Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Probing stability of exocyclic BN-doped fulvenes in ground state: 1-aminoboroles *vs* 1-pyrroloboranes

Alvi Muhammad Rouf,*[a] Ahmad Raza Ashraf,[a] Areej Fatima,[a] Imra Kousar,[a] Muhammad Faizan Nazar,*[a] and Shahbaz Ahmed[a]

[a] *Department of Chemistry, Division of Science and Technology, University of Education, Lahore, 54770, Pakistan. E-mail: rouf.alvi@ue.edu.pk; raufasham@hotmail.com; faizan.nazar@ue.edu.pk*

Supporting Information

1. Infra Red (IR) Spectra

The infra red (IR) frequency analysis exhibit positive values for vibrational modes of all BN-fulvenes indicating energy minima (Figures S1–S3). The major IR frequencies recognizing important bonds are given in Table S1 and summarized as (1) 570–914 cm^{-1} (wagging: ring C–H bonds, may also include C–B/ C–N bonds), (2) 1318–1725 cm^{-1} (stretching: B–N bond) and (3) 1551–1718 cm^{-1} (asymmetric stretching: ring C=C bonds).

Table S1: Global charge and multiplicity analysis for the parent BN-fulvenes P-1H and B-1H. Frequencies are given in cm^{-1}. The abbreviations (w) and (v.w) represent weak and very weak vibrations, respectively.

BN-fulvenes	**Ring C–H bonds (Wagging)**	**B–N bond (Stretching)**	**Ring C=C bonds (Stretching)**	**BN-fulvenes**	**Ring C–H bonds (Wagging)**	**B–N bond (Stretching)**	**Ring C=C bonds (Stretching)**
P1-H	783	1387, 1478, 1539		**B1-H**	570, 676	1443, 1653	
P-1NH$_2$	761	1393, 1425, 1455, 1533		**B-1NH$_2$**	774	1527, 1725	
P-1OMe	770	1395, 1407, 1467, 1535, 1540		**B-1OMe**	758	1549 (w)	
P-1CN	787	1407, 1515, 1553		**B-1CN**	765	1330, 1391	1622 (w)
P-1F	695, 778	1418, 1434, 1508, 1545		**B-1F**	749	1619 (v.w)	
P-1Cl	779, 839	1384, 1475, 1536		**B-1Cl**	757	1438	
P-2NH$_2$	806	1402, 1410, 1473	1688, 1730	**B-2NH$_2$**	728 (w)	1657, 1632, 1670	1690
P-2OMe	765	1409, 1459, 1483	1680, 1685	**B-2OMe**	709 (w), 840 (w)	1366, 1499 (w) 1640	1678
P-2CN	850 (w)	1353, 1451		**B-2CN**	710	1475 (w), 1662	
P-2F	803	1365, 1410, 1467	1690, 1716	**B-2F**	695	1349, 1498, 1650	1718
P-2Cl	815 (w)	1318, 1355, 1428	1551, 1647	**B-2Cl**	684	1474	1677 (w)
P-3NH$_2$	818 (w)	1445, 1502	1680	**B-3NH$_2$**	658, 702, 830	1431, 1644	1678
P-3OMe	792 (w)	1440, 1504	1651	**B-3OMe**	853	1386, 1658	1689
P-3CN	885 (w)	1398, 1458	1599	**B-3CN**	914 (w)	1462, 1663	
P-3F	829 (w)	1455, 1492	1660	**B-3F**	864	1403, 1652	1707
P-3Cl	844 (w)	1360, 1469	1570 (w)	**B-3Cl**	867	1264, 1447, 1657	1648 (v.w)

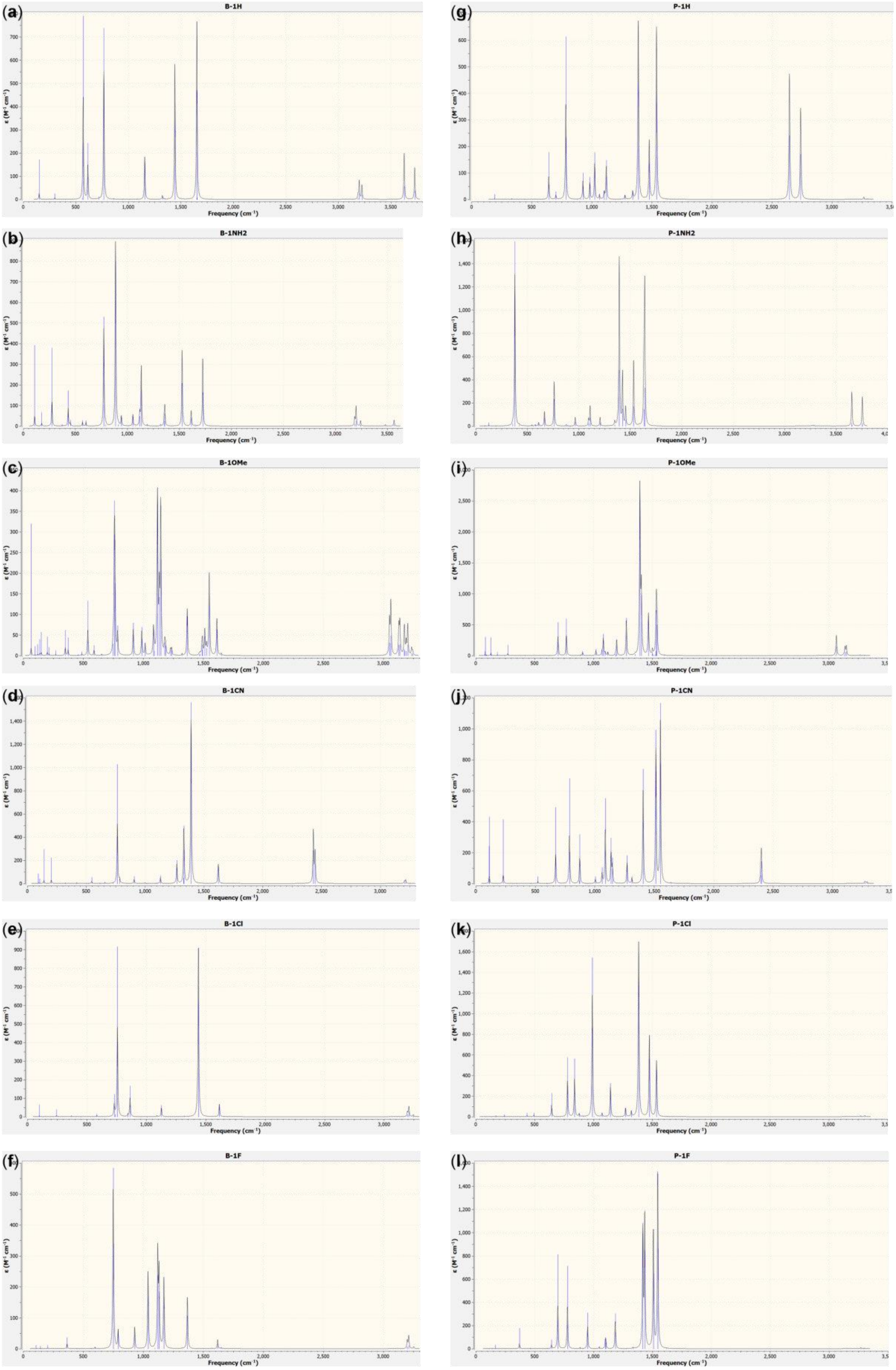


Figure S1. IR spectra of **B-1X** (**a** – **f**) and **P-1X** fulvenes (**g** – **l**).

Figure S2. IR spectra of **B-2Y** (**a** – **e**) and **P-2Y** fulvenes (**f** – **j**).

