Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Bonding and Optical Properties of Spirocyclic-phosphazene Derivatives. A DFT Approach

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Supplementary Information

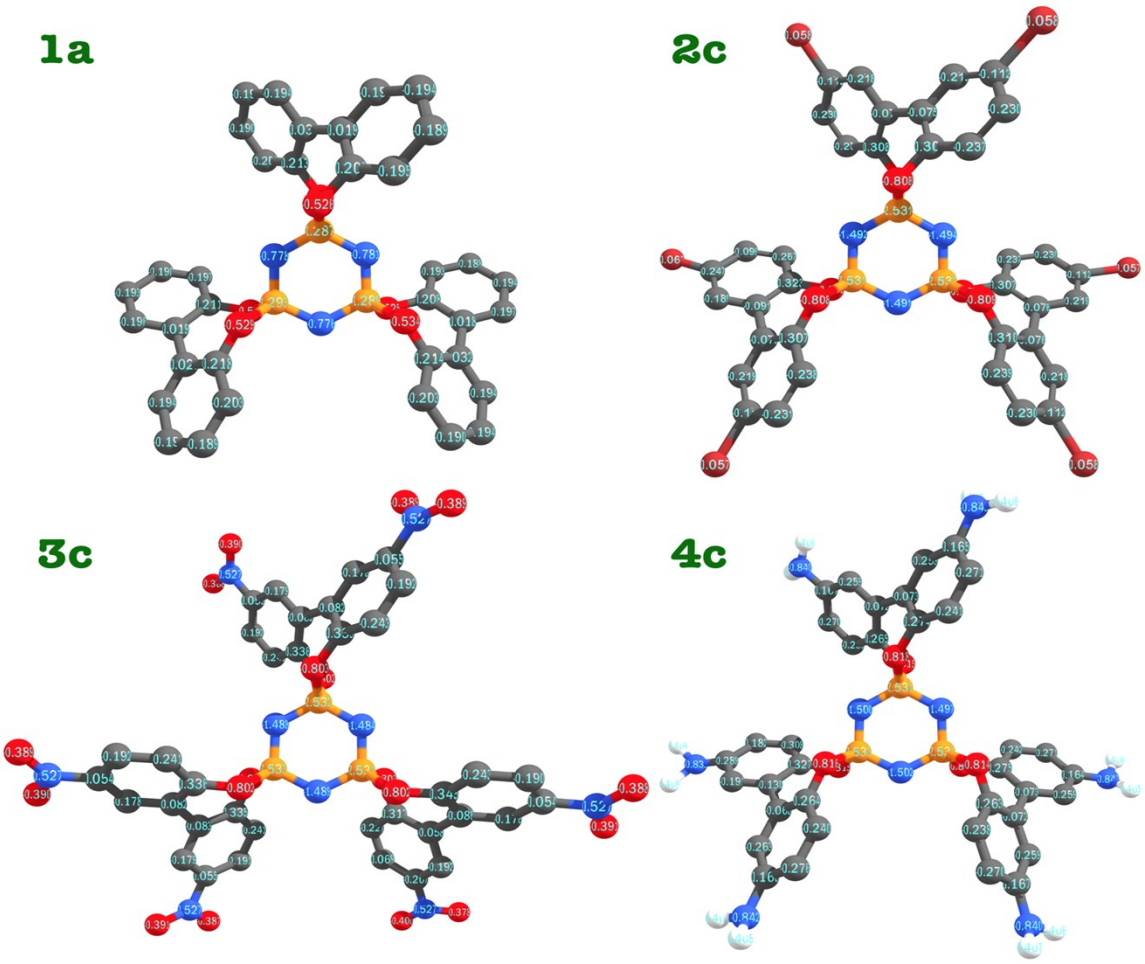

Figure S1. In the figure are shown the NBO Natural charges of the corresponding systems.

