

Supplement

Table S1. Dependence of the S-T energy separations ($-\Delta E_{S-T}$, in kcal/mol), C_i symmetry imposed on optimized geometries.

Basis sets

Method	TZVP	TZVPP	QZVP
RI-BP86-D	9.4	11.5	
RI-MP2(fc)	18.7	24.7	27.3
RI-MP2(fc)(SCS)	14.4	20.2	22.8
RI-MP2(fc)(SOS)	12.2	17.9	20.5

RI = resolution of the identity.

BP86 = Becke-Perdew density functional.

MP2(fc) = Moller-Plesset second order perturbation theory, with frozen core approximation.

SCS = spin correction according to Grimme et al..

SOS = spin correction according to Head-Gordon et al..

Basis sets:

TZVP, A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **100**, 5829 (1994).

TZVPP, F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.* **294**, 143 (1998).

QZVP, F. Weigend, F. Furche and R. Ahlrichs, *J. Chem. Phys.* **119**, 12753 (2003).

Table S2. Dependence of the S-T energy separation ($-\Delta E_{S-T}$, in kcal/mol) at optimized CCSD level utilizing the TZVP basis set and partitioning of the energy components of the overall CCSD wavefunction.

Component	$-\Delta E_{S-T}$ (in kcal/mol)
HF	-34.7
MP2	17.6
MP3	2.2
MP4D	4.7
MP4DQ	0.0
MP4SDQ	0.8
CCSD	-1.2
CCSD(t)	5.5 (10.6) ^a

^aCCSD(t)/cc-pVTZ//CCSD/TZVP; see Table 3.

For the bulky systems dispersion corrections are of considerable importance on the S-T energy separation. The matter is illustrated for the case **1** R(P) = Mes*, R(C) = TMS.

Table S3. Energy difference between singlet and triplet ($-\Delta E_{S-T}$, in kcal/mol) at BP86/TZVP (L1) and BP86-D/TZVP (L2) level. Absolute energies are in hartree.

State	L1	L2	ΔE (L1-L2)
S	-2513.029862	-2513.19355	0.16369
T	-2512.992786	-2513.16365	0.17086
$-\Delta E$ (S-T)	23.2	18.8	

The dispersion corrections ($E(L1)-E(L2)$) are larger for the stronger pyramidalized triplet than the singlet (see last column in the table).