10.1071/CH08043_ AC

Accessory Publication: Australian Journal of Chemistry, 2008, 61(3), 209-215.

Accessory Publication for

Aromaticity in Heterocyclic and Inorganic Benzene Analogs

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Figure S1. Schematic □ MO interaction diagram of benzene (**1**) constructed from two $(CH)_3^{9\bullet}$ fragments in their decet valence configuration, based on Kohn-Sham MO analyses at BP86/TZ2P. There are 3 □ electrons in each of the two fragments, which have mutually opposite spin. The effect on orbital energies of the localization mode defined in Scheme 1 and represented here with curved arrows is indicated by + (stabilization) and – (destabilization).

Figure S2. Alternative bond energy decomposition of **4** and **5**, each constructed from two rigid fragments, as function of the distortion mode (in deg) from delocalized to localized structure as defined for **4** and **5** in Scheme 2. The diagram shows the *changes* relative to $\theta = 60°$ ($\Delta\Delta E$) in the indicated terms $\Delta E_{int} = (\Delta E_{Pauli} + \Delta E_{\sigma}) + [\Delta E_{\pi}] + \Delta V_{elstat}$ = (total σ) + [total □] + ΔV_{elstat} computed at BP86/TZ2P.

Table S1. Cartesian coordinates, point-group symmetry, total energy relative to ADF's basic atoms and number of imaginary frequencies (NIMAG) of species occurring in this study, optimized at BP86/TZ2P.