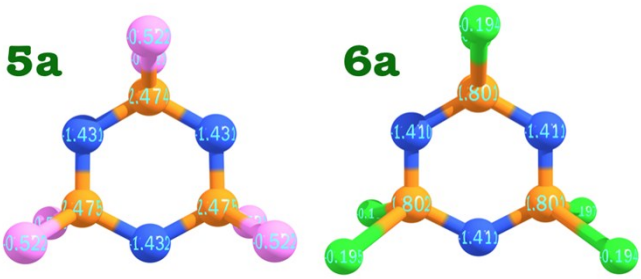

Figure S2. In the figure are shown the NBO Natural charges of the corresponding systems.

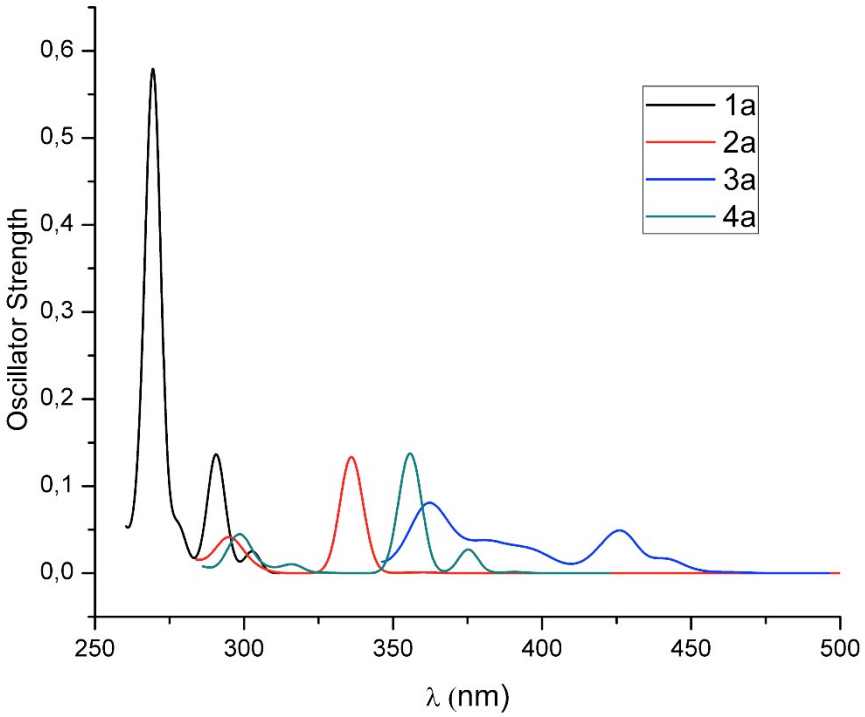

Figure S3. The TD-DFT UV-vis spectra for molecules in study.

