

Enhancing Magnetic Couplings through Protonation of Benzylideneaniline-Bridged Diradicals and Comparison with Stilbene-, Azobenzene-Based Diradicals

Fengying Zhang^{*,†}, Yiwei Feng[‡], Xinyu Song[‡], Yuxiang Bu[‡]

† Department of Materials Science and Engineering, Jinzhong University, Jinzhong, 030619, People's Republic of China

‡ School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, People's Republic of China

The Corresponding Authors: zfy13233005848@163.com

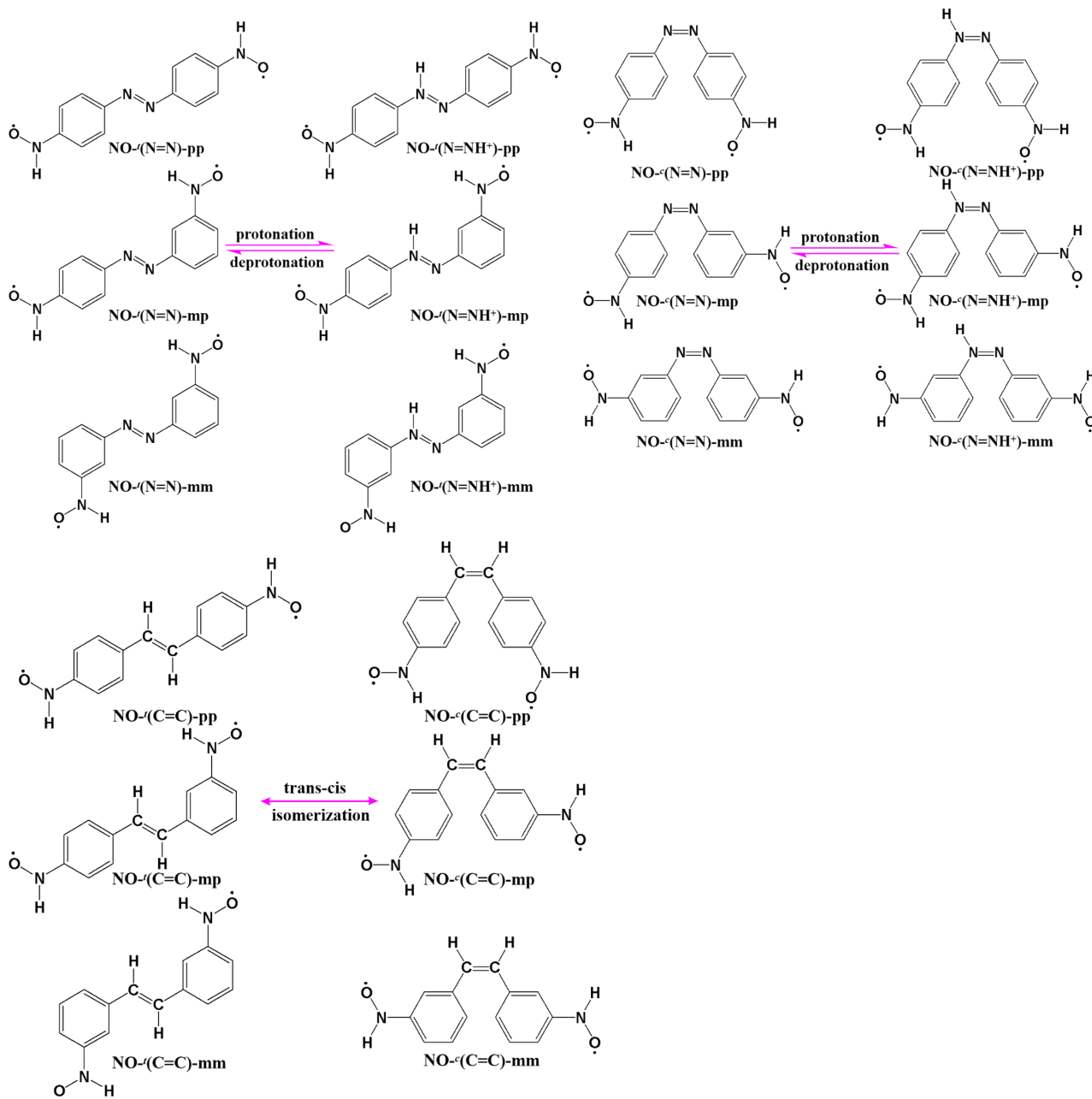
Electronic Supplementary Information

Contents

- 1. Schematic Diagram of Unprotonated and Protonated Structures of AB-Bridged Nitroxide (NO) Diradicals and Stilbene-Bridged Ones for Trans- and Cis-forms of Three Series**
- 2. Relevant Data of Describing Ground States for All Designed Diradicals, Their Diradical Character and Magnetic Behaviors**
- 3. Optimized Molecular Geometries for Ground States of All Diradicals**
- 4. Distributions of Mulliken Atomic Spin Density of All Diradicals**
- 5. Schematic Diagram of Exchange Coupling between Two Radical Groups through HOMO or LUMO of Coupler**
- 6. SOMO Plots and Spin Density Maps for All Diradicals**
- 7. Spin Alteration Plots for BA-, AB- and Stilbene-Bridged Diradicals**

1. Schematic Diagram of Unprotonated and Protonated Structures of AB-Bridged Nitroxide (NO) Diradicals and Stilbene-Bridged Ones for *Trans*- and *Cis*-forms of Three Series

Scheme S1. Schematic diagram of the unprotonated and protonated structures of AB-based diradicals and stilbene-based ones for the *trans*- and *cis*-forms with two nitroxide (NO) radical groups at the para-/para- (pp), meta-/para- (mp) or meta-/meta- (mm) sites.