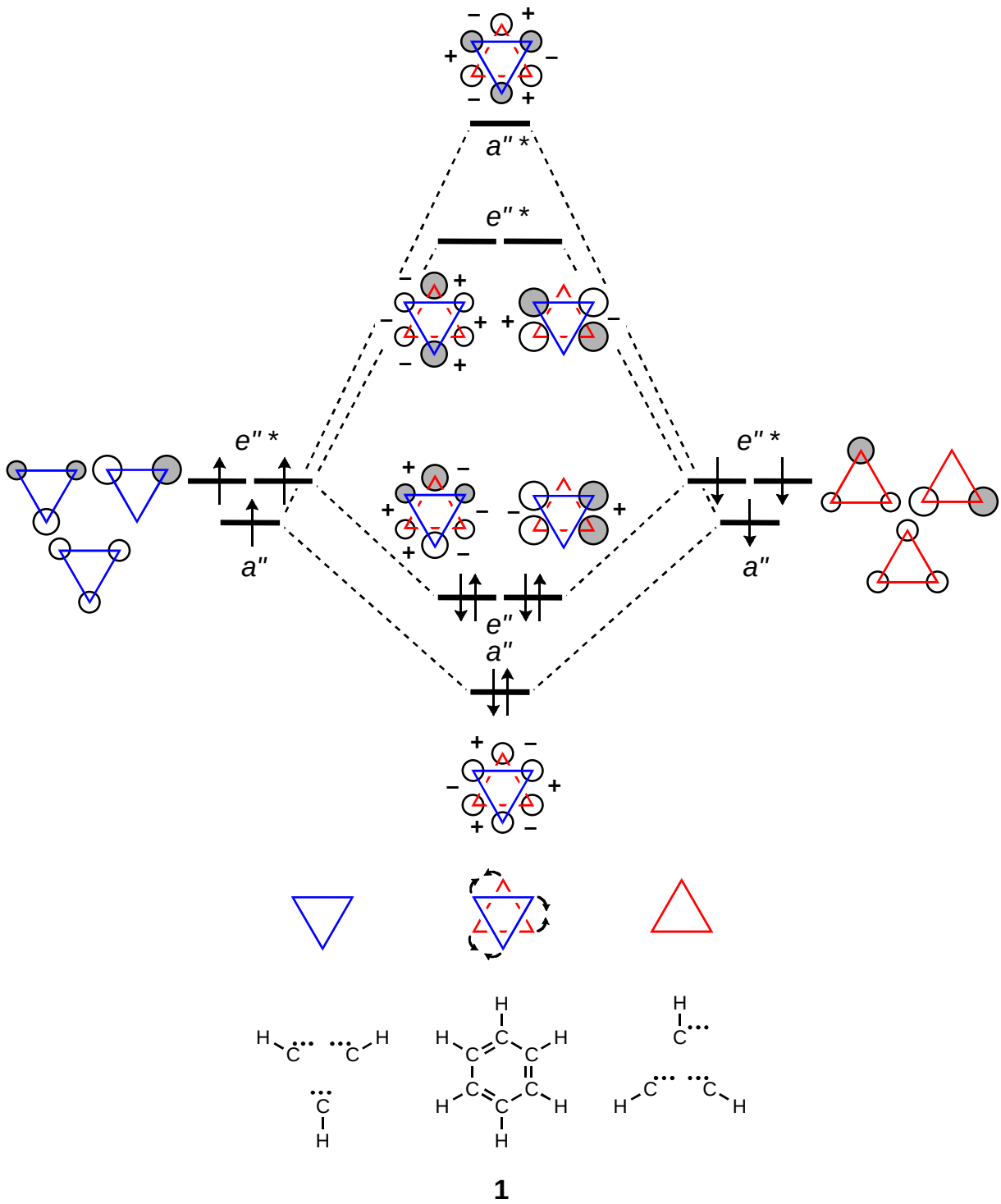

Figure S1. Schematic □ MO interaction diagram of benzene (**1**) constructed from two $(CH)_3^{9\bullet}$ fragments in their decet valence configuration, based on Kohn-Sham MO analyses at BP86/TZ2P. There are 3 □ electrons in each of the two fragments, which have mutually opposite spin. The effect on orbital energies of the localization mode defined in Scheme 1 and represented here with curved arrows is indicated by + (stabilization) and – (destabilization).

