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

Supporting Information

The role of the multiconfigurational character of nitronyl-nitroxide in the singlet-triplet energy gap of its biradicals

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We show in this Supporting Information how the differences between CAS(2,2)+DDCI and CAS(4,4)+DDCI in calculating the singlet–triplet energy gap ($\Delta E_{TS}=E_S-E_T$) are common to the species characterized by a fragment bearing the unpaired electron with a π backbone. In Figure S1 the two model diradicals that we have utilized, characterized by a triplet ground state, are schematized. The torsional angle O-N-C-N is the same for both and is fixed to 70°. In part (a) we have a nitronyl nitroxide diradical which is basically that of Figure 1a of the paper, while in part (b) we have replaced one of the N-O with a C-H.

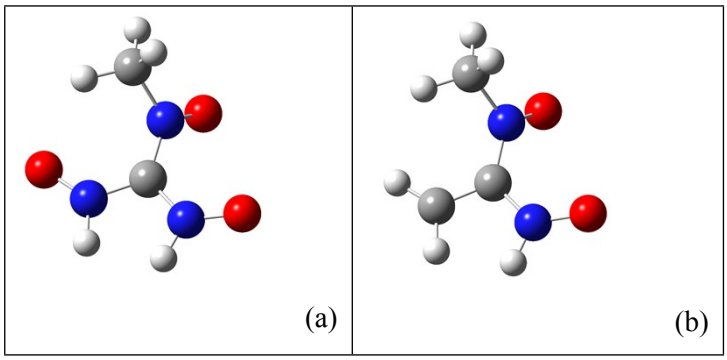

Figure S1 – model diradicals: (a) nitronyl nitroxide; (b) the same species of (a) where one NO has been replaced by CH

We have performed full variational/full MOs set DDCI calculations employing the 6-311G* basis set without any MOs localization. The values of ΔE_{TS} obtained, in cm^{-1}, are summarized in Table S1.

Table S1 – ΔE_{TS} (cm^{-1}) for the two model diradicals of Figure S1

Species	CAS(2,2)	CAS(4,4)	CAS(2,2)+DDCI	CAS(4,4)+DDCI
(a)	302.8	466.5	687.9	964.0
(b)	171.7	220.1	331.4	494.8

Differences are already evident at the CAS level. With DDCI the CAS(4,4) are 276.1 (28.6%) and 163.4 (33%) larger than the CAS(2,2) values, respectively for species (a) and (b).

While the absolute value of the gap is seen to depend from the presence of one single or two nitroxides, the difference between the CAS(2,2)+DDCI and the CAS(4,4)+DDCI values are in percent about the same, therefore in both cases the largest CAS should be considered as the reference space for DDCI.

Table S2 – MCSCF Orbital occupation for the triplet state of the two model diradicals of Figure S1

Species	HOMO-2	HOMO-1	HOMO	LUMO
(a)	1.83	1.00	1.00	0.17
(b)	1.91	1.00	1.00	0.09

In Table S2 we show the occupation numbers of the 4 MOs of the CAS(4,4) space obtained, for the triplet state at MCSCF level, with DALTON. We can see that the MCSCF character is evident even for the C-C-N-O (b) species.

We now give some details on the computational cost of the DDCI2/DDCI calculations for the phenyl-bridged bis nitronyl nitroxide diradical with CAS(6,6) reference space. DDCI2 calculation has been performed on a 16 CPU Intel(R) Xeon(R) CPU E5-2670 0 @ 2.60GHz with 125 GB RAM in 20.13 h of CPU. The largest DDCI calculation with 74 virtual MOs (Nvar=103 in Table3) has been performed on a 240 CPU Intel(R) Xeon(R) CPU E5-4650 v2 @ 2.40GHz with 6 TB RAM in 22.6 d of CPU.