–Supplementary Material–

Electronic structure of rhombus-shaped nanographenes: system size evolution from closed- to open-shell ground states

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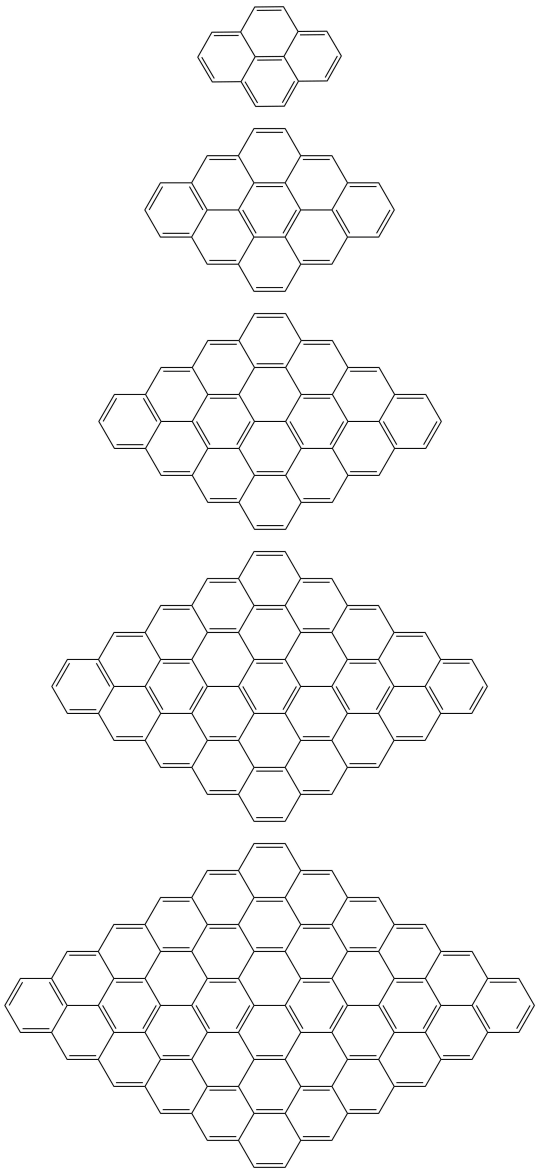

Figure 1: Chemical structures of the n-rhombenes studied (H atoms are not shown).

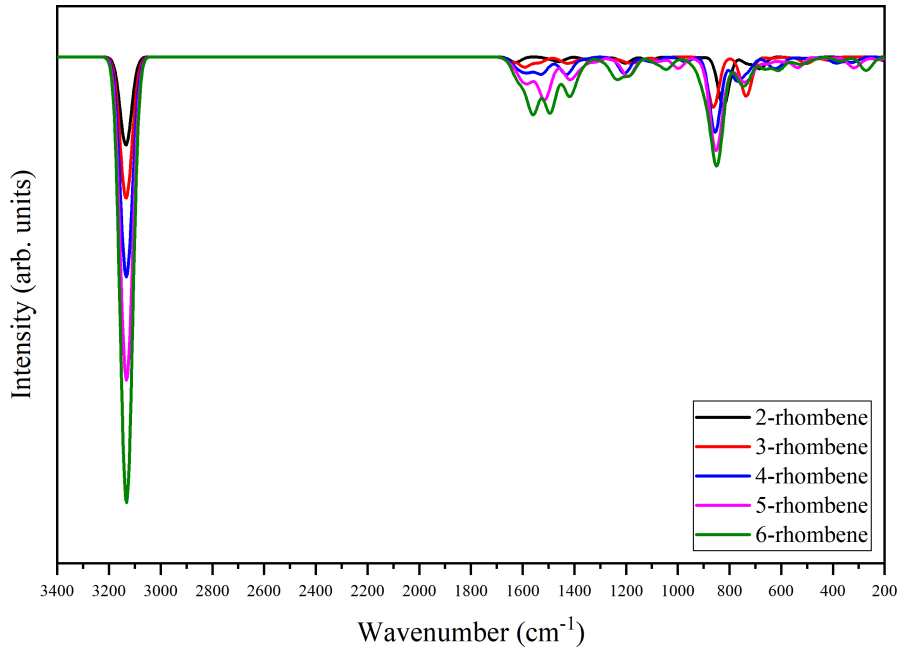

Figure 2: Simulated IR spectra for n-rhombenes, as calculated at the B97-3c level.

