

Supplementary Information

June 19, 2009

HF molecular dissociation

Table S1: SF-XCIS and RAS(6,4)-SF absolute energies (in Hartrees) along the HF molecular dissociation. All calculations were obtained using the 6-31G basis set.

r (Å)	SF-XCIS	RAS(6,4)-SF
0.8	-99.997399	-99.998034
1.0	-100.026411	-100.027513
1.2	-99.998433	-99.999573
1.4	-99.959763	-99.960871
1.6	-99.925181	-99.926227
1.8	-99.899047	-99.900029
2.0	-99.881652	-99.882582
2.2	-99.871225	-99.872118
2.4	-99.865433	-99.866301
2.6	-99.862367	-99.863221
2.8	-99.860785	-99.861633
3.0	-99.859975	-99.860821
3.2	-99.859559	-99.860403
3.4	-99.859344	-99.860188

Singlet-triplet gap in linear acenes

Figure S1: Exponential fitting ($a + be^{-\alpha n}$) to the computed RAS(4,4)-SF singlet-triplet gap of the linear n -acenes. The adjusted parameters for $2 \leq n \leq 20$ correspond to 1.59 ± 0.44 kcal/mol, 165.94 ± 5.32 kcal/mol and 0.428 ± 0.013 for a , b and α respectively.

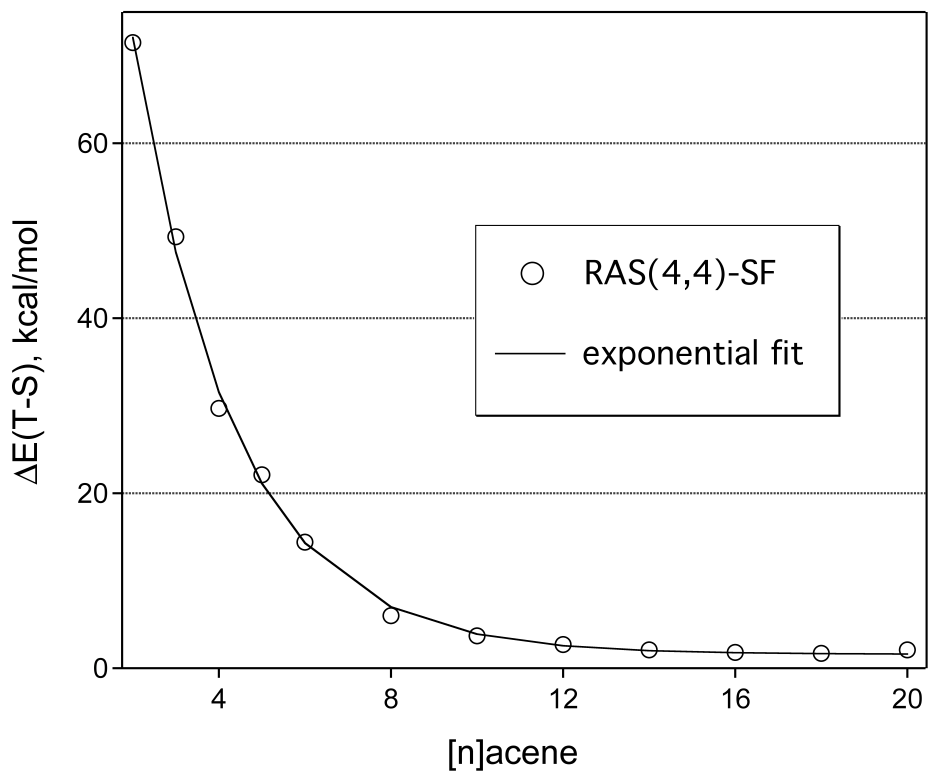
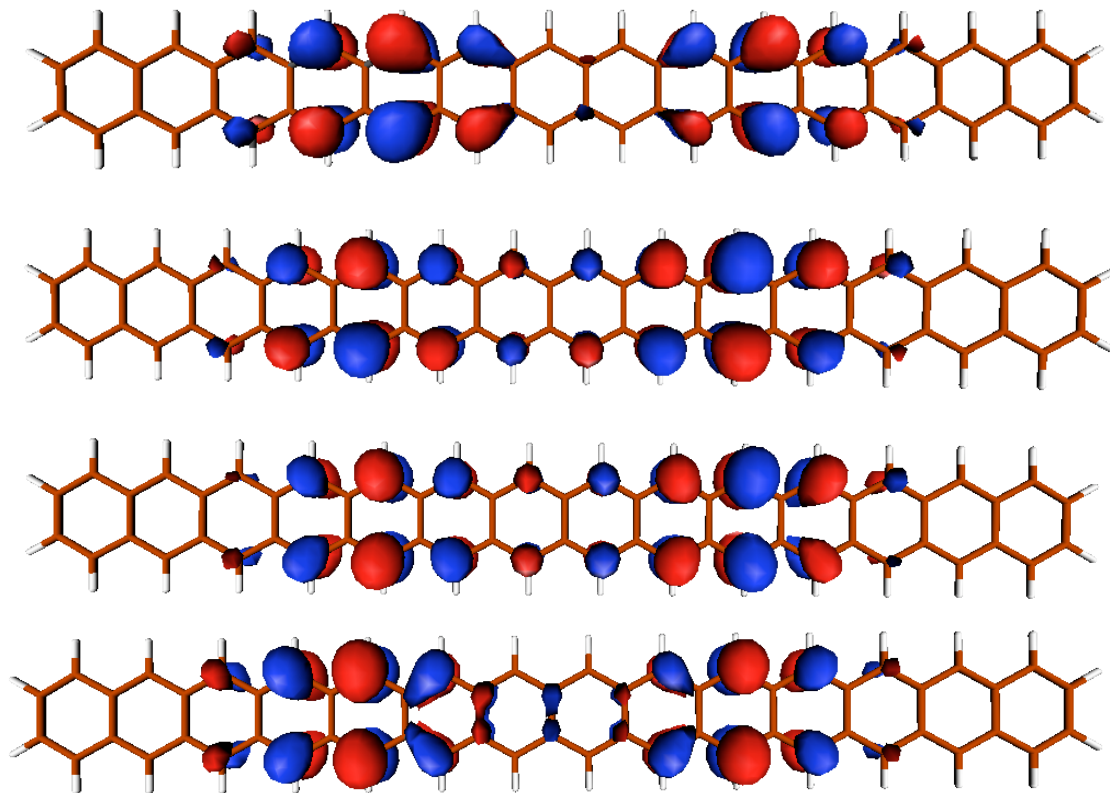