Figure S3. IR spectra of **B-3Z** (**a** – **e**) and **P-3Z** fulvenes (**f** – **j**).

2. Relative Energy

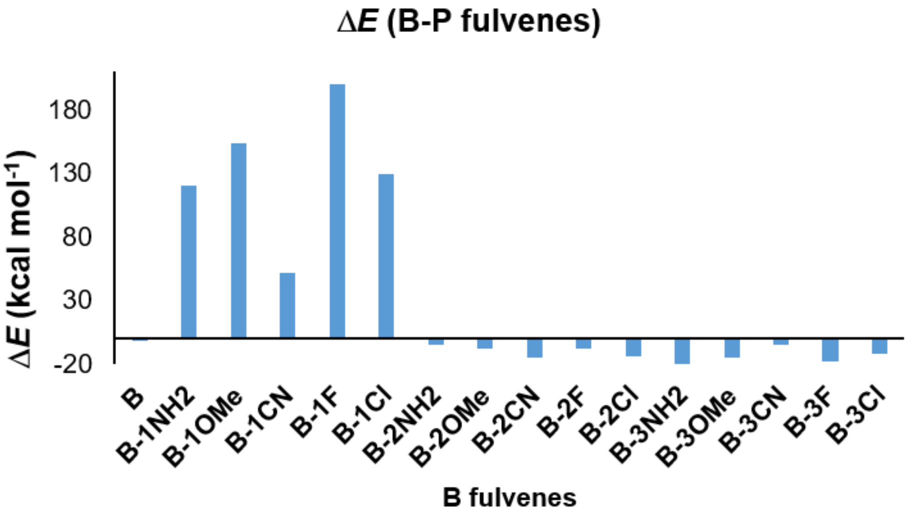


Figure S4. Relative energy (Δ*E*) of BN-fulvenes. Where Δ*E* = electronic energy of **B** – electronic energy of **P**.

3. Stability of Charge and Multiplicity

A sweep of charge and multiplicity of the parent **P-1H** and **B-1H** fulvenes reveals that the former is stabilized and the latter is multiplicity stabilized and charge destabilized. Charge destabilization of the latter is associated with the high electron deficieny of the borole structure that becomes stabilized when it gains electron.

Table S2: Global charge and multiplicity analysis for the parent BN-fulvenes P-1H and B-1H.

BN-fulvene	Charge	Multiplicity	*E* (hartrees)	Δ*E* (hartrees)	Δ*E* (kcal mol^{-1})	Δ*E* (eV)
P1-H	0	1	-235.600831	0	0	0
	0	3	-235.487559	0.113272	71.07931272	3.082287435
	0	5	-235.306907	0.293924	184.4402492	7.998077655
	1	2	-235.289207	0.311624	195.5471762	8.479719081
	-1	2	-235.591794	0.009037	5.67080787	0.245909241
B1-H	0	1	-235.6031875	0	0	0
	0	3	-235.546136	0.0570515	35.80038677	1.552450046
	0	5	-235.38353	0.2196575	137.8372778	5.977183702
	1	2	-235.302252	0.3009355	188.8400356	8.188870246
	1	4	-235.205277	0.3979105	249.6928179	10.82769382
	1	6	-235.017032	0.5861555	367.8184378	15.95010005
	-1	2	-235.609879	-0.0066915	-4.198983165	-0.182084949
	-1	4	-235.509211	0.0939765	58.97119351	2.557230253

4. Positional Isomerization Energies in BN-Fulvenes P and B

Table S3: Positional isomers of BN-Fulvenes P and B, and their relative isomer energies (ΔE-iso).

Fulvene	**ΔE-iso**	**Fulvene**	**ΔE-iso**
P-1NH2	0	**B-1NH2**	0
P-2NH2	72.4	**B-2NH2**	-53
P-3NH2	73.7	**B-3NH2**	-66.1
P-1OMe	0	**B-1OMe**	0
P-2OMe	81.7	**B-2OMe**	-79.2
P-3OMe	84.2	**B-3OMe**	-83.9
P-1CN	0	**B-1CN**	0
P-2CN	24.2	**B-2CN**	-42.7
P-3CN	22.3	**B-3CN**	-34.1
P-1F	0	**B-1F**	0
P-2F	106.4	**B-2F**	-101.7
P-3F	108.9	**B-3F**	-109.8
P-1Cl	0	**B-1Cl**	0
P-2Cl	73.9	**B-2Cl**	-69.7
P-3Cl	71.5	**B-3Cl**	-70.2

5. Bond Dissociation Energy (BDE)

Some interesting outcomes (other than given in the main text) related to bond strength, its trends and its link to the relarive thermodynamic stability of BN-fulvenes are given here in ESI. Notably, BDE pattern is given in Fig. 3, BDE values are given in Table 1, and bond order (BO) data is given in Fig. 6, in the main text.

1- Homolytic cleavage of the N/B–X bond in **P-1X/B-1X** fulvenes leads to higher value of BDE$_1$ for **P-1X** conforming their higher relative stability than the corresponding **B-1X**: such that **P-1F/B-1F** = 337.7/162.3 kcal mol^{-1}, **P-1OMe/B-1OMe** = 273.8/130.9 kcal mol^{-1}, **P-1Cl/B-1Cl** = 240.7/136.1 kcal mol^{-1}, **P-1NH$_2$/B-1NH$_2$** = 273.7/155.4 kcal mol^{-1} and **P-1CN/B-1CN** = 280.6/251.6 kcal mol^{-1}, respectively.

2- Notably, the highest and the lowest BDE$_2$ differences (143.2/116.5 and 145.4/144.5 kcal mol^{-1}) are observed for the pairs of isomers **P-1F/B-1F** and **P-1CN/B-1CN**, respectively, with the highest and the lowest ΔE (200.5 kcal mol^{-1}) among the **P/B-1X** isomers.

3- The calculated BDE (i.e., BDE$_3$) supports stronger N–C$_{(ring)}$ bond in **P-1X** than B–C$_{(ring)}$ bond in **B-1X**: such that **P-1F/B-1F** = 274.4/242.9 kcal mol^{-1}, **P-1OMe/B-1OMe** = 270.4/246.2 kcal mol^{-1}, **P-1NH$_2$/B-1NH$_2$** = 264.5/251.0 kcal mol^{-1} and **P-1CN/B-1CN** = 279.8/256.1 kcal mol^{-1}.

4- According to the BO data, the butadiene part of the borole ring in **B-1X** fulvenes is not significantly affected by the exocylic substitution, and the ring substitutions induce a small perturbation.

5- The BO data of fulvenes **B-2Y/P-2Y** and **B-3Y/P-3Y** are given as **B-2CN/P-2CN** = 1.14/1.10 and **B-3CN/P-3CN** = 1.10/1.10, **B-2Cl/P-2Cl** = 1.42/1.42 and **B-3Cl/P-3Cl** = 1.42/143, **B-2OMe/P-2OMe** = 1.38/1.37 and **B-3OMe/P-3OMe** = 1.39/1.38, **B-2F/P-2F** 1.38/1.41 and **B-3F/P-3F** = 1.41/1.40, **B-2NH$_2$/P-2NH$_2$** = 1.29/1.27 and **B-3NH$_2$/P-3NH$_2$** = 1.31/1.27.

6- The ΔBO of the B–N bond in **B-3Z** (compared to **P-3Z**) fails to relate with ΔE, where high bond strength meets with low stability and *vice versa*: **B-3NH$_2$** (0.06, -19.6 kcal mol^{-1}), **B-3OMe** (0.06, -14.8 kcal mol^{-1}), **B-3F** (0.15, -18.2 kcal mol^{-1}), **B-3Cl** (0.17, -11.7 kcal mol^{-1}) and **B-3CN** (0.25, -4.8 kcal mol^{-1}).