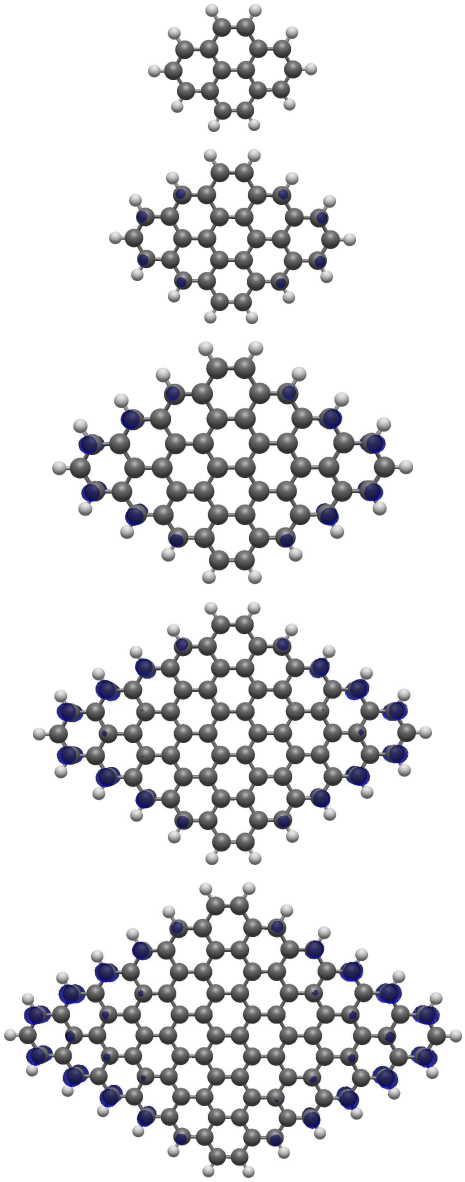

Figure 3: Density plots of $\rho_U(\mathbf{r})$ ($\sigma = 0.005$ e/bohr^3) of n-rhombenes, as calculated by the FT-TPSS/def2-TZVP method.

Table 1: Number of unpaired electrons (N_U) and diradical (Y_0), tetraradical (Y_1) and hexaradical (Y_2) index of the ground state of n-rhombenes at the RAS-SF/6-31G* level.

$[n]$	N_U	Y_0	Y_1	Y_2
2	0.20	0.056	0.034	0.002
3	0.45	0.145	0.038	0.030
4	1.06	0.313	0.080	0.043
5	2.17	0.670	0.263	0.049
6	2.78	0.892	0.374	0.101

Table 2: HOMO and LUMO energies (ev) of n-rhombenes, as calculated by DFT/def2-TZVP methods.

$[n]$	PBE		PBE0		PBEHH	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
2	–5.073	–2.396	–5.809	–1.689	–6.438	–0.849
3	–4.474	–3.114	–5.013	–2.618	–5.460	–1.960
4	–4.177	–3.513	–4.553	–3.196	–4.842	–2.707
5	–4.136	–3.625	–4.980	–2.814	–	–
6	–4.185	–3.619	–4.942	–2.884	–	–

Table 3: Energy differences (eV) between the ground-state (S_0) and S_1 (ΔE_{SS}), T_1 (ΔE_{ST}), and Q_1 (ΔE_{SQ}) states of n-rhombenes. All calculations were carried out at the RAS-SF/6-31G* level.

$[n]$	ΔE_{ST}	ΔE_{SS}	ΔE_{SQ}
2	2.835	4.240	8.285
3	1.281	3.338	5.243
4	0.535	2.298	2.781
5	0.139	1.257	0.868
6	0.056	0.762	0.235

Table 4: Energy differences (eV) between the ground-state (S_0) and S_1 (ΔE_{SS}), T_1 (ΔE_{ST}), and Q_1 (ΔE_{SQ}) states of n-rhombenes, as calculated by DFT/def2-TZVP methods and corrected by the Yamaguchi expression.

$[n]$	PBE			PBE0		
	ΔE_{ST}	ΔE_{SS}	ΔE_{SQ}	ΔE_{ST}	ΔE_{SS}	ΔE_{SQ}
2	2.314	–	6.089	2.360	–	6.475
3	1.089	–	3.754	0.994	–	3.701
4	0.423	–	1.836	0.576	0.170	1.952
5	0.174	0.040	0.846	1.403	0.630	0.882
6	0.235	0.176	0.324	1.181	1.214	0.474

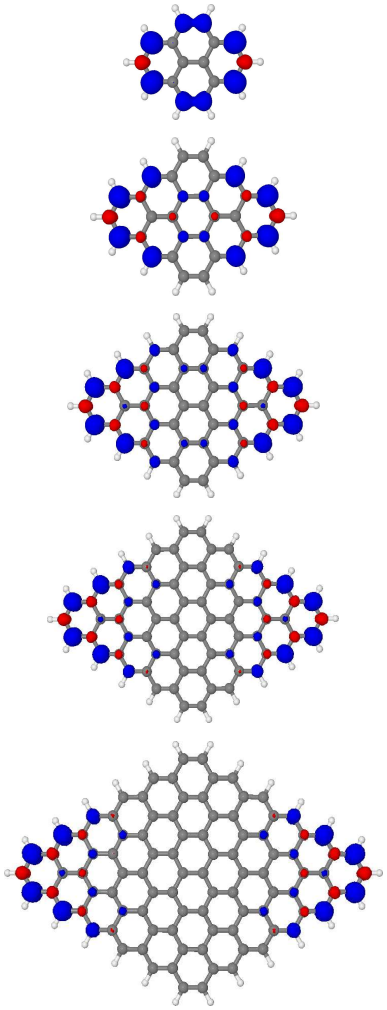

Figure 4: Spin Density plots (σ = 0.005 e/bohr^3) of triplet state of n-rhombenes, as calculated by the PBE0/def2-TZVP method.

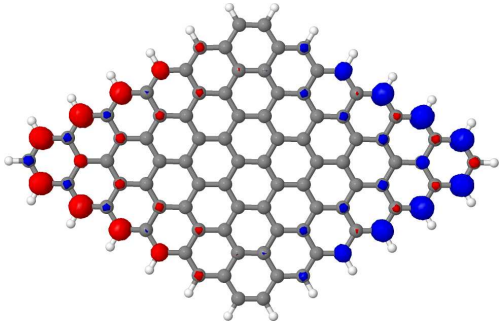

Figure 5: Spin Density plot ($\sigma = 0.005$ e/bohr^3) of open-shell singlet state of 6-rhombenes, as calculated by the PBE/def2-TZVP method.