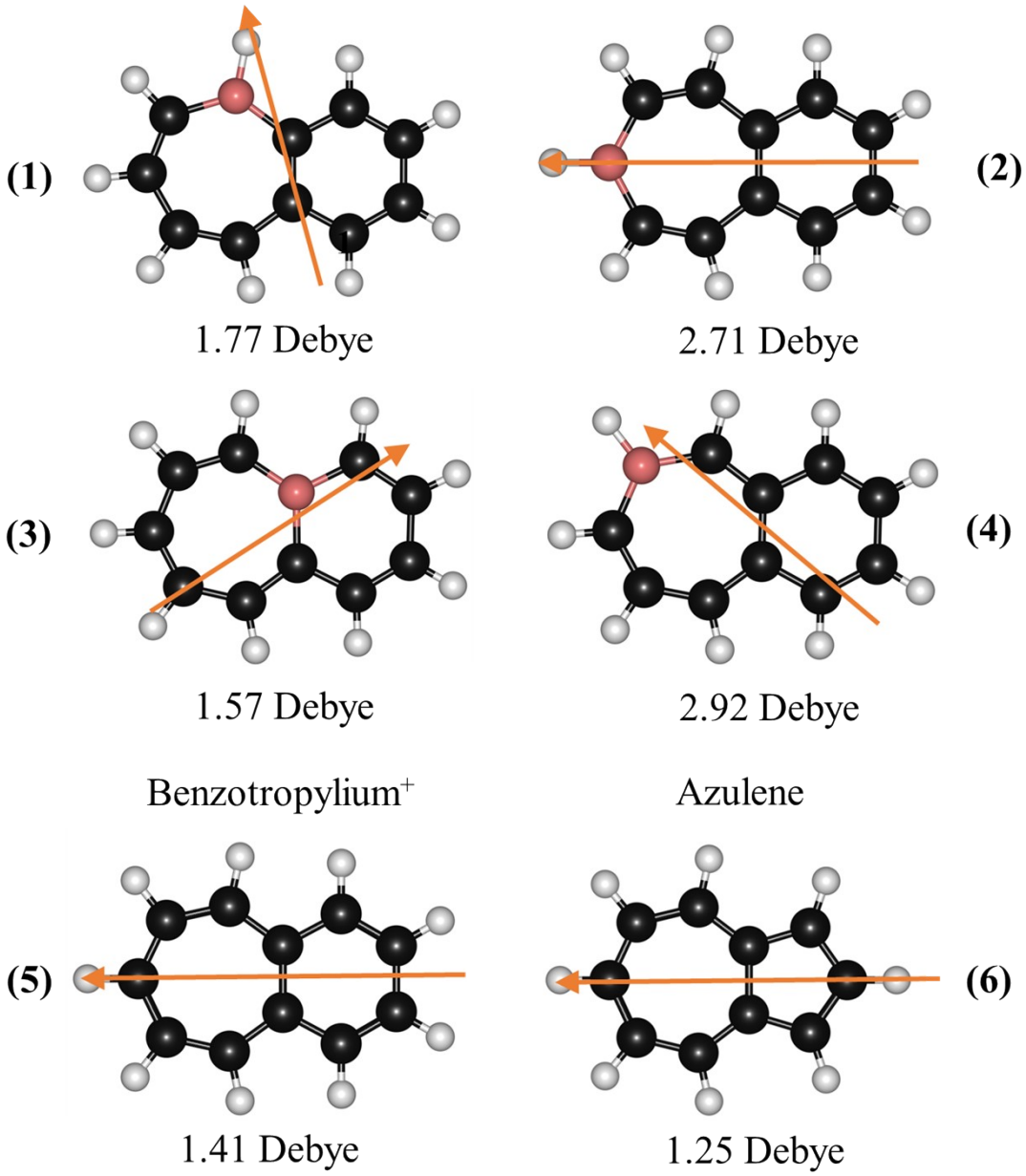


Figure S3. Complete ring current strength (in nA.T^{-1}) values for benzoborepin isomers, benzene and borepin computed at the ωB97X-D/def2-TZVP level of theory.