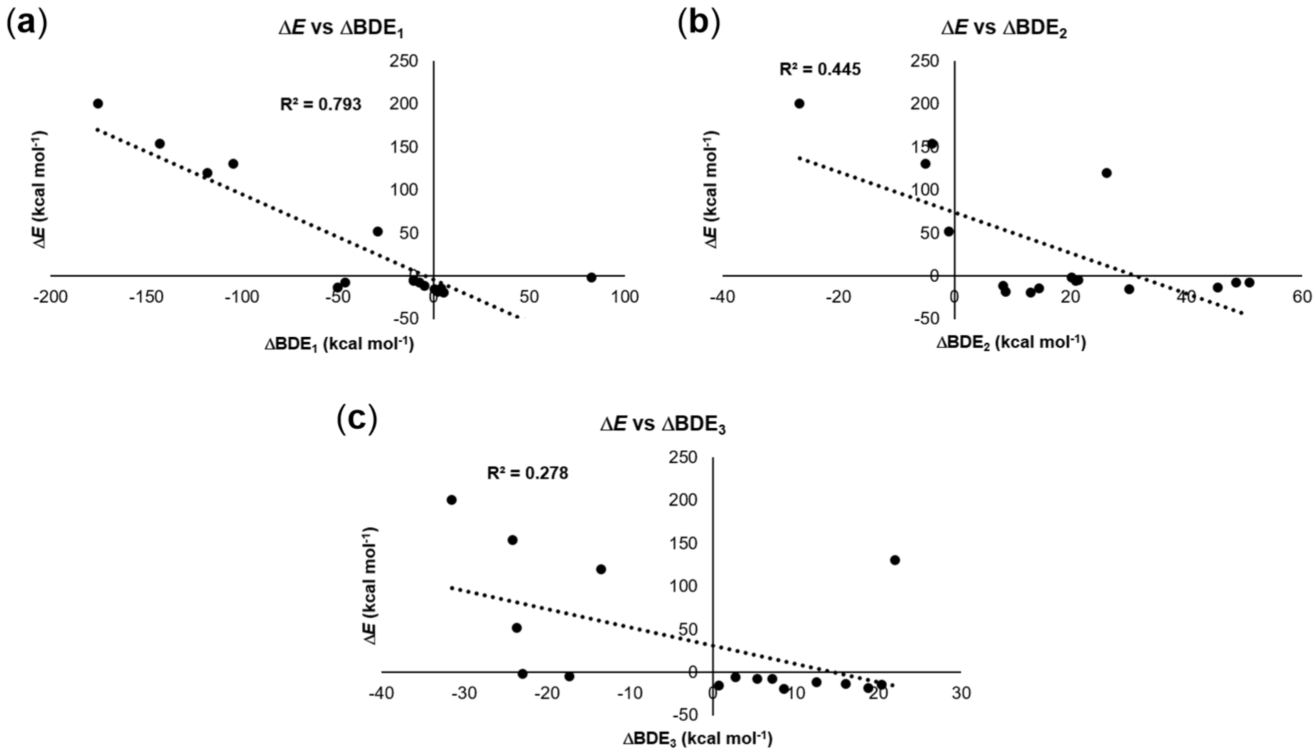


Figure S5: The linear relationship between ΔE and (**a**) $\Delta \mathrm{BDE}_1$ calculated for the fulvene-substituent bond, (**b**) $\Delta \mathrm{BDE}_2$ calculated for the B–N bond, and (**c**) $\Delta \mathrm{BDE}_3$ calculated for the ring B/N–$\mathrm{C}_{\mathrm{ring}}$ bond.

6. Aromaticity Indices: NICS(1)$_{zz}$, ΔBL, and Electron Density of Delocalized Bonds (EDDB)

Although the parent fulvene shows values of delocalization indices in-between **P** and **B** fulvenes, i.e., EDDB(G) = 2.021 *e* and EDDB(P) = 0.426 *e* (Fig. S7). The negative NICS(1)$_{zz}$ (-12.3 to -29.5 ppm), smaller ΔBL (0.054–0.108 Å) and larger EDDB(G) values (3.154–4.939 *e*) (Table 2) affirm **P** fulvenes (**P-1X**, **P-2Y** and **P-3Z**) as aromatic species. However, their lower aromaticity compared to the parent pyrrole (C_4H_5N that have NICS(1)$_{zz}$ = -32.5 ppm and ΔBL = 0.050 Å, (Table 2) is linked to the presence of an exocyclic boryl group (in each structure) mounted at the ring N atom that interacts with the N's delocalized lone-pair (that one can visualize through EDDB(G) in Fig. S8a). The EDDB(G) value in **P** fulvenes is found more or less than that of the parent pyrrole (4.100 *e*) because of the consideration of delocalization of the whole system (Fig. S8a). However, ring EDDB index, EDDB(P) of **P** fulvenes (0.936–2.497 *e*) show lower values than that of pyrrole (2.978 *e*) (Fig. S8b) revealing reduced aromaticity, thus complying NICS(1)$_{zz}$ and ΔBL results. EDDB(P) isosurfaces of **P** fulvenes reveal strong ring delocalization that correlate well to their geometry revealing CC bond (that is next to endocylic N) is the strongest ring bond in all **P** fulvenes, and CC bond opposite to endocylic N is the weakest in **P-3Z** fulvenes. On the other hand, **B** fulvenes are revealed to be significantly less antiaromatic (NICS(1)$_{zz}$ = 11.2–27.7 ppm, ΔBL = 0.142–0.184 Å, and EDDB(P) = 0.138–0.241 *e*) compared to the parent borole C_4H_5B (NICS(1)$_{zz}$ = 34.8 ppm, ΔBL = 0.179 Å, and EDDB(P) = 0.115 *e*) (Table 2, Fig. S7 and S8b). The reduction in the antiaromaticity of **B** fulvenes could be linked to lone-pair donation by the exocyclic amine group (in each structure) mounted on B atom of the ring. Further, substituents also actively participate in enhancing ring π-delocalization, displayed by EDDB(G) values (1.217–3.047 *e*). However, EDDB(P) isosurafces of **B-1X** fulvenes visualized in Fig. 8a reveal delocalization is divided into two parts; the exocyclic framework and two separate ring CC bonds. On the other hand, ring-substitution in **B** fulvenes interacts well with the butadiene fragment, bypassing the endycyclic B atom, as observed from the EDDB(G) isosurafces (Fig. S8a). The EDDB(P) isosurafces reveal almost no ring delocalization (Fig. S8b).

Generally, it is found that a substituent reducing aromaticity of **P** fulvene also reduces its relative stability compared to the corresponding **B** fulvene, and contrarily, a substituent reducing antiaromaticity of **B** fulvene enhances its stability compared to the relevent **P** fulvene. Therefore, in general, based on NICS(1)$_{zz}$, **P** fulvenes display the following decreasing order of aromaticity for π-ED groups **P-1X** > **P-3Z** > **P-2Y**, and for σ-/π-EW CN group **P-2Y** ≈ **P-3Z** > **P-1X**. Interestingly, this aromaticity trend in **P** fulvenes is quite similar to the previously reported trend for undoped fulvenes.[1] Further, aromaticity trend of **P** fulvenes, except CN-substituted ones, follow the stability trend of their positional isomers (Table S3). On the other hand, the decreasing antiaromaticity trend observed for **B** fulvenes is given as for those having π-ED groups **B-2Y** > **B-1X** > **B-3Z** and bearing CN groups **B-1X** > **B-3Z** ≈ **B-2Y**.