2. Relevant Data of Describing Ground States for All Designed Diradicals, Their Diradical Character and Magnetic Behaviors

Table S1. (U)B3LYP/6-311++G(d,p) level estimated energies (in a.u.) of the closed-shell (CS) singlet, broken-symmetry (BS) open-shell singlet and triplet (T) state, corresponding $\langle S^2 \rangle$ values, intramolecular magnetic coupling constants (J , in cm^{-1}) for all the studied diradicals

| Species | $E_{(\text{CS})}$ | $E_{(\text{BS})} (\langle S^2 \rangle)$ | $E_{(\text{T})} (\langle S^2 \rangle)$ | J (cm^{-1}) |
|--|-------------------|---|--|-----------------------------|
| NO- ^t (C=N)-pp | -816.7673728 | -816.7865587(1.023) | -816.7850358(2.027) | -332.6 |
| NO- ^t (C=NH ⁺)-pp | -817.1519864 | -817.1649505(0.958) | -817.1609693(2.024) | -819.0 |
| NO- ^c (C=N)-pp | -816.7547584 | -816.7744392(1.028) | -816.7740769(2.031) | -79.2 |
| NO- ^c (C=NH ⁺)-pp | -817.1419546 | -817.1555869(0.990) | -817.1541171(2.029) | -310.2 |
| NO- ^t (C=N)-mp | -816.7358730 | -816.7839190(1.027) | -816.7842677(2.038) | 75.6 |
| NO- ^t (C=NH ⁺)-mp | -817.1124189 | -817.1522706(1.027) | -817.1531664(2.053) | 191.5 |
| NO- ^c (C=N)-mp | -816.7261365 | -816.7722347(1.029) | -817.7723369(2.032) | 22.3 |
| NO- ^c (C=NH ⁺)-mp | -817.0997151 | -817.1440134(1.026) | -817.1444744(2.040) | 99.7 |
| NO- ^t (C=N)-mm | -816.7306591 | -816.7825639(1.030) | -816.7824946(2.027) | -15.2 |
| NO- ^t (C=NH ⁺)-mm | -817.1020315 | -817.1540855(1.030) | -817.1539732(2.032) | -24.8 |
| NO- ^c (C=N)-mm | -816.7261143 | -816.7724169(1.028) | -816.7723736(2.028) | -9.5 |
| NO- ^c (C=NH ⁺)-mm | -817.1011093 | -817.1442902(1.028) | -817.1442098(2.027) | -17.6 |
| NO- ^t (N=N)-pp | -832.7912209 | -832.8039351(1.016) | -832.8006354(2.026) | -716.4 |
| NO- ^t (N=NH ⁺)-pp | -833.1736256 | -833.1774699(0.750) | -833.1670631(2.027) | -1787.1 |
| NO- ^c (N=N)-pp | -832.7433633 | -832.7757799(1.052) | -832.7740492(2.030) | -388.1 |
| NO- ^c (N=NH ⁺)-pp | -833.1392491 | -833.1595056(0.613) | -833.1515378(2.036) | -1227.9 |
| NO- ^t (N=N)-mp | -832.7519877 | -832.7993847(1.029) | -832.8001179(2.054) | 156.9 |
| NO- ^t (N=NH ⁺)-mp | -833.1303975 | -833.1588446(1.044) | -833.1601730(2.102) | 275.3 |
| NO- ^c (N=N)-mp | -832.7260858 | -832.7731900(1.032) | -832.7734935(2.047) | 65.6 |
| NO- ^c (N=NH ⁺)-mp | -833.1102405 | -833.1409742(1.038) | -833.1427276(2.100) | 362.1 |
| NO- ^t (N=N)-mm | -832.7434203 | -832.7961128(1.038) | -832.7959225(2.027) | -42.2 |
| NO- ^t (N=NH ⁺)-mm | -833.1054873 | -833.1526605(1.056) | -833.1523585(2.033) | -67.8 |
| NO- ^c (N=N)-mm | -832.7213777 | -832.7716133(1.030) | -832.7715707(2.027) | -9.4 |
| NO- ^c (N=NH ⁺)-mm | -833.0911304 | -833.1365620(1.041) | -833.1364858(2.036) | -16.8 |
| NO- ^t (C=C)-pp | -800.7238342 | -800.7413050(1.023) | -800.7387645(2.026) | -555.4 |
| NO- ^c (C=C)-pp | -800.7121709 | -800.7322195(1.029) | -800.7310125(2.028) | -264.9 |
| NO- ^t (C=C)-mp | -800.6895999 | -800.7375431(1.028) | -800.7381467(2.048) | 129.8 |
| NO- ^c (C=C)-mp | -800.6825073 | -800.7300552(1.029) | -800.7303325(2.038) | 60.3 |
| NO- ^t (C=C)-mm | -800.6853285 | -800.7369079(1.036) | -800.7367539(2.027) | -34.1 |
| NO- ^c (C=C)-mm | -800.6834698 | -800.7290559(1.030) | -800.7289318(2.027) | -27.3 |

Table S2. (U)M06-2X/6-311++G(d,p) level estimated energies (in a.u.) of the broken-symmetry (BS) open-shell singlet and triplet (T) state, corresponding $\langle S^2 \rangle$ values, intramolecular magnetic coupling constants (J , in cm^{-1}) for trans-BA and trans-BAH⁺-based diradicals

| Species | $E_{(\text{BS})} (\langle S^2 \rangle)$ | $E_{(\text{T})} (\langle S^2 \rangle)$ | J (cm^{-1}) |
|--|---|--|-----------------------------|
| NO- ^t (C=N)-pp | -816.4414892(1.035) | -816.4409045(2.028) | -129.1 |
| NO- ^t (C=NH ⁺)-pp | -816.8096809(1.050) | -816.8080863(2.034) | -355.4 |
| NO- ^t (C=N)-mp | -816.4402716(1.026) | -816.4404214(2.031) | 32.7 |
| NO- ^t (C=NH ⁺)-mp | -816.7997140(1.026) | -816.8000542(2.039) | 73.6 |
| NO- ^t (C=N)-mm | -816.4394732(1.027) | -816.4394412(2.025) | -7.0 |
| NO- ^t (C=NH ⁺)-mm | -816.8034161(1.024) | -816.8033579(2.024) | -12.8 |