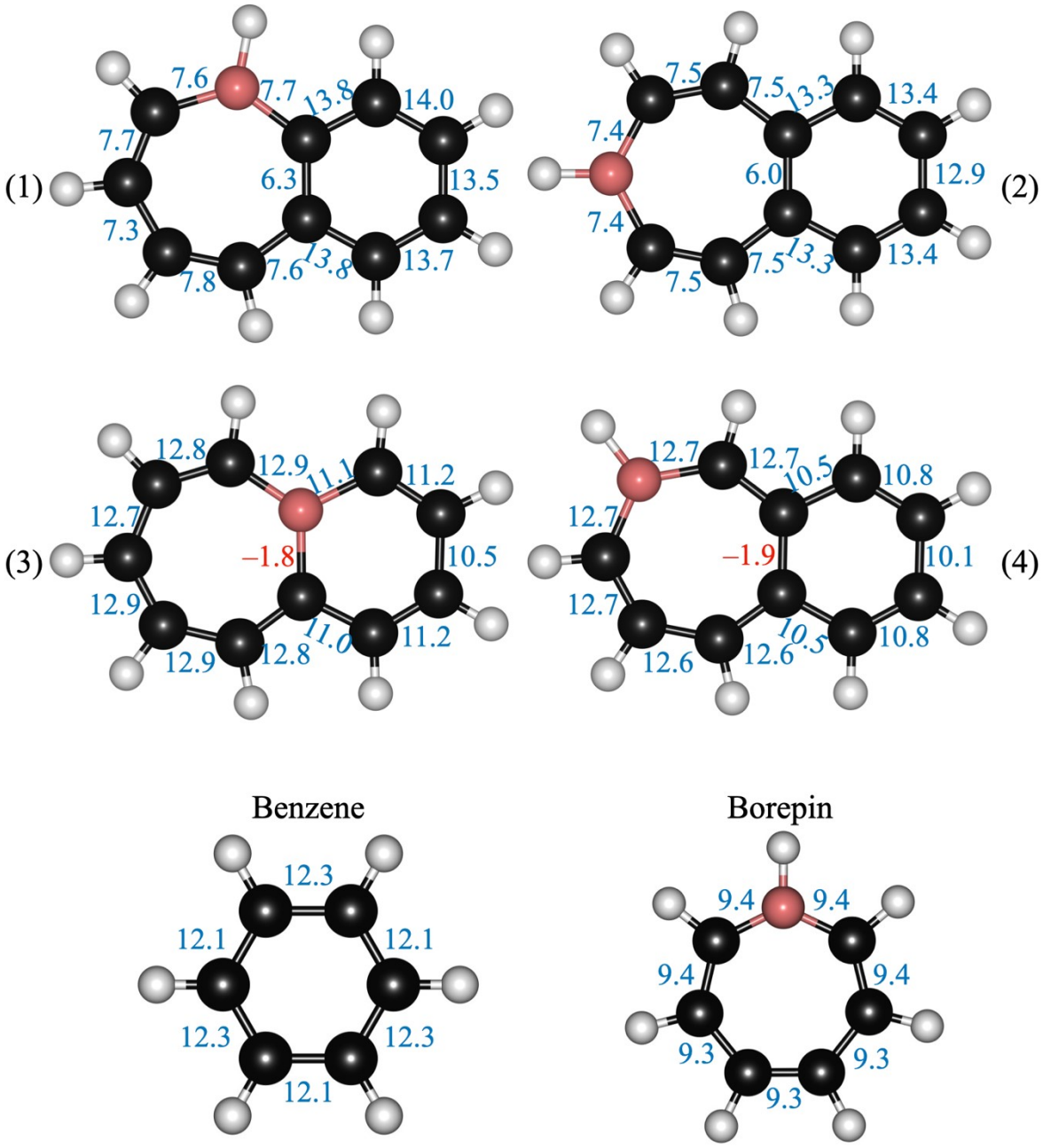


Figure S4. Complementary resonance structures contributing to aromaticity stabilization of the six-membered ring of isomers 1 and 2.