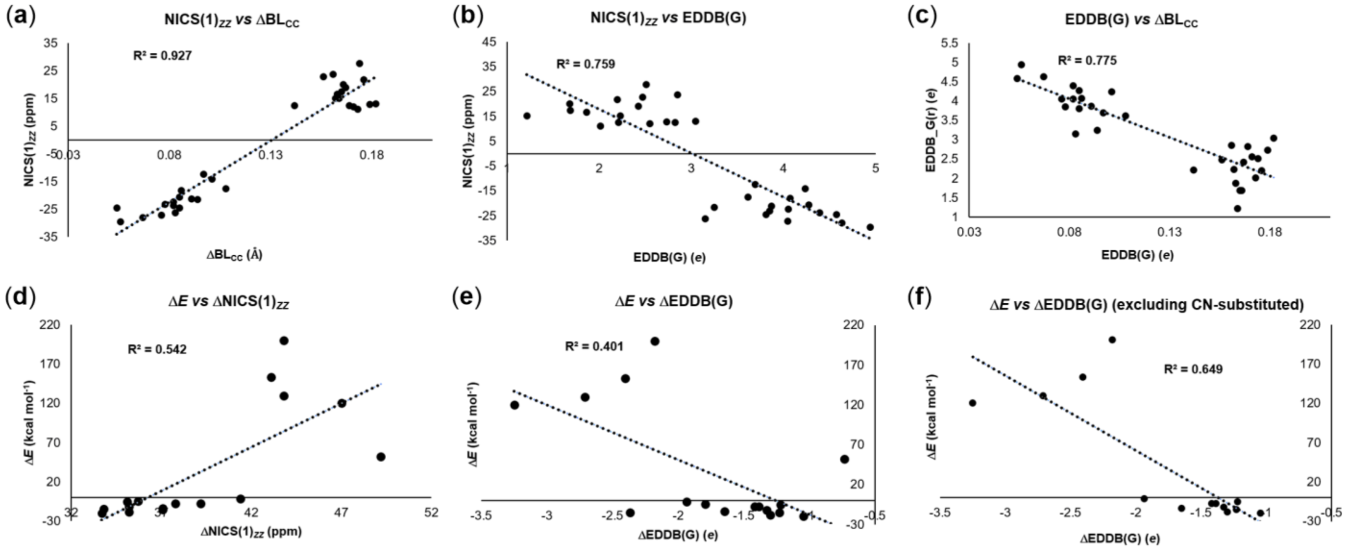


Figure S6: (Above) Linear relation between aromaticity indices themselves (**a**-**c**). (Below) Linear relationship between Δ*E* and aromaticity indices (**d**-**f**) of the corresponding BN-fulvenes. Data is taken from Table 2.

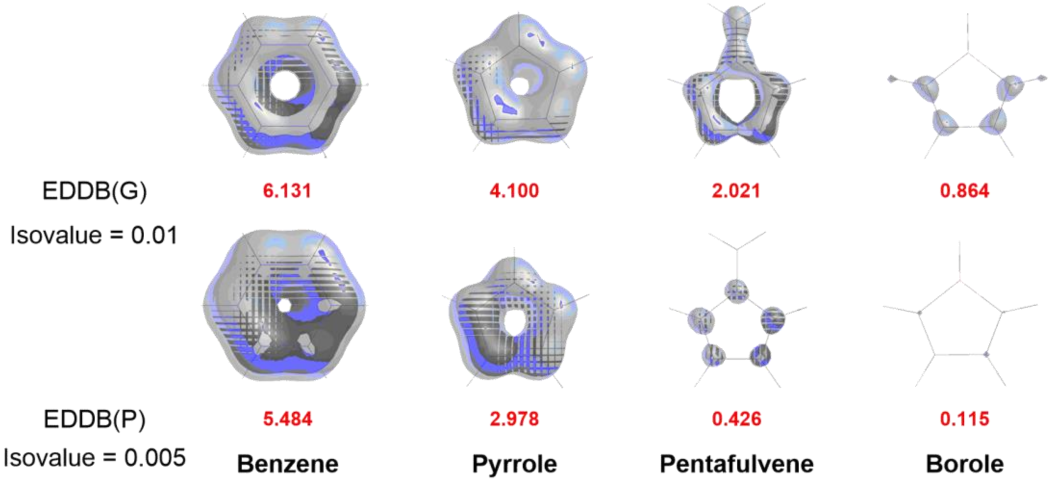
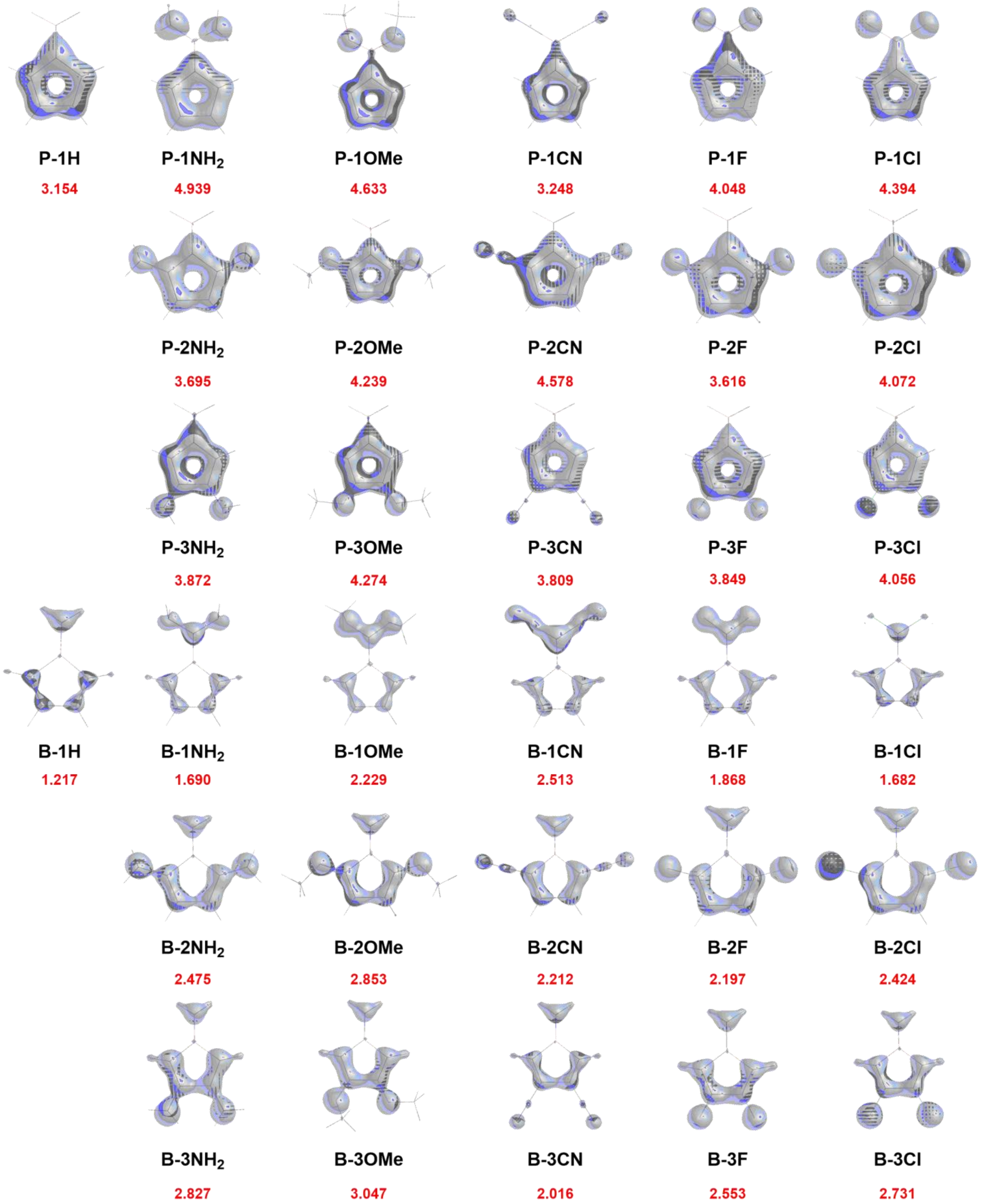


Figure S7. EDDB values (*e*) of the parent benzene, pyrrole, fulvene, and borole: (above) the total population of delocalized electrons in molecule (i.e., EDDB(G)), and (below) total population of delocalized electrons in 5-membered ring (5MR) (i.e., EDDB(P)). The given isosurfaces are visualized in Avogadro software from the corresponding EDDB(G/P) fchk files.