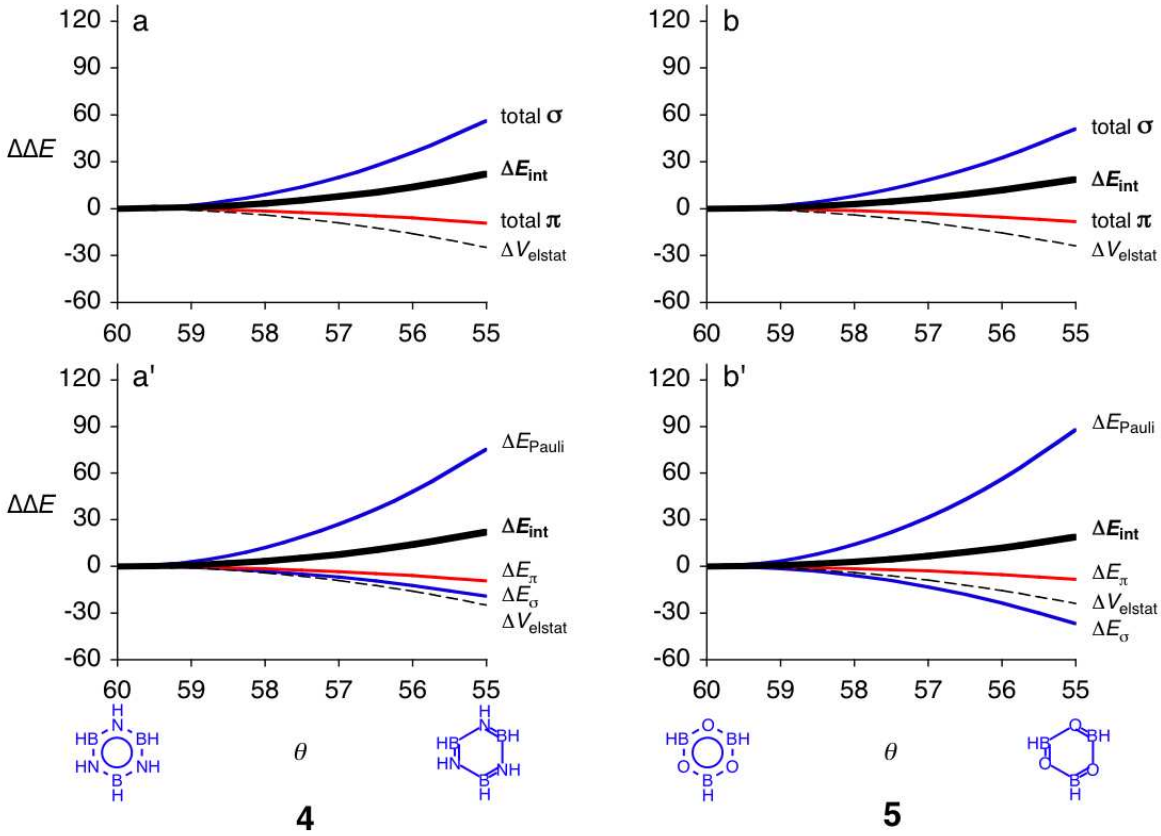

Figure S2. Alternative bond energy decomposition (in kcal/mol) of **4** and **5**, each constructed from two rigid *neutral* fragments (see text), as function of the distortion mode (in deg) from delocalized to localized structure as defined in Scheme 2. The diagram shows the *changes* relative to $\theta = 60°$ ($\Delta\Delta E$) in the indicated terms $\Delta E_{int} = (\Delta E_{Pauli} + \Delta E_{\sigma}) + [\Delta E_{\pi}] + \Delta V_{elstat}$ = (total σ) + [total □] + ΔV_{elstat} computed at BP86/TZ2P.

Table S1. Cartesian coordinates (in Å), point-group symmetry, total energy relative to ADF's basic atoms, and number of imaginary frequencies (NIMAG) of species occurring in this study, optimized at BP86/TZ2P.

1 C_6H_6 (D_{6h}) –1728.98 kcal/mol NIMAG = 0

C	0.000000	1.397664	0.000000
H	0.000000	2.487887	0.000000
C	0.000000	-1.397664	0.000000
H	0.000000	-2.487887	0.000000
C	1.210412	0.698832	0.000000
H	2.154573	1.243944	0.000000
C	1.210412	-0.698832	0.000000
H	2.154573	-1.243944	0.000000
C	-1.210412	-0.698832	0.000000
H	-2.154573	-1.243944	0.000000
C	-1.210412	0.698832	0.000000
H	-2.154573	1.243944	0.000000

2 $C_3H_3N_3$ (D_{3h}) –1409.07 kcal/mol NIMAG = 0

C	-1.296848	0.000000	0.000000
H	-2.389197	0.000000	0.000000
C	0.648424	1.123103	0.000000
H	1.194598	2.069105	0.000000
C	0.648424	-1.123103	0.000000
H	1.194598	-2.069105	0.000000
N	1.378496	0.000000	0.000000
N	-0.689248	1.193812	0.000000
N	-0.689248	-1.193812	0.000000

3 N_6 (D_{6h}) –974.41 kcal/mol NIMAG = 3 (B_{2u}: *i*322 cm^{-1}, E_2: *i*390 cm^{-1})

N	1.328875	0.000000	0.000000
N	-1.328875	0.000000	0.000000
N	0.664438	1.150840	0.000000
N	-0.664438	1.150840	0.000000
N	-0.664438	-1.150840	0.000000
N	0.664438	-1.150840	0.000000

4 $B_3N_3H_6$ (D_{3h}) –1637.39 kcal/mol NIMAG = 0

B	-1.455612	0.000000	0.000000
H	-2.654775	0.000000	0.000000
B	0.727806	1.260597	0.000000
H	1.327388	2.299103	0.000000
B	0.727806	-1.260597	0.000000
H	1.327388	-2.299103	0.000000
N	1.410075	0.000000	0.000000
H	2.423851	0.000000	0.000000
N	-0.705037	1.221161	0.000000
H	-1.211926	2.099117	0.000000
N	-0.705037	-1.221161	0.000000
H	-1.211926	-2.099117	0.000000