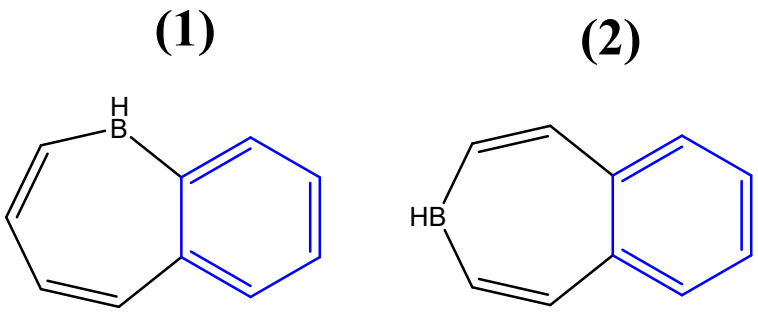


Table S2. Cartesian coordinates of benzene, borepin and benzoborepin isomers at the ωB97XD/def2TZVP level of theory.

Benzoborepin (1)				Benzoborepin (2)			
C	0.709169733	0.003623303	0.000000000	C	0.708846049	0.000000000	0.000000000
C	-0.709169733	-0.003623303	0.000000000	C	-0.708846049	0.000000000	0.000000000
B	-1.628768998	-1.240731691	0.000000000	C	-1.591055115	-1.147970081	0.000000000
C	-1.198666644	-2.703226714	0.000000000	C	-1.345337099	-2.476682177	0.000000000
C	0.062566151	-3.197435382	0.000000000	B	0.000000000	-3.198618230	0.000000000
C	1.305402497	-2.486829564	0.000000000	C	1.345337099	-2.476682177	0.000000000
C	1.563545816	-1.160127336	0.000000000	C	1.591055115	-1.147970081	0.000000000
H	-2.809346682	-1.013867943	0.000000000	H	-2.637881190	-0.850757060	0.000000000
H	-1.982534798	-3.456835000	0.000000000	H	-2.244313163	-3.089017223	0.000000000
H	0.180473528	-4.278829478	0.000000000	H	0.000000000	-4.399274316	0.000000000
H	2.184245409	-3.123266363	0.000000000	H	2.244313163	-3.089017223	0.000000000
H	2.620278338	-0.909372910	0.000000000	H	2.637881190	-0.850757060	0.000000000
C	0.710069909	2.435933784	0.000000000	C	0.696648053	2.442930177	0.000000000
C	-0.684154371	2.442621581	0.000000000	C	-0.696648053	2.442930177	0.000000000
C	-1.362688367	1.246849882	0.000000000	C	-1.368184100	1.246690091	0.000000000
H	1.260322379	3.368628337	0.000000000	H	1.246213088	3.375339241	0.000000000
H	-1.225018545	3.380485489	0.000000000	H	-1.246213088	3.375339241	0.000000000
H	-2.445627274	1.251178748	0.000000000	H	-2.451327175	1.248869089	0.000000000
C	1.385669434	1.240879755	0.000000000	C	1.368184100	1.246690091	0.000000000
H	2.469226928	1.242352559	0.000000000	H	2.451327175	1.248869089	0.000000000
Benzoborepin (3)				**Benzoborepin (4)**			
C	0.773477378	0.008239024	0.000000000	C	0.723679572	-0.016827328	0.000000000
B	-0.773477378	-0.008239024	0.000000000	C	-0.723679572	0.016827328	0.000000000
C	-1.622995922	-1.269957141	0.000000000	C	-1.572670433	-1.082119324	0.000000000
C	-1.236198531	-2.581412848	0.000000000	B	-1.315819893	-2.569911443	0.000000000
C	0.073085432	-3.106057384	0.000000000	C	0.070115490	-3.173438708	0.000000000
C	1.287655135	-2.467811154	0.000000000	C	1.275771419	-2.515735216	0.000000000
C	1.601393885	-1.098682056	0.000000000	C	1.541128171	-1.141803141	0.000000000
H	-2.703214263	-1.127573427	0.000000000	H	-2.621639116	-0.788419872	0.000000000
H	-2.017329707	-3.337472218	0.000000000	H	-2.266662146	-3.304045139	0.000000000
H	0.128138362	-4.190334782	0.000000000	H	0.159132364	-4.258029675	0.000000000
H	2.150051005	-3.126534223	0.000000000	H	2.174313842	-3.128294677	0.000000000
H	2.671888500	-0.896143822	0.000000000	H	2.600771563	-0.904271270	0.000000000
C	0.725719577	2.453248128	0.000000000	C	0.781976936	2.432261601	0.000000000
C	-0.708494444	2.494968306	0.000000000	C	-0.639609676	2.470890529	0.000000000
C	-1.458141760	1.366058492	0.000000000	C	-1.344487078	1.319339357	0.000000000
H	1.265526529	3.393143758	0.000000000	H	1.347064927	3.355357244	0.000000000
H	-1.173972793	3.476403545	0.000000000	H	-1.151827318	3.424605666	0.000000000
H	-2.539585804	1.474834413	0.000000000	H	-2.426855036	1.348373195	0.000000000
C	1.422578576	1.292122926	0.000000000	C	1.421120591	1.242528368	0.000000000
H	2.508510607	1.327904173	0.000000000	H	2.503837240	1.214590626	0.000000000
Benzotropylium cation (5)				**Benzene**			
C	-0.522087891	0.567895106	0.000000000	C	0.693435052	1.201129086	0.000000000
C	0.000000000	-0.771200237	0.000000000	C	-0.693435052	1.201129086	0.000000000
C	1.363654194	-1.128778084	0.000000000	C	-1.386841101	0.000000000	0.000000000
C	2.509568217	-0.363431515	0.000000000	C	-0.693435052	-1.201129086	0.000000000
C	2.618446955	1.020866158	0.000000000	C	0.693435052	-1.201129086	0.000000000