P-1H 3.154 **P-1NH$_2$** 4.939 **P-1OMe** 4.633 **P-1CN** 3.248 **P-1F** 4.048 **P-1Cl** 4.394

P-2NH$_2$ 3.695 **P-2OMe** 4.239 **P-2CN** 4.578 **P-2F** 3.616 **P-2Cl** 4.072

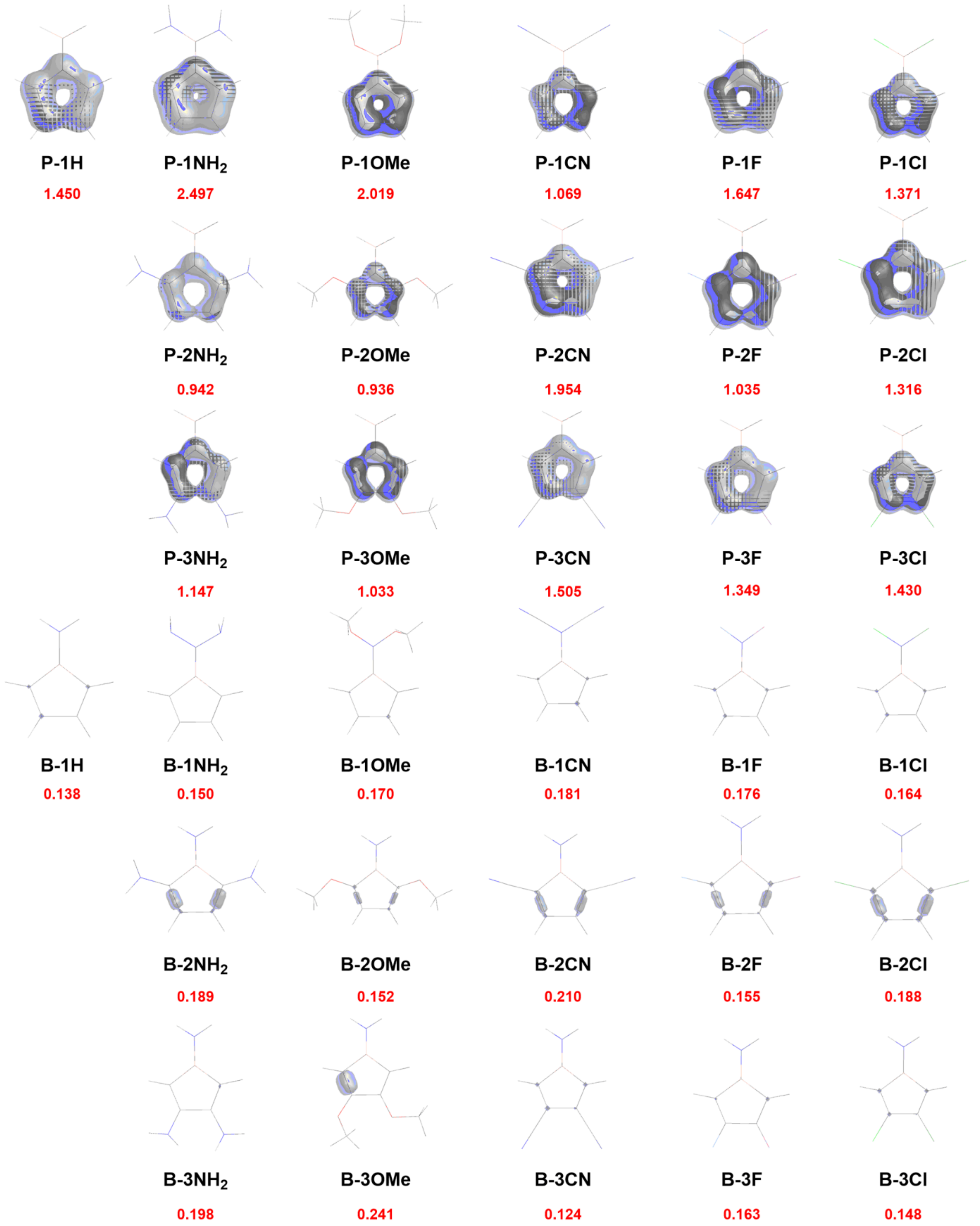
P-3NH$_2$ 3.872 **P-3OMe** 4.274 **P-3CN** 3.809 **P-3F** 3.849 **P-3Cl** 4.056

B-1H 1.217 **B-1NH$_2$** 1.690 **B-1OMe** 2.229 **B-1CN** 2.513 **B-1F** 1.868 **B-1Cl** 1.682

B-2NH$_2$ 2.475 **B-2OMe** 2.853 **B-2CN** 2.212 **B-2F** 2.197 **B-2Cl** 2.424

B-3NH$_2$ 2.827 **B-3OMe** 3.047 **B-3CN** 2.016 **B-3F** 2.553 **B-3Cl** 2.731

Figure S8a. Total population of delocalized electrons in molecule (i.e., EDDB(G)) values (*e*) of BN-fulvenes. The given isosurfaces are visualized in Avogadro software from the fchk files of EDDB(G), where the isosurface value = 0.01.



P-1H 1.450
P-1NH$_2$ 2.497
P-1OMe 2.019
P-1CN 1.069
P-1F 1.647
P-1Cl 1.371

P-2NH$_2$ 0.942
P-2OMe 0.936
P-2CN 1.954
P-2F 1.035
P-2Cl 1.316

P-3NH$_2$ 1.147
P-3OMe 1.033
P-3CN 1.505
P-3F 1.349
P-3Cl 1.430

B-1H 0.138
B-1NH$_2$ 0.150
B-1OMe 0.170
B-1CN 0.181
B-1F 0.176
B-1Cl 0.164

B-2NH$_2$ 0.189
B-2OMe 0.152
B-2CN 0.210
B-2F 0.155
B-2Cl 0.188

B-3NH$_2$ 0.198
B-3OMe 0.241
B-3CN 0.124
B-3F 0.163
B-3Cl 0.148

Figure S8b. Total population of delocalized electrons in 5-membered ring (5MR) (i.e., EDDB(P)) values (*e*) of BN-fulvenes. The given isosurfaces are visualized in Avogadro software from the fchk files of EDDB(P), where the isosurface value = 0.005.

7. Diploe Moment and Natural Population Analysis (NPA) Charges

Dipole moment (μ) measured in debye (D) demonstrates that its higher value indicates higher polarity and stronger interactions. The calculated μ of the parent fulvene (0.6 D) is intermediate to that of pyrrole (1.9 D) and borole (-0.8 D). BN-doping reduces μ of the parent fulvene to approximately zero in **P-1H** (Fig. S9), and μ of **B-1H** is 1.6 D that is closer to pyrrole. The μ for the exoxylic BN-fulvenes **P-1X** and **B-1X** are very close to each other. However, NH_2-, OMe- and CN-substituted fulvenes show higher μ than those of F- and Cl-substituted ones.