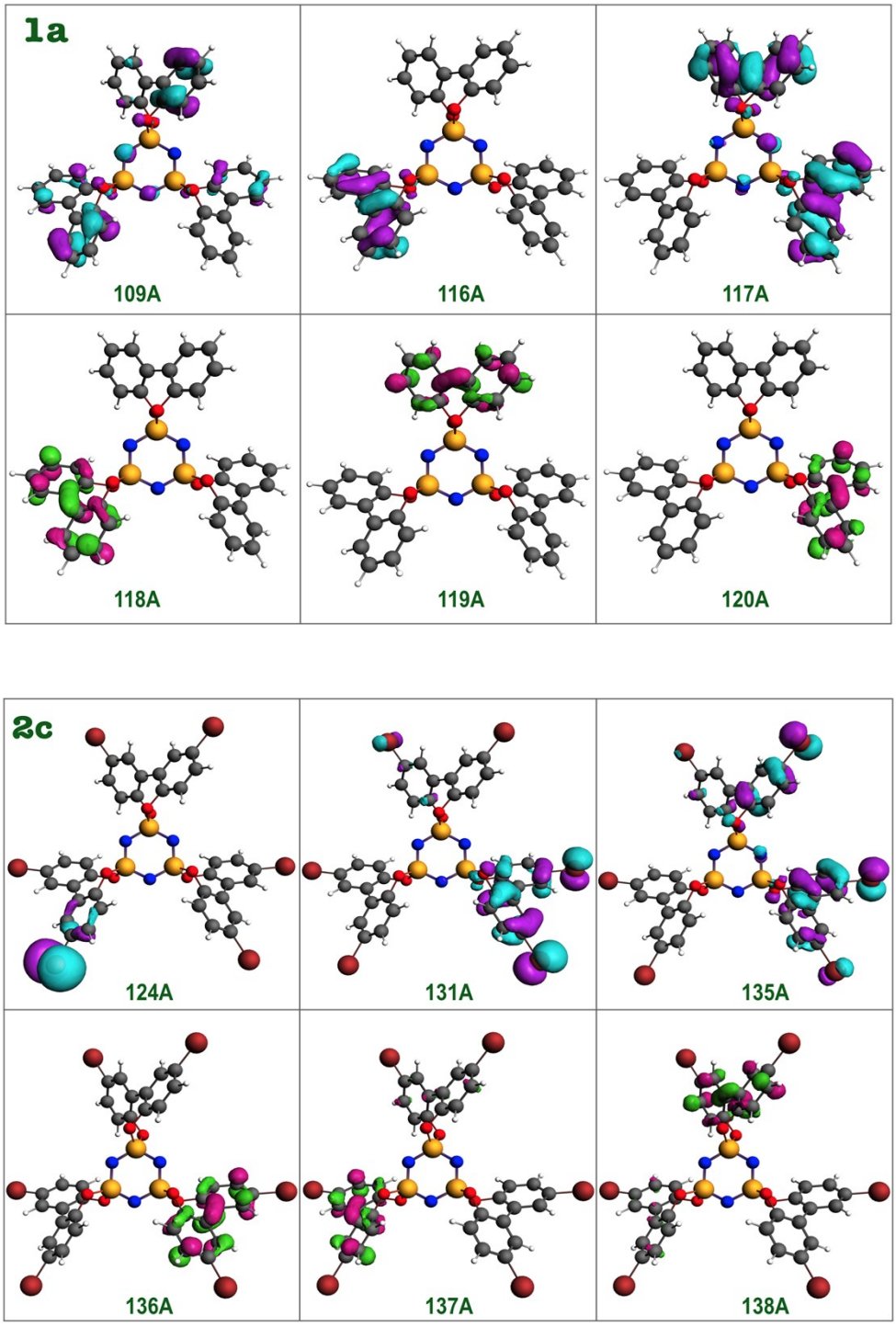

Figure S4. Plotted molecular orbital functions involved at the electronic transitions of spiro-cyclic phosphazene derivatives.