Figure S2: Graphical representation of the four singly occupied orbitals of the ROHF quintet of the 14-fused ring acene.



Ni(II) Octahedral Complexes

Table S2: Experimental cartesian coordinates (in Angstroms) from Ref. 1 of $[\text{NiF}_6]^{4-}$.

Ni	0.0000	0.0000	0.0000
F	2.0070	0.0000	0.0000
F	-2.0070	0.0000	0.0000
F	0.0000	2.0070	0.0000
F	0.0000	-2.0070	0.0000
F	0.0000	0.0000	2.0070
F	0.0000	0.0000	-2.0070

Table S3: Experimental cartesian coordinates (in Angstroms) from Ref. 2 of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

Ni	2.24235	4.18561	0.00000
O	0.51846	3.13729	-0.27492
O	3.31666	2.64823	-0.86984
O	1.16805	5.72300	0.86984
O	2.00575	5.06886	-1.82676
O	2.47896	3.30236	1.82676
O	3.96624	5.23394	0.27492
H	0.52676	5.54654	1.28487
H	1.56101	6.32102	1.30527
H	4.24974	5.28245	0.92796
H	4.35405	5.75971	-0.25493
H	2.15230	4.64769	-2.45757
H	1.28409	5.44812	-2.01908
H	3.20062	2.92311	2.01908
H	3.95794	2.82468	-1.28487
H	2.92370	2.05020	-1.30527
H	0.13066	2.61151	0.25493
H	0.23496	3.08878	-0.92796
H	2.33241	3.72353	2.45757

Table S4: Experimental cartesian coordinates (in Angstroms) from Ref. 3 of $[\text{Ni}(\text{NH}_3)_6]^{2+}$.

Ni	-15.00062	-10.13881	21.00868
N	-14.96264	-8.07406	21.55052
N	-14.97831	-12.20459	20.46988
N	-16.44043	-9.72196	19.45109
N	-16.60312	-10.50397	22.41279
N	-13.45518	-9.72602	19.63158
N	-13.61644	-10.60138	22.53356
H	-14.60307	-12.29800	19.66846
H	-14.66698	-7.99205	22.38577
H	-15.78477	-7.73642	21.49237
H	-15.81309	-12.51407	20.44444
H	-14.42139	-7.63212	20.99956
H	-14.51052	-12.66368	21.07174
H	-16.42228	-10.37585	18.84670
H	-16.62372	-9.85004	23.01706
H	-16.23791	-8.95028	19.05753
H	-16.46749	-11.28139	22.82341
H	-17.25485	-9.66926	19.80652
H	-17.37897	-10.52964	21.97714
H	-13.26468	-8.85761	19.65014
H	-13.45458	-11.47578	22.53278
H	-13.71903	-9.95238	18.81380
H	-13.95341	-10.36481	23.32103
H	-12.72983	-10.19444	19.84957
H	-12.85739	-10.15819	22.39045