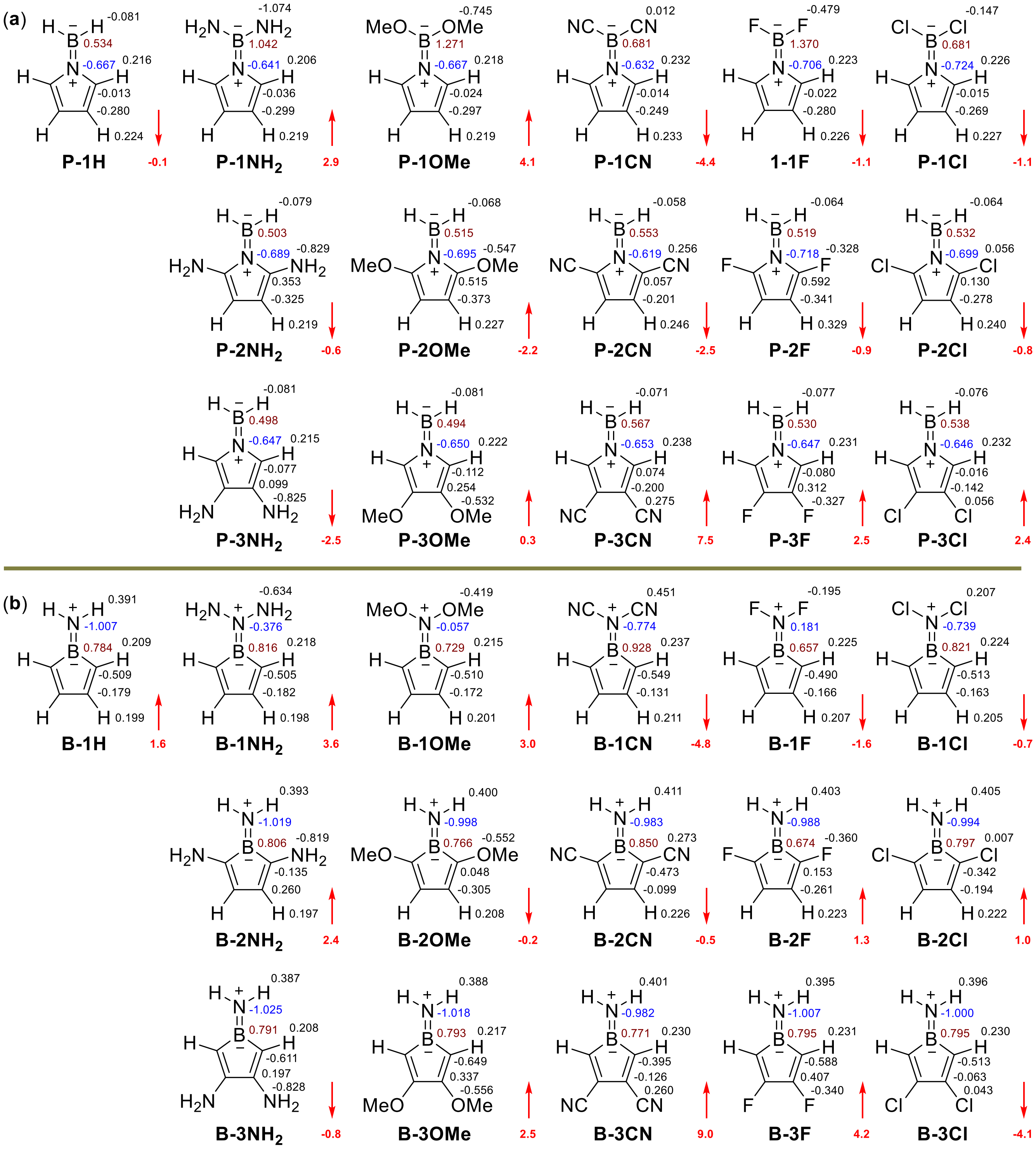


Figure S9. NPA charges (*e*) given on the corresponding atoms and dipole moments (D, given in red color) of BN-fulvenes (**a**) **P** and (**b**) **B**.

When NPA charges on N and B across the B=N bond within a BN-fulvene are added, irrespective of their signs, lead to the the term Δq(N-B), that is represented as $\Delta q(\text{N-B})_P$ and $\Delta q(\text{N-B})_B$ for **P** and **B** fulvenes, respectively (Table 3). This term reveals greater charge accumulation across the B=N bond leads to more stable BN-fulvene isomer and *vice versa*. Further, the relative term $\Delta\Delta q$(N-B) for the two corresponding isomers reflects the amount of Δq(N-B) could define the magnitude of the relative stability ($R^2 = 0.865$, in Fig. S10a).

However, the term Σq(N+B) that calculates the net charge across the B=N bonds, i.e., the sum of B and N charges in the corresponding **P** and **B** fulvenes (where $\Sigma q(\text{N+B})_P = q(\text{N})_P + q(\text{B})_P$ and $\Sigma q(\text{N+B})_B = q(\text{N})_B + q(\text{B})_B$, respectively), explains that **P** isomers are stabilized when the B=N bond accumulates more positive charge, while **B** isomers are stabilized when this charge sum is more negative. Therefore, linking to the electron-rich and electron-deficient behavior of the rings in the two BN-fulvenes, respectively, where the former could stabilize positive charge and the latter could stabilize negative charge. This trend is exemplified by the most stable species at each position, namely **P-1F**, **B-2CN** and **B-3NH$_2$** (Fig. S4). These correlations exhibit excellent linear relationship ΔE (R^2 = 0.816 and 0.902, respectively, in Fig. S10b and 10c).

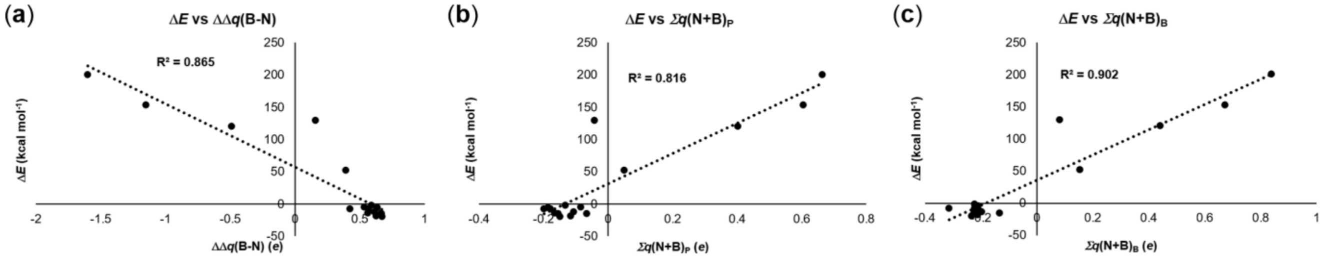


Figure S10. (**a**) Linear relationship between ΔE and the difference of NPA charges (*e*) across the B=N bond of **B** fulvene relative to **P** fulvene, i.e., $\Delta\Delta q$ (= Δq(B) - Δq(N) or = Δq(B-N)), and (**b** and **c**) the sum of charges across the B=N bond, i.e., Σq(N+B) in **P** fulvenes and **B** fulvenes, respectively.