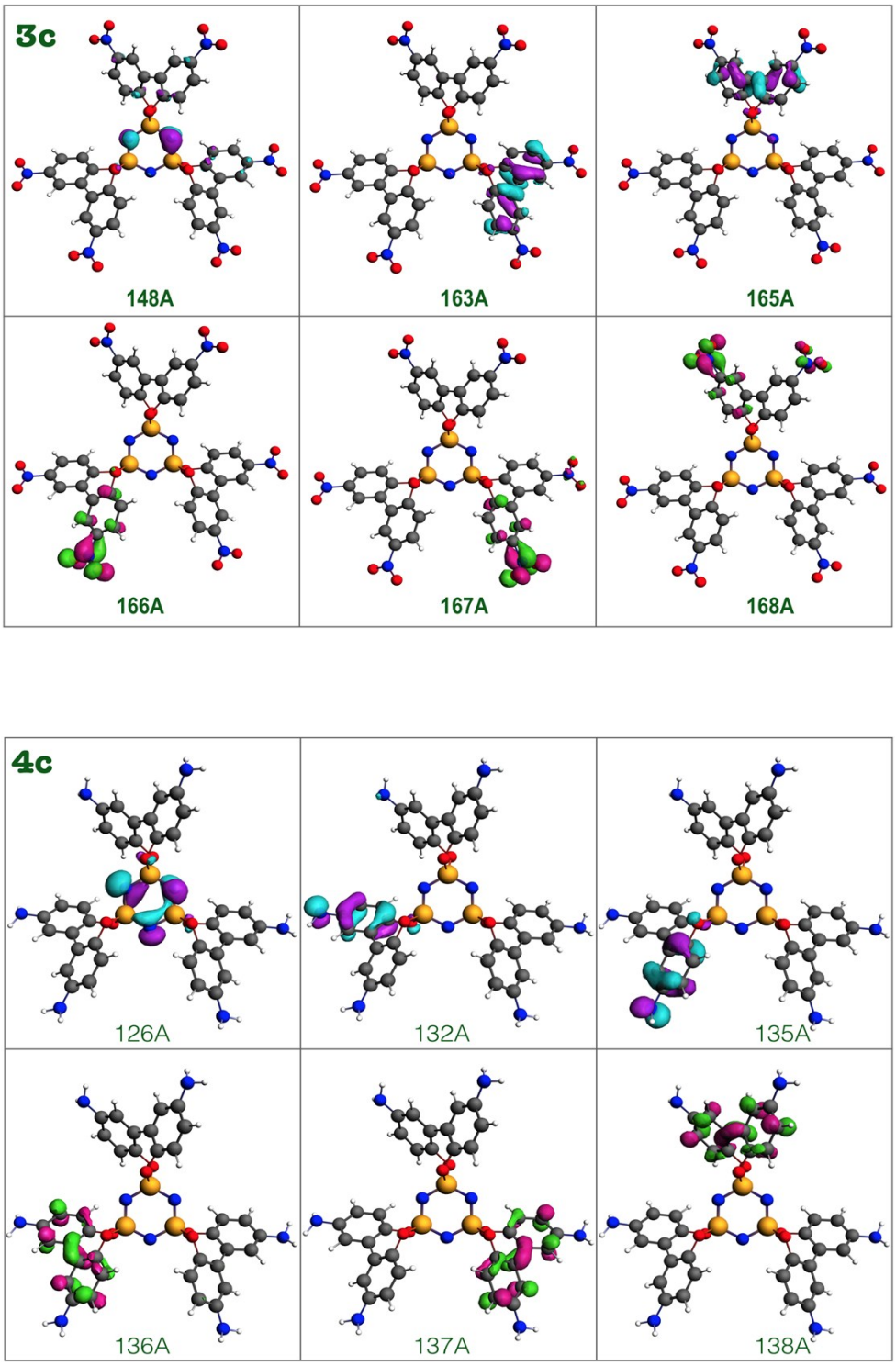

Figure S4. Plotted molecular orbital functions involved at the electronic transitions of spiro-cyclic phosphazene derivatives.