Table S3. The single-point calculated energies (in a.u.) of the broken-symmetry (BS) open-shell singlet and triplet (T) state, singlet-triplet energy differences (ΔE_{ST} , kcal/mol), intramolecular magnetic coupling constants (J , in cm^{-1}) for trans-BA and trans-BAH⁺-based diradicals using CASSCF(4,6)/6-311++G(d,p) level

| Species | $E_{(\text{BS})}$ | $E_{(\text{T})} (\langle S^2 \rangle)$ | ΔE_{ST} (kcal/mol) | J (cm^{-1}) |
|--|-------------------|--|--------------------------------------|-----------------------------|
| NO- ^t (C=N)-pp | -811.8289807 | -811.8280313 | 0.59 | -208.2 |
| NO- ^t (C=NH ⁺)-pp | -812.1943054 | -812.1917782 | 1.58 | -554.2 |
| NO- ^t (C=N)-mp | -811.8137236 | -811.8139543 | -0.14 | 50.6 |
| NO- ^t (C=NH ⁺)-mp | -812.1898241 | -812.1903800 | -0.35 | 121.9 |
| NO- ^t (C=N)-mm | -811.8147608 | -811.8147216 | 0.02 | -8.6 |
| NO- ^t (C=NH ⁺)-mm | -812.1951189 | -812.1950524 | 0.04 | -14.6 |

Note: Herein, the expression of singlet-triplet energy difference is given as $\Delta E_{\text{ST}} = E(S = 1) - E(S = 0)$, in which $E(S = 0)$ refers to the energy of the BS open-shell singlet and $E(S = 1) - E(S = 0) = -J$. In Table S1, we observed the diradicals NO-^t(C=N)-pp, NO-^t(C=NH⁺)-pp, NO-^t(C=N)-mm and NO-^t(C=N)-mm with the energy orders of the CS singlet, BS open-shell singlet and T state $E_{(\text{BS})} < E_{(\text{T})} < E_{(\text{CS})}$, and the diradicals NO-^t(C=N)-mp and NO-^t(C=NH⁺)-mp with the energy orders $E_{(\text{T})} < E_{(\text{BS})} < E_{(\text{CS})}$. Therefore, it is more reasonable to choose the BS open-shell singlet of the diradical to do single point calculation for a singlet.