8. Frontier Molecular Orbitals (FMOs)

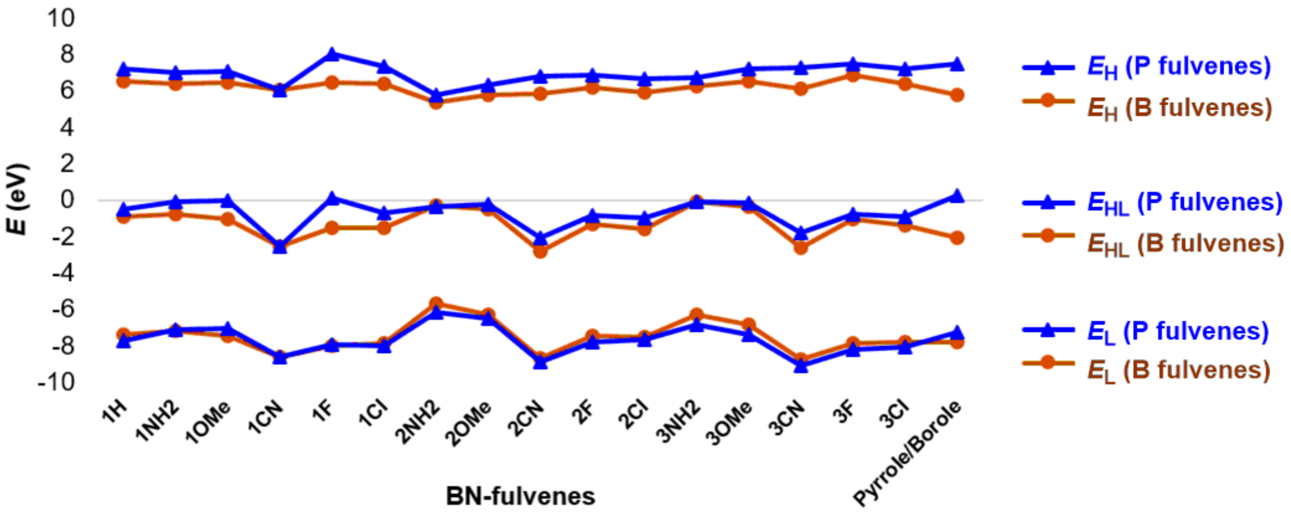


Figure S11. Frontier molecular orbital (FMOs) energies and gaps of BN-fulvenes.

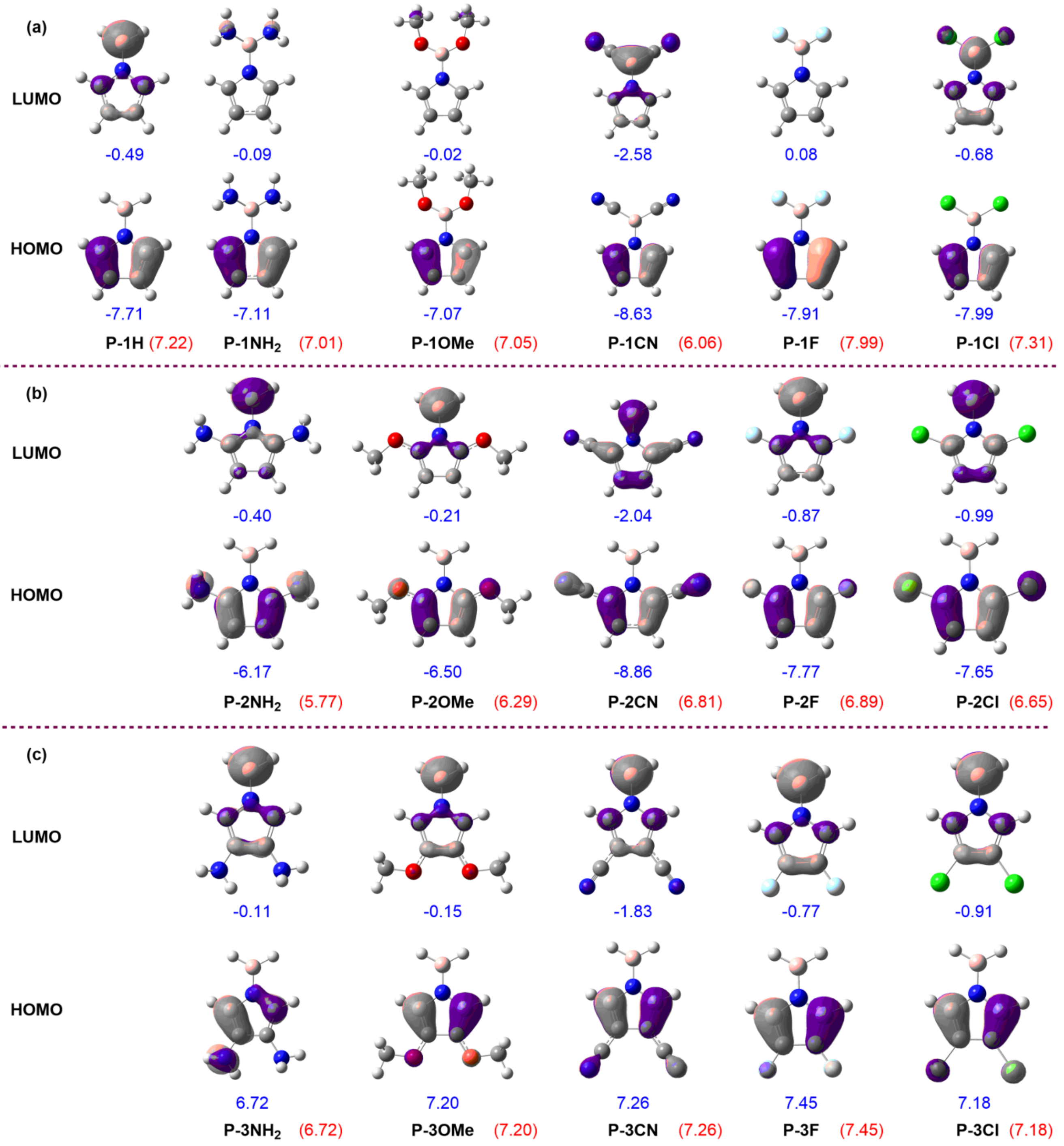


Fig. S12. FMOs of **P** fulvenes, their energies (in blue color) and gaps (in red color). Atom's color code: H (white), C (grey), N (blue), B (pink), O (red), F (cyan), and Cl (green).