Table S1. Selected structural parameters of phosphazene derivatives

	1a	**2a**	**2b**	**2c**	**6(3b)**	**4a**	**[a]Exp.**
P_1-N_1	1.581	1.581	1.583	1.580	1.586	1.580	
P_1-N_2	1.582	1.585	1.583	1.580	1.587	1.581	1.585,1.568
P_2-N_2	1.582	1.578	1.578	1.580	1.572	1.584	1.585,1.582
P_2-N_3	1.582	1.579	1.581	1.581	1.581	1.581	1.585,1.586
P_3-N_1	1.581	1.581	1.578	1.580	1.573	1.584	1.585
P_3-N_3	1.580	1.584	1.581	1.580	1.582	1.589	
P_1-O_1	1.605	1.606	1.610	1.608	1.611	1.608	1.586
P_1-O_2	1.604	1.604	1.600	1.604	1.592	1.608	1.581
P_2-O_3	1.605	1.609	1.603	1.608	1.610	1.601	1.584
P_2-O_4	1.604	1.609	1.601	1.602	1.611	1.605	
C-C_{ar}	1.391	1.392	1.391	1.388	1.391	1.392	1.393
C-C	1.480	1.480	1.480	1.479	1.480	1.480	
C-C_{ar2}	1.392	1.388	1.388	1.388	1.388	1.401	
C-C_2	1.480	1.480	1.478	1.478	1.479	1478	
Br-C	-	1.913	1.913	1.912	-	-	
O_2N-C	-	-	-	-	1.479	-	
H_2N-C	-	-	-	-	-	1.398	
O-C_{ar}	1.393	1.387	1.390	1.390	1.384	1.391	1.395
P_1-N_2-P_2	122.2	121.9	122.3	122.6	122.7	121.9	122.9,120.8
P_1-N_1-P_3	122.3	122.5	122.5	122.3	122.6	122.1	122.9,121.2
N_1-P_1-N_2	117.6	117.4	117.2	117.6	116.4	118.2	118.5,118.6
N_1-P_3-N_3	117.5	117.9	117.7	117.5	118.3	117.3	118.5,118.3
O_1-P_1-O_2	102.0	102.3	102.4	102.0	103.2	101.7	102.4
O_3-P_2-O_4	102.1	101.6	101.8	102.0	101.0	102.5	103.0
P_1-O_1-C_9	123.7	122.0	122.7	122.6	121.1	122.9	121.8
P_2-O_3-C_5	123.7	123.9	122.2	121.99	120.3	124.8	

[a]Ref. [24]

Table S2. Second order stabilization energies, ΔE^2, εj-εi from NBO analysis for the selected systems.

CSF	Donor	Acceptor	ΔE2	εj-εi
Electron W-D			(Kcal/mol)	a.u.
1				
	BD (2)C1-C2	BD* (2)C3-C6	19.74	0.28
	BD (2)C1-C2	BD* (2)C5-C7	20.92	0.29
Overall	BD (2)C-C	BD* (2)C-C	729.63	
2c	BD (2)C1-C2	BD* (2)C3-C6	19.43	0.28
	BD (2)C1-C2	BD* (2)C5-C7	21.41	0.27
Overall	BD (2)C-C	BD*(2)C-C	725.36	
	BD (1)C1-C2	BD*(1)C5-Br71	5.03	0.79
	BD (1)C6-C7	BD* (1)C5-Br71	4.68	0.81
	LP (3)Br71	BD* (2)C5-C 7	9.78	0.31
	LP (2)Br71	BD* (1)C2-C 5	2.88	0.86
	LP (2)Br71	BD* (1)C5-C7	2.98	0.87
3c				
	BD (2)C1-C2	BD* (2)C3-C6	21.64	0.27
	BD (2)C1-C2	BD* (2)C5-C7	20.98	0.28
Overall	BD (2)C-C	BD* (2)C-C	735.78	
	BD (2)C18-C19	BD* (2)N76-O77	26.93	0.15
	BD (2) C-C7	BD*(2) N73-O74	26.27	0.15
	BD* (2)N73-O74	BD* (2)C5-C7	15.03	0.14
	BD*(2)N76-O77	BD* (2)C18-C19	14.5	0.14
4c	BD (2)C1-C2	BD* (2)C3-C6	15.73	0.29
	BD (2)C1-C2	BD* (2)C5-C7	22.1	0.26
Overall	BD (2)C-C	BD* (2)C-C	717.03	
	LP (1)N67	BD* (2)C5-C7	29.32	0.32
	LP (1)N68	BD* (2)C18-C19	27.19	0.32
	BD (1)C1-C2	BD* (1)C5-N67	3.83	1.15
	BD (1)C6 - C 7	BD* (1)C5-N67	3.64	1.16
	BD (1)C19-C23	BD* (1)C18-N68	3.51	1.13
	BD (1)C20-C24	BD* (1)C18-N68	3.82	1.14