3. Optimized Molecular Geometries for Ground States of All Diradicals

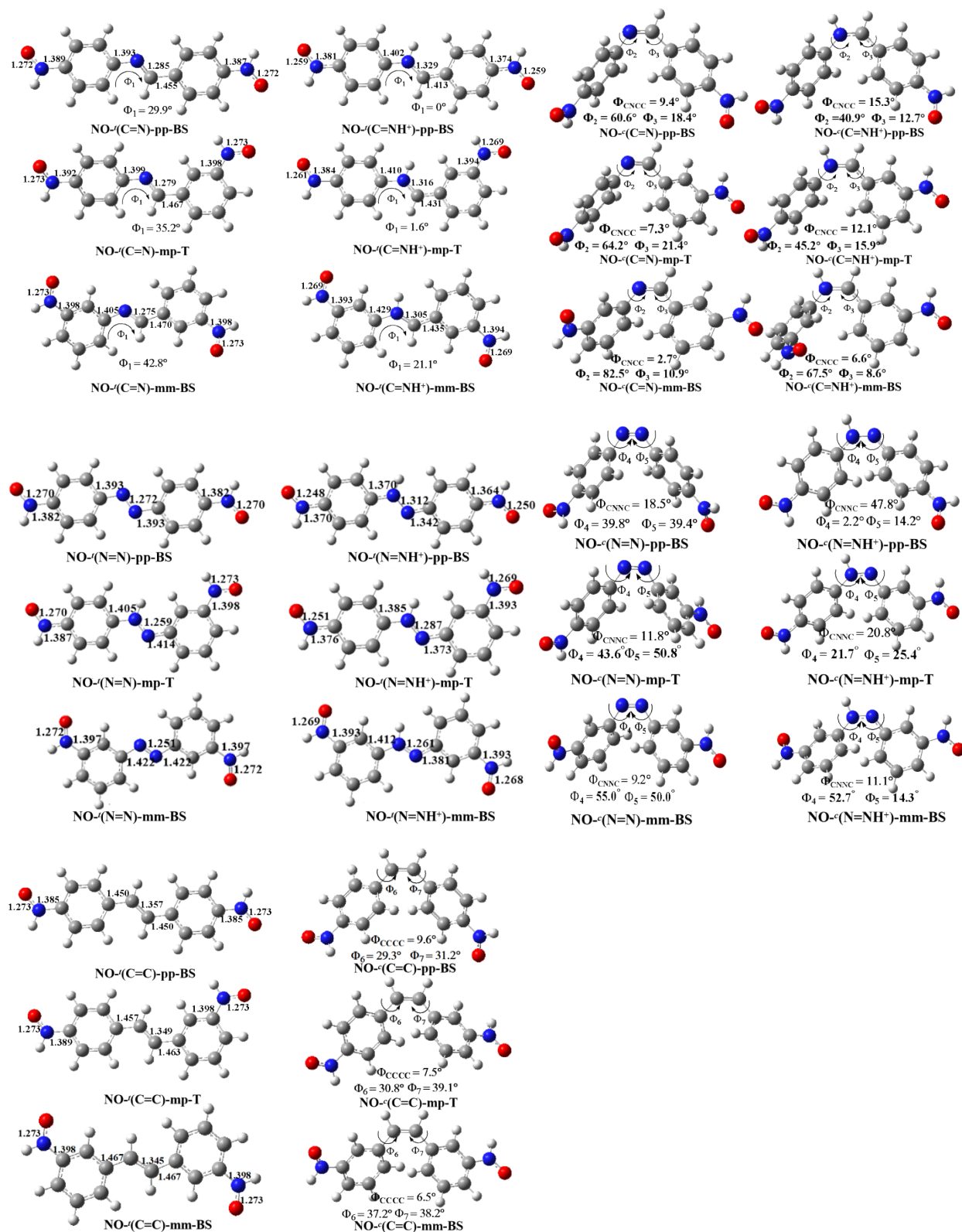
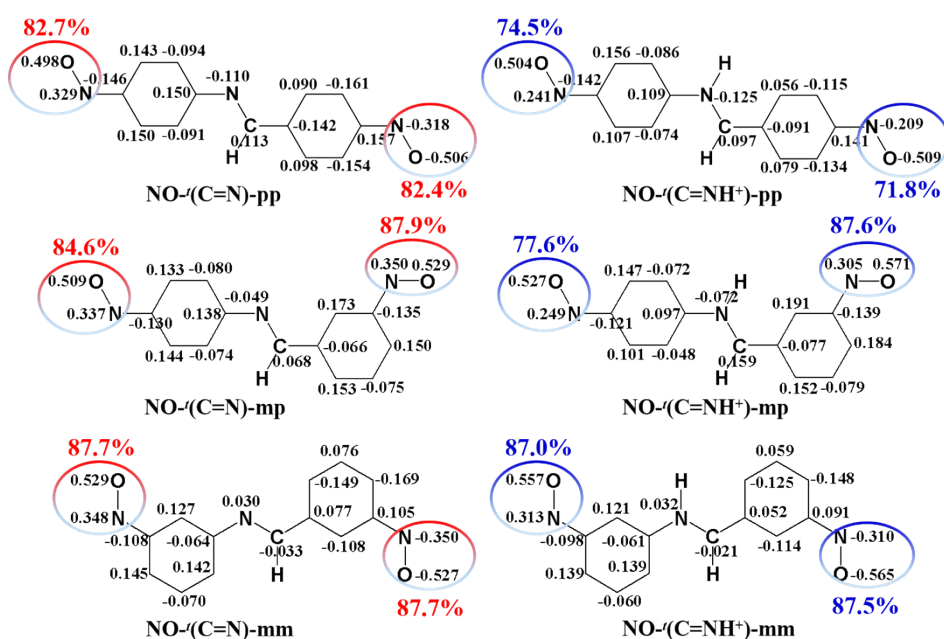
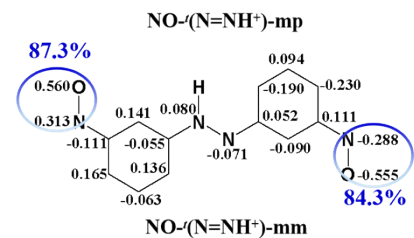
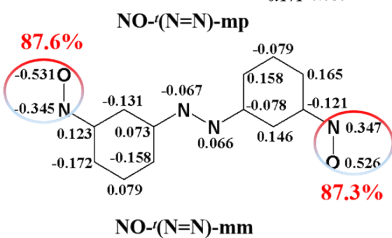
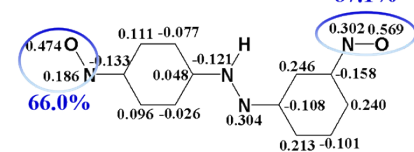
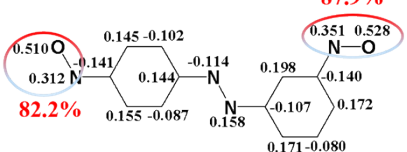
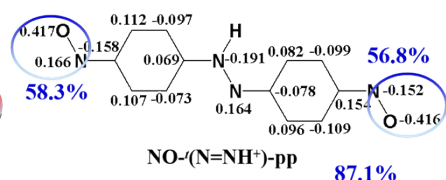
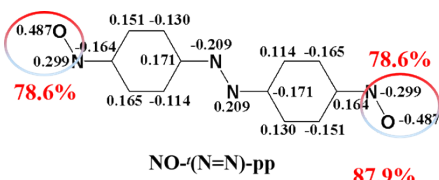
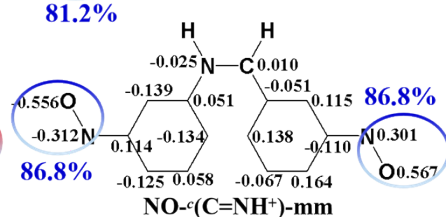
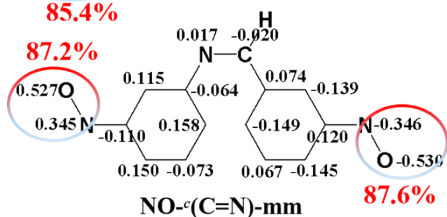
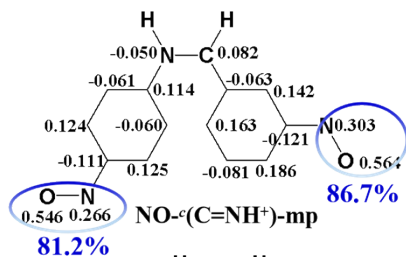
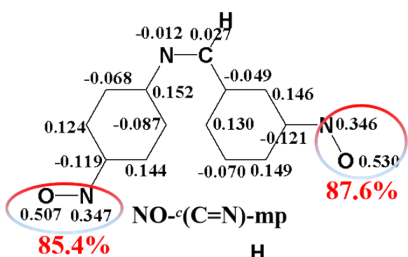
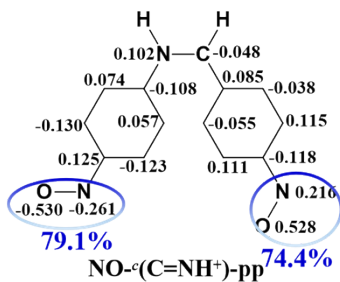
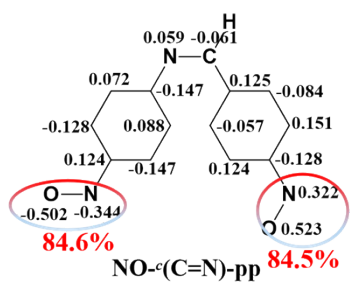