C	1.601291504	1.965921796	0.000000000	C	1.386841101	0.000000000	0.000000000
C	0.239844406	1.754081221	0.000000000	H	1.234822087	2.138774153	0.000000000
H	1.537318631	-2.199856347	0.000000000	H	-1.234822087	2.138774153	0.000000000
H	3.442523847	-0.913933618	0.000000000	H	-2.469549177	0.000000000	0.000000000
H	3.629004428	1.414723556	0.000000000	H	-1.234822087	-2.138774153	0.000000000
H	1.915827184	3.002557743	0.000000000	H	1.234822087	-2.138774153	0.000000000
H	-0.357136863	2.660232029	0.000000000	H	2.469549177	0.000000000	0.000000000
C	-2.779266037	-0.329235297	0.000000000				
C	-2.268613024	-1.638906507	0.000000000				
C	-0.919834654	-1.848450887	0.000000000				
H	-3.849171300	-0.168448445	0.000000000				
H	-2.947364075	-2.481429900	0.000000000				
H	-0.531929717	-2.858647710	0.000000000				
C	-1.928337654	0.738034037	0.000000000				
H	-2.327068266	1.744027917	0.000000000				

Borepin

B	1.727960164	0.000000000	0.000000000
C	1.011687113	1.345256098	0.000000000
C	-0.328163982	1.597418117	0.000000000
C	-1.413474062	0.681096047	0.000000000
C	-1.413474062	-0.681096047	0.000000000
C	-0.328163982	-1.597418117	0.000000000
C	1.011687113	-1.345256098	0.000000000
H	2.928816253	0.000000000	0.000000000
H	1.629524158	2.241004159	0.000000000
H	-0.638736006	2.639851190	0.000000000
H	-2.395391129	1.143628083	0.000000000
H	-2.395391129	-1.143628083	0.000000000
H	-0.638736006	-2.639851190	0.000000000
H	1.629524158	-2.241004159	0.000000000