5 $B_3H_3O_3$ (D_{3h}) –1294.44 kcal/mol NIMAG = 0

B	-1.383456	0.000000	0.000000
H	-2.576574	0.000000	0.000000
B	0.691728	1.198108	0.000000
H	1.288287	2.231379	0.000000
B	0.691728	-1.198108	0.000000
H	1.288287	-2.231379	0.000000
O	1.382565	0.000000	0.000000
O	-0.691282	1.197336	0.000000
O	-0.691282	-1.197336	0.000000

6 Si_6H_6 (D_{6h}) –1057.09 kcal/mol

NIMAG = 1 (B_{2g}: *i*134 cm^{-1})

Si	2.227832	0.000000	0.000000
H	3.721264	0.000000	0.000000
Si	-2.227832	0.000000	0.000000
H	-3.721264	0.000000	0.000000
Si	1.113916	1.929359	0.000000
H	1.860632	3.222709	0.000000
Si	-1.113916	1.929359	0.000000
H	-1.860632	3.222709	0.000000
Si	-1.113916	-1.929359	0.000000
H	-1.860632	-3.222709	0.000000
Si	1.113916	-1.929359	0.000000
H	1.860632	-3.222709	0.000000

7 P_6 (D_{6h}) –644.66 kcal/mol NIMAG = 2 (E_2: *i*93 cm^{-1})

P	2.134514	0.000000	0.000000
P	-2.134514	0.000000	0.000000
P	1.067257	1.848543	0.000000
P	-1.067257	1.848543	0.000000
P	-1.067257	-1.848543	0.000000
P	1.067257	-1.848543	0.000000

3' N_6 (D_2) –983.43 kcal/mol NIMAG = 0

N	-1.246674	-0.064273	0.000010
N	1.246674	0.064273	0.000010
N	-0.693391	1.096688	0.242723
N	0.576947	1.162169	-0.242735
N	0.693391	-1.096688	0.242723
N	-0.576947	-1.162169	-0.242735

6' Si_6H_6 (D_{3d}) **–1060.11 kcal/mol**

NIMAG = 0

Si	1.911711	1.103727	0.238272
H	3.188862	1.841090	-0.042527
Si	-1.911711	-1.103727	-0.238272
H	-3.188862	-1.841090	0.042527
Si	0.000000	2.207453	-0.238272
H	0.000000	3.682181	0.042527
Si	-1.911711	1.103727	0.238272
H	-3.188862	1.841090	-0.042527
Si	0.000000	-2.207453	0.238272
H	0.000000	-3.682181	-0.042527
Si	1.911711	-1.103727	-0.238272
H	3.188862	-1.841090	0.042527

7' P_6 (D_2) **–648.32 kcal/mol** NIMAG = 0

P	-2.009635	0.000000	0.000000
P	2.009635	0.000000	0.000000
P	-0.973788	1.794284	0.435079
P	0.973788	1.794284	-0.435079
P	0.973788	-1.794284	0.435079
P	-0.973788	-1.794284	-0.435079

N_2 ($D_{\infty h}$) **–383.34 kcal/mol**

NIMAG = 0

N	0.000000	0.000000	0.550855
N	0.000000	0.000000	-0.550855

CH_3NH_2 (C_s) **–813.22 kcal/mol** NIMAG = 0

N	0.572854	-0.108718	-0.166118
H	0.329265	-1.003324	0.261330
H	2.183714	0.337383	1.242641
C	1.255365	0.753443	0.809169
H	0.567622	0.976517	1.635422
H	1.505245	1.709717	0.331106
H	1.196398	-0.325086	-0.945056