Figure S1. Optimized geometries for the ground states of all diradicals at the (U)B3LYP/6-311++G (d,p) level, including N-O and C-N bond lengths as well as CCNC (ϕ_1) dihedral angles for *trans*-BA-bridged diradicals, associated with CNCC (ϕ_{CNCC}), CCNC (ϕ_2) and CCCN (ϕ_3) dihedral angles for

cis-BA-bridged ones; N-O and N-N bond lengths for *trans*-AB-bridged diradicals, as well as CNNC (ϕ_{CNNC}) and CCNN (ϕ_4 and ϕ_5) dihedral angles for *cis*-AB-bridged ones; N-O and C-C bond lengths for *trans*-stilbene-bridged diradicals, as well as CCCC (ϕ_{CCCC}) and CCCC (ϕ_6 and ϕ_7) dihedral angles for *cis*-stilbene-bridged ones.

4. Distributions of Mulliken Atomic Spin Density of All Diradicals





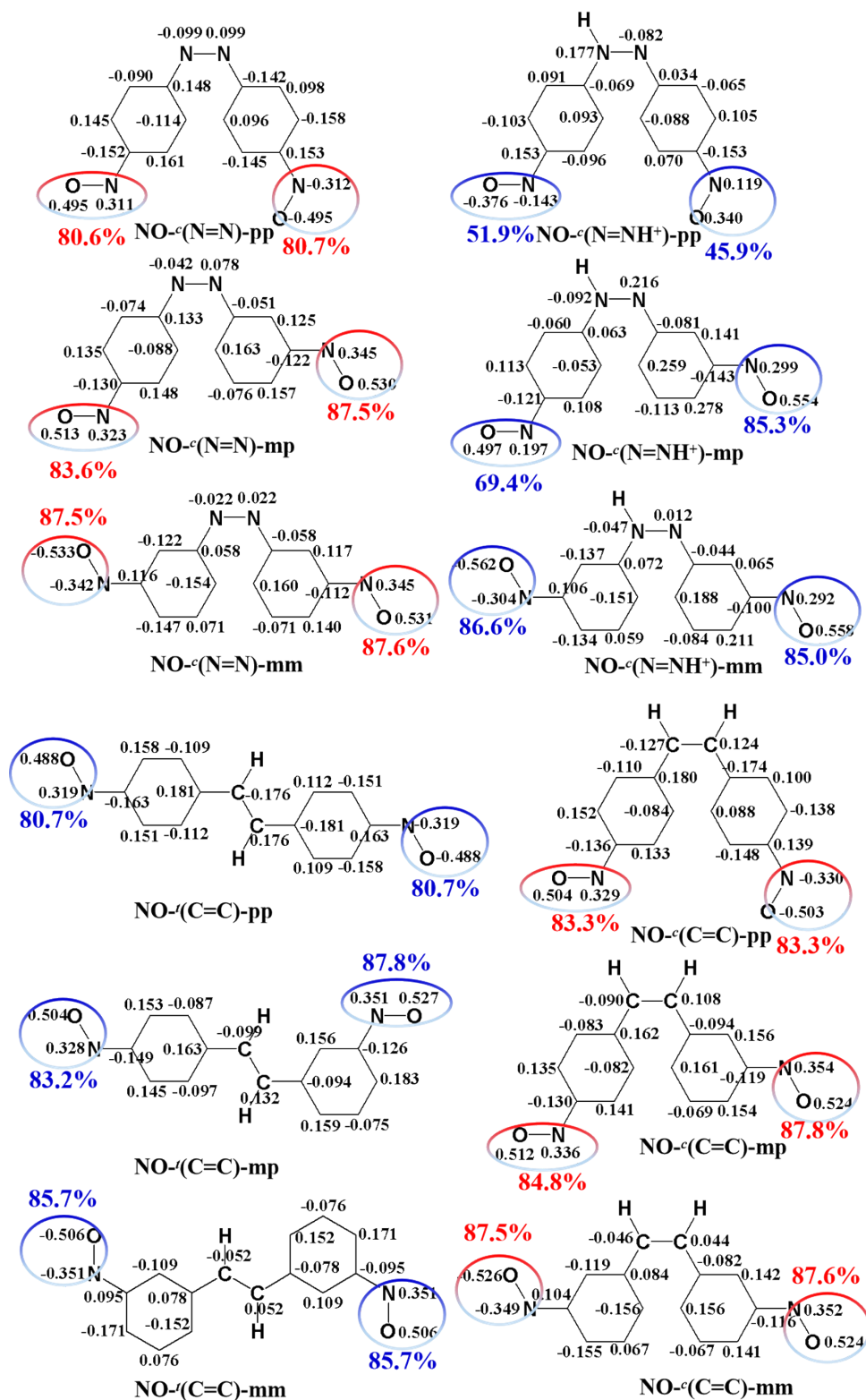


Figure S2. Comparison of spin polarization and the Mulliken atomic spin density distributions of BA- and AB-bridged diradicals before and after protonation in trans and cis forms as well as stilbene-bridged diradicals in trans and cis forms.