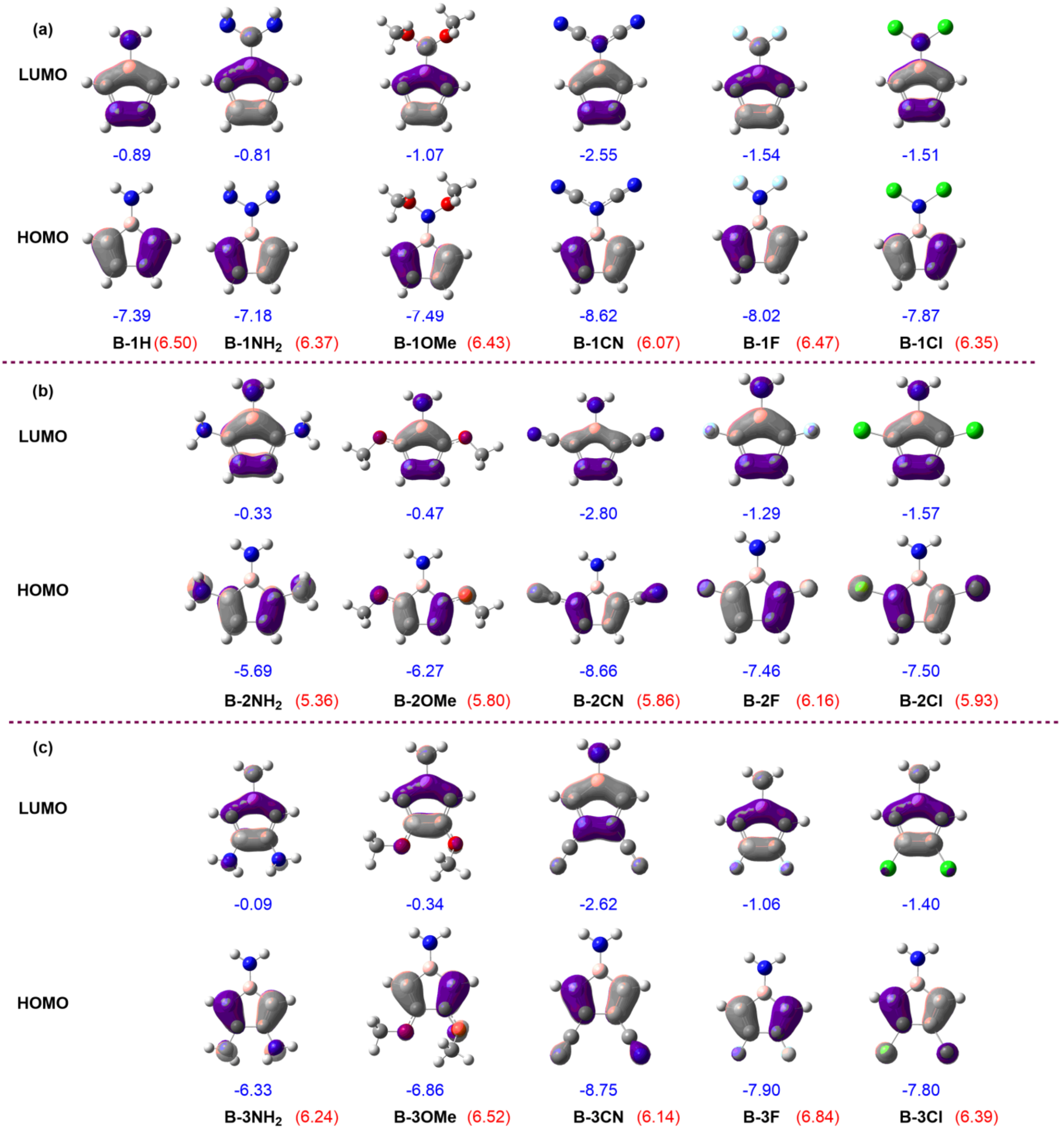


Figure S13. FMOs of **B** fulvenes, their energies (in blue color) and gaps (in red color). Atom's color code: H (white), C (grey), N (blue), B (pink), O (red), F (cyan), and Cl (green).

Generally, **P** isomers display stabilized HOMOs (E_H = -6.17 to -9.09 eV) compared to the corresponding **B** isomers (E_H = -5.69 to -8.75 eV), except for the exocyclic substituted fulvenes **B-1NH$_2$**, **B-1OMe** and **B-1F** that display slightly more stable HOMOs than the corresponding isomers **P-1NH$_2$**, **P-1OMe**, and **P-1F** (E_H = -7.18 *vs* -7.11 eV, -7.49 *vs* -7.0 eV, and -8.02 *vs* -7.91 eV, respectively). On the other hand, LUMOs of **B** isomers are found stabilized (E_L = -0.09 to -2.80 eV) than the corresponding **P** isomers (E_L = 0.08 to -2.58 eV), except **B-1CN**, **B-2NH$_2$** and **B-3NH$_2$** that are more stable than **P-1CN**, **P-2NH$_2$**, and **P-3NH$_2$** (E_L = -2.55 *vs* -2.58 eV, -0.33 *vs* -0.40 eV and -0.09 *vs* -0.11 eV, respectively). It generalizes lower electron affinity and higher reactivity of **B** compounds.

On substituting **B-1H** fulvenes derivatives display reduced HOMO-LUMO gap (here denoted as E_{HL}) (E_{HL} = 5.36–6.50 eV), except **B-3OMe** and **B-3F** that get slightly higher E_{HL} (6.52 and 6.84 eV). The σ- and π-EW CN-substituted **B** fulvenes (**B-1CN**, **B-2CN** and **B-3CN**) get the lowest E_{HL} (6.07, 5.86 and 6.16 eV) among BN-fulvene due to higher gain in stability of their LUMOs (1.66–1.91 eV) compared to the parent **B-1H**. Thus announcing these species as the most reactive among BN-fulvenes. However, competition between π-ED and σ-EW character in the other groups gives mixed results.

On the other hand, most of the **P** fulvenes display higher E_{HL} (6.65–7.99 eV) than the parent fulvene (6.45 eV), indicating higher stability. However, few examples like **P-1CN**, **P-2NH$_2$** and **P-2OMe** (where ΔE_{HL} = 6.06, 5.77 and 6.29 eV, respectively) exhibit enhanced reactivity. Further, every **P** fulvene shows higher gap than the corresponding **B** fulvene, indicating latter fulvenes are prone to higher reactivity, and easy to excite.

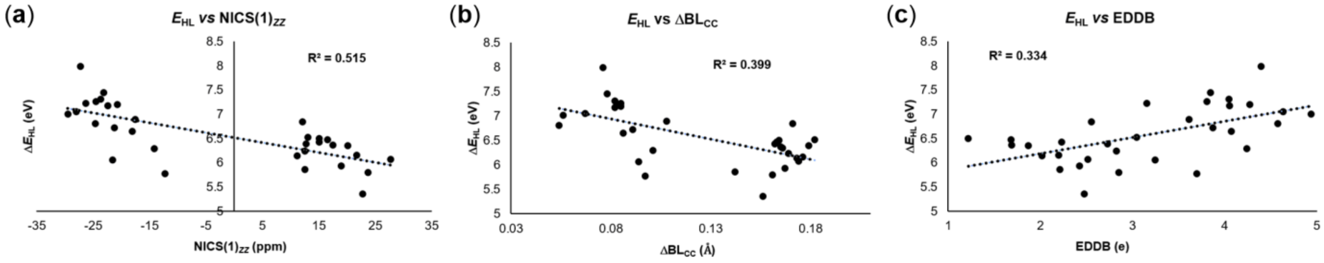


Figure S14. Linear relationships between HOMO-LUMO energy gaps (E_{HL}) and aromaticity indices: (**a**) E_{HL} *vs* NICS(1)$_{ZZ}$, (**b**) E_{HL} *vs* ΔBL$_{CC}$ and (**c**) E_{HL} *vs* EDDB(G) of BN-fulvenes (data from Table 2).

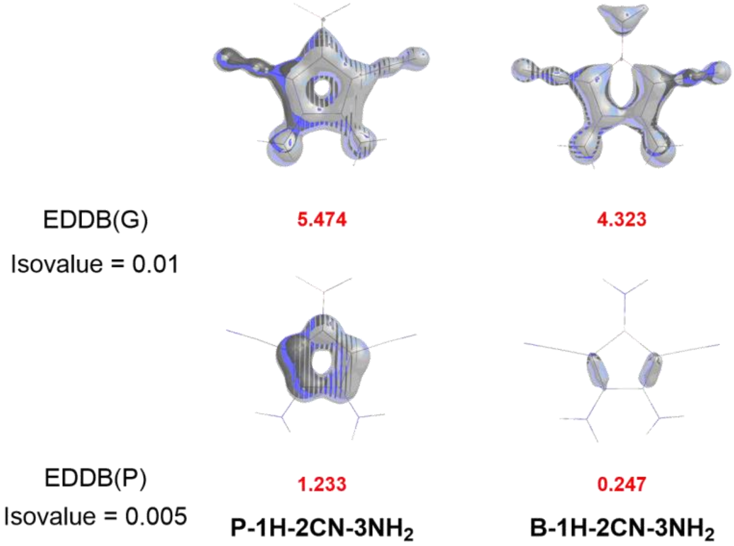


Figure S15. Total population of delocalized electrons in molecule and 5-membered ring (5MR) (i.e., EDDB(G), above, and EDDB(P), below) values (*e*) of BN-fulvene complexes. The given isosurfaces are visualized in Avogadro software from the fchk files of EDDB(G/P).

9. Cartesian Coordinates and Absolute Energies (Es)

Absolute energies and Cartesian coordinates are provided separately in .xyz file.

10. Reference

---

[1] S. Yadav,O E. Bakouri, K. Jorner, H. Tong, C. Dahlstrand, M. Solà, H. Ottosson, *Chem. Eur. J.*, 2019, **14**, 1870.