Table S5: Experimental and RAS-SF with two different active spaces, i.e. (8,5) and (18,10), energy gaps (in eV) for the $[\text{NiF}_6]^{4-}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complexes.

symmetry	$[\text{NiF}_6]^{4-}$			$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$			$[\text{Ni}(\text{NH}_3)_6]^{2+}$		
	(8,5)	(18,10)	Exp ^a	(8,5)	(18,10)	Exp ^{b,c}	(8,5)	(18,10)	Exp ^{b,c}
$^3T_{2g}$	0.79	0.87	0.90	0.92	0.99	1.05, 1.06	1.08	1.25	1.33
$^3T_{1g}(^3F)$	2.05	1.49	1.55	2.09	1.69	1.67, 1.77	1.85	2.08	2.17
1E_g	2.30	2.19	1.91	2.28	2.19	1.91	2.22	2.11	
$^1T_{2g}$	3.12	2.97	2.59	3.20	3.09		3.22	3.31	
$^3T_{1g}(^3P)$	3.74	3.39	2.95	3.96	3.58	3.14, 3.15	3.70	3.85	3.50, 3.49
$^1A_{1g}$	4.32	3.60		3.72	3.50		3.67	3.51	

^aRef 4. ^bRef. 5. ^cRef 6.

Tetraradicals from weakly interaction triplets

Table S6: Singlet-quintet adiabatic energy gaps (in kcal/mol) for the organic tetraradical studied systems computed by HF, MP2 and B3LYP.

molecule	S-Q Energy gaps			Ground state			
	HF	MP2	B3LYP	HF	MP2	B3LYP	Expt.
1	34.3	17.1	16.0	Q	Q	Q	Q
2	-9.7	8.3	12.4	S	Q	Q	S
3	20.1	-4.9	1.1	T	T	Q	Q
4	33.4	15.8	13.1	Q	Q	Q	Q
5	68.1	7.4	13.8	Q	Q	Q	Q
6	33.4	22.6	10.4	Q	Q	Q	Q
7	1.1	0.4	0.4	Q	Q	Q	Q
8	37.2	29.2	20.4	Q	Q	Q	Q
9	41.0	27.3	-21.2	Q	Q	S	S
10	12.9	10.0	1.8	Q	Q	Q	Q
11	36.5	25.2	1.9	Q	Q	Q	Q
12	35.5	24.7	5.4	Q	Q	Q	Q
13	13.2	12.5	-4.0	Q	Q	S	Q
14	6.9	-2.3	7.5	Q	S	Q	T
15	35.6	25.3	17.1	Q	Q	Q	Q
16	0.1	-8.3	-33.7	T	T	S	S
17	-65.2	-82.6	0.7	T	T	S	Q
18	-52.9	-60.9	15.2	S	S	Q	S
19	34.8	23.4	15.8	Q	T	Q	S
20	34.8	23.6	16.1	Q	Q	Q	S
21	34.9	23.6	16.0	Q	Q	Q	S
22	37.7	15.9	0.2	Q	Q	Q	Q
23	-131.0	-133.2	-1.7	S	S	T	S~T
24	34.3	22.4	-4.5	Q	Q	S	S
25	34.4	22.0	8.1	Q	Q	Q	Q
26	34.3	21.8	15.9	Q	Q	Q	Q
27	28.3	22.9	16.2	Q	T	S	S~Q
28	-58.1	-116.8	16.3	S	S	S	S~Q

References

- [1] A. Okazaki and Y. Suemune, *J. Phys. Soc. Jpn.* **16**, 671 (1961).
- [2] S. Banerjee, A. R. Choudhury, T. G. Row, S. Chaudhuri, and A. Ghosh, *Polyhedron* **26**, 24 (2007).
- [3] B. Paul et al., *CrystEngComm* **6**, 293 (2004).
- [4] K. Knox, R. G. Shulman, and S. Sugano, *Phys. Rev.* **130**, 512 (1963).
- [5] C. K. Jørgensen, *Acta Chem. Scand.* **9**, 1362 (1955).
- [6] M.-C. Nolet, A. Michaud, C. Bain, D. Zargarian, and C. Reber, *Photochem. Photobiol.* **82**, 57 (2006).