5. Schematic Diagram of Exchange Coupling between Two Radical Groups through HOMO or LUMO of Coupler

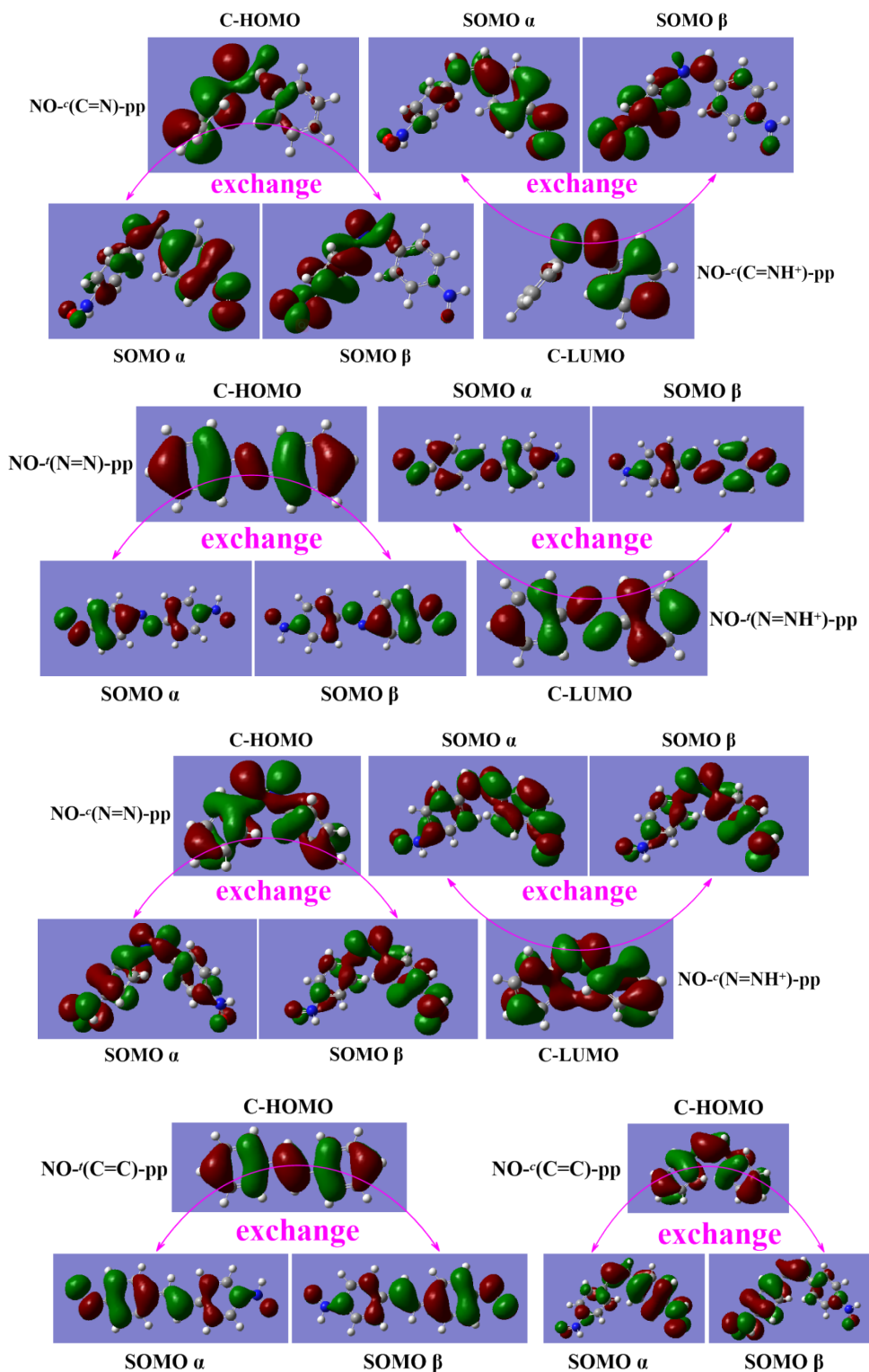


Figure S3. Exchange couplings between two SOMOs of diradicals $\text{NO}^{\cdot}(\text{C}=\text{N})\text{-pp}$, $\text{NO}^{\cdot}(\text{C}=\text{NH}^+)\text{-pp}$, $\text{NO}^{\cdot}(\text{N}=\text{N})\text{-pp}$, $\text{NO}^{\cdot}(\text{N}=\text{NH}^+)\text{-pp}$, $\text{NO}^{\cdot}(\text{C}=\text{C})\text{-pp}$ and $\text{NO}^{\cdot}(\text{N}=\text{N})\text{-pp}$, $\text{NO}^{\cdot}(\text{N}=\text{NH}^+)\text{-pp}$, $\text{NO}^{\cdot}(\text{C}=\text{C})\text{-pp}$ and $\text{NO}^{\cdot}(\text{N}=\text{N})\text{-pp}$.

$\sigma(\text{C}=\text{C})$ -pp though their corresponding couplers (C) HOMO or LUMO.