CH_2NH (C_s) **–625.67 kcal/mol** NIMAG = 0

N	-0.433217	-0.289635	-0.768396
H	0.049976	-1.174559	-0.981053
H	1.171502	0.074542	0.551747
C	0.218416	0.385256	0.090992
H	-0.182258	1.355794	0.412569

N_2H_4 (C_2) **–691.33 kcal/mol** NIMAG = 0

N	0.702431	-0.414895	-0.282858
H	-0.259367	-0.455532	0.066418
H	0.675632	-0.613716	-1.282598
N	1.282279	0.895141	-0.123071
H	1.715221	0.923584	0.799685
H	0.575710	1.635658	-0.156113

N_2H_2 (C_{2h}) **–502.94 kcal/mol** NIMAG = 0

N	0.924056	-0.299319	-0.119599
N	1.800796	-0.015292	0.723551
H	0.222897	-0.892128	0.376291
H	2.501956	0.577517	0.227661

BH_3NH_3 (C_{3v}) **–841.23 kcal/mol** NIMAG = 0

N	-0.565707	-0.399658	-0.925306
H	-0.803000	-1.324825	-0.559882
H	1.369499	-0.233229	0.294386
B	0.371288	0.445227	0.148171
H	-0.307303	0.535596	1.152888
H	-0.079760	-0.531759	-1.815352
H	-1.440985	0.092589	-1.118583
H	0.583365	1.512748	-0.393613

BH_2NH_2 (C_{2v}) **–686.78 kcal/mol** NIMAG = 0

N	-0.647405	-0.337497	-0.674249
H	-0.757593	-1.342407	-0.594645
H	1.303478	-0.256371	0.411585
B	0.444015	0.357204	-0.158259
H	-1.411789	0.110741	-1.167322
H	0.491203	1.547881	-0.299468

BH_3OH_2 (C_s) **–704.16 kcal/mol** NIMAG = 0

O	-0.777192	-0.249061	-0.613435
B	0.656692	0.516221	-0.001785
H	-0.815539	-1.143129	-0.228042
H	1.533814	-0.250737	-0.338077
H	0.625244	1.570428	-0.588305
H	0.413851	0.553440	1.179733
H	-0.654825	-0.369642	-1.572520

BH_2OH (C_s) **–565.69 kcal/mol** NIMAG = 0

O	-0.641331	-0.335650	-0.671091
B	0.430130	0.327964	-0.161949
H	-0.606368	-1.293859	-0.516428
H	1.304240	-0.269843	0.413911
H	0.445495	1.516830	-0.320803

Si_2H_6 (D_{3d}) **–700.14 kcal/mol** NIMAG = 0

Si	-0.648245	-0.908239	-0.589785
Si	0.687136	0.858719	0.240575
H	-2.087653	-0.686416	-0.239428
H	2.126601	0.637078	-0.109701
H	0.251907	2.165623	-0.348003
H	0.570405	0.947960	1.731311
H	-0.531596	-0.997390	-2.080533
H	-0.213177	-2.215253	-0.001310

Si_2H_4 (C_{2h}) **–497.00 kcal/mol** NIMAG = 0

Si	-0.322389	-0.945227	-0.661461
Si	0.361279	0.895718	0.312240
H	-0.024242	2.201578	-0.308637
H	0.299575	0.962811	1.805913
H	-0.260697	-1.012405	-2.155137
H	0.063155	-2.251046	-0.040502

P_2H_4 (C_2) **–547.98 kcal/mol** NIMAG = 0

P	-0.345610	-0.165186	-1.006695
P	-0.004343	1.563254	0.399251
H	0.942852	2.309553	-0.372890
H	1.020484	0.891674	1.140494
H	0.742040	0.051571	-1.912439
H	-1.269847	0.554009	-1.830873

P_2H_2 (C_{2h}) **–367.76 kcal/mol** NIMAG = 0

P	-0.378135	-0.035759	-0.988514
P	0.042614	1.440657	0.369171
H	1.007051	0.638378	1.078292
H	-1.342572	0.766522	-1.697633