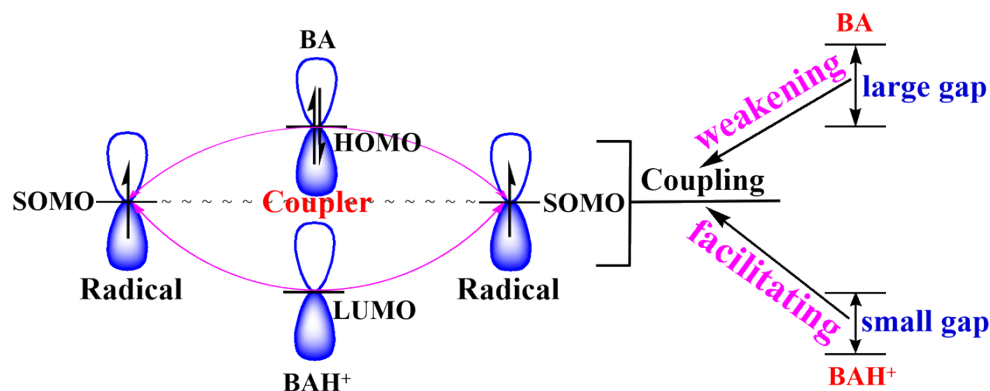
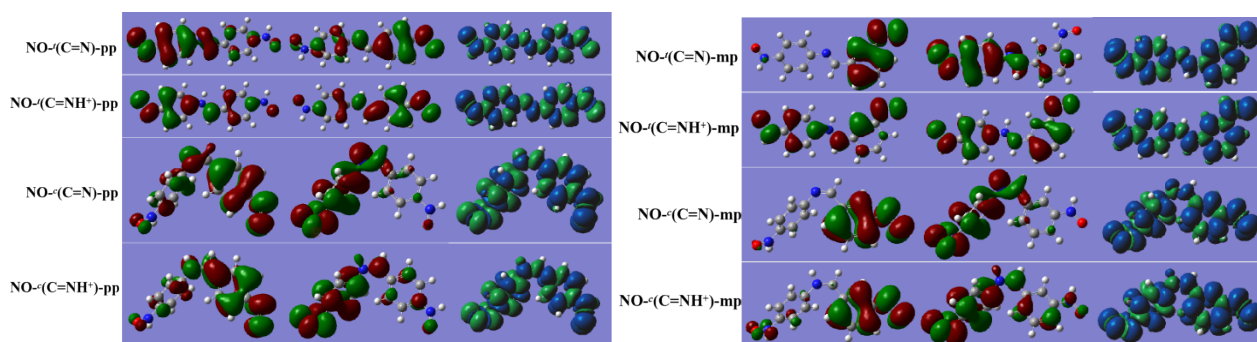


Figure S4. Schematic diagram of exchange coupling between two radical groups through HOMO of the coupler BA and LUMO of the coupler BAH⁺. A small HOMO-LUMO energy gap of the protonated coupler BAH⁺ in trans or cis forms is in favor of strong magnetic coupling in contrast to that of unprotonated BA. Location of the molecular orbitals (SOMOs, HOMO and LUMO) roughly represent the high- or low-level in energy.

6. SOMO Plots and Spin Density Maps for All Diradicals



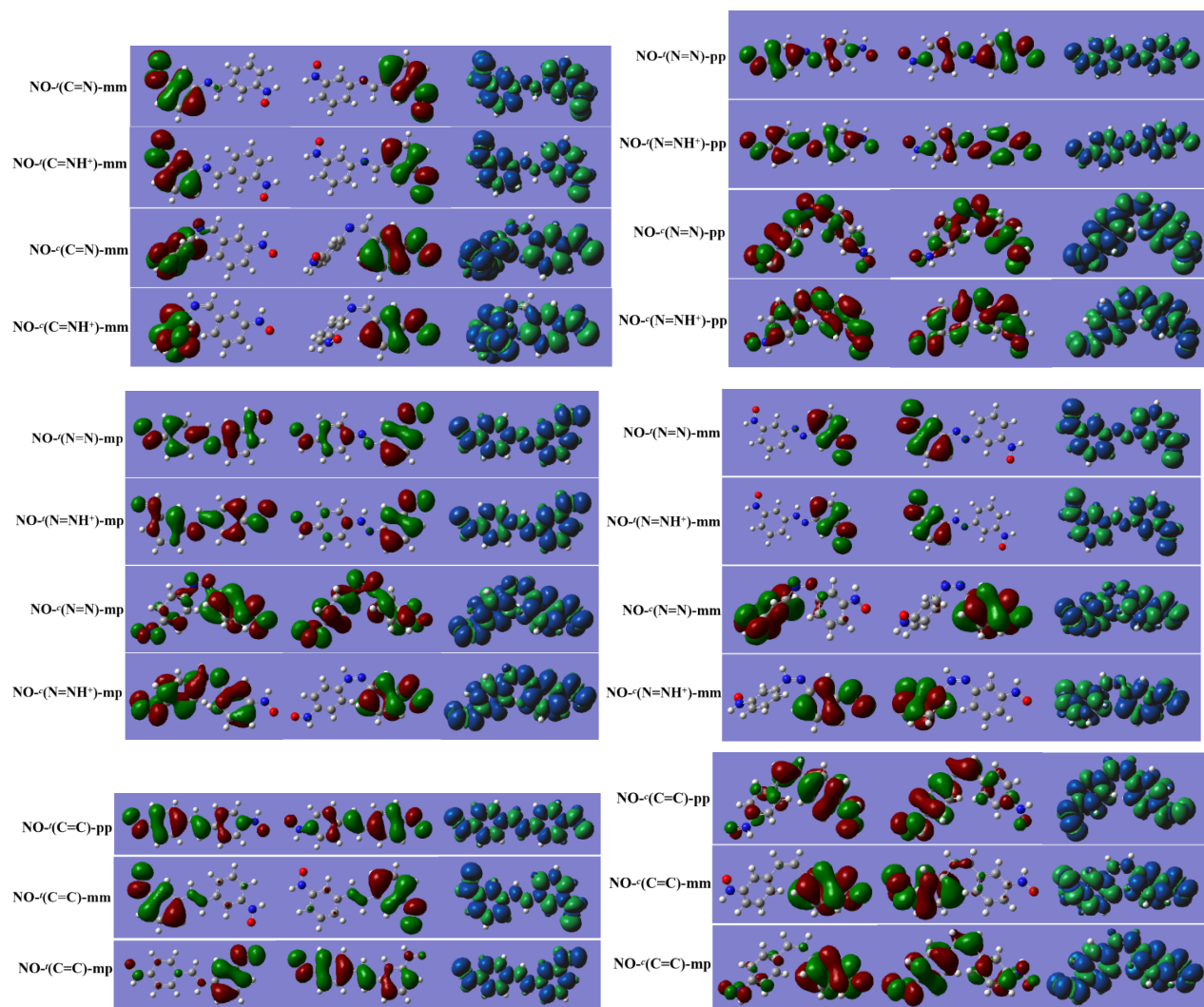


Figure S5. SOMOs (isovalue = 0.02) and spin density map (isovalue = 0.0004) of the ground states for all diradicals.

7. Spin Alteration Plots for BA-, AB- and Stilbene-Bridged Diradicals

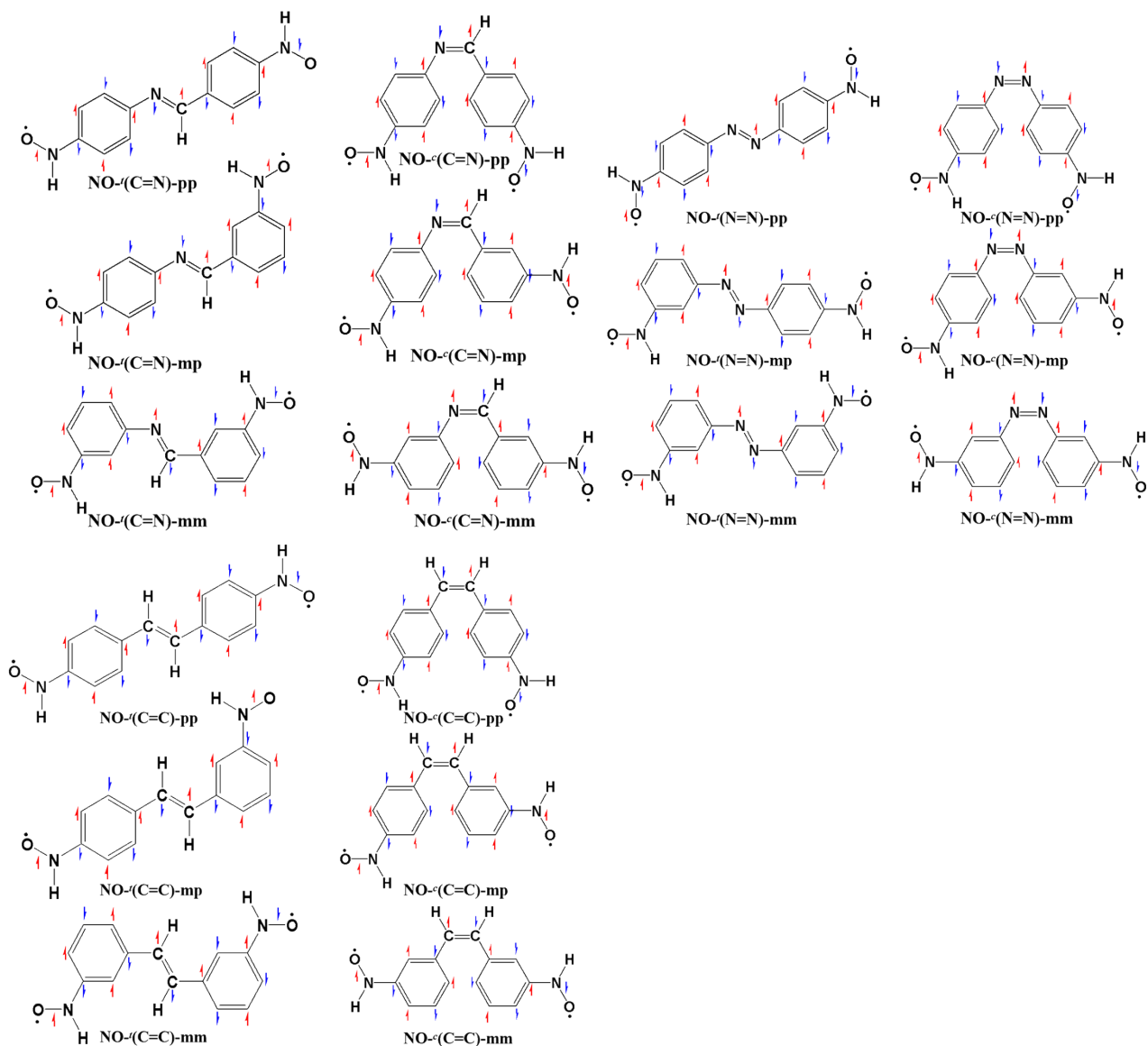


Figure S6. Scheme of spin alteration rule for *trans*-diradicals $\text{NO}^t(\text{C}=\text{N})\text{-pp}$, $\text{NO}^t(\text{C}=\text{N})\text{-mp}$, $\text{NO}^t(\text{C}=\text{N})\text{-mm}$, $\text{NO}^t(\text{N}=\text{N})\text{-pp}$, $\text{NO}^t(\text{N}=\text{N})\text{-mp}$, $\text{NO}^t(\text{N}=\text{N})\text{-mm}$, $\text{NO}^t(\text{C}=\text{C})\text{-pp}$, $\text{NO}^t(\text{C}=\text{C})\text{-mp}$ and $\text{NO}^t(\text{C}=\text{C})\text{-mm}$, as well as *cis*-diradicals $\text{NO}^c(\text{C}=\text{N})\text{-pp}$, $\text{NO}^c(\text{C}=\text{N})\text{-mp}$, $\text{NO}^c(\text{C}=\text{N})\text{-mm}$, $\text{NO}^c(\text{N}=\text{N})\text{-pp}$, $\text{NO}^c(\text{N}=\text{N})\text{-mp}$, $\text{NO}^c(\text{N}=\text{N})\text{-mm}$, $\text{NO}^c(\text{C}=\text{C})\text{-pp}$, $\text{NO}^c(\text{C}=\text{C})\text{-mp}$ and $\text{NO}^c(\text{C}=\text{C})\text{-mm}$. The spin alteration of the corresponding protonated counterparts of BA- and AB-bridged diradicals are exactly the same as that of them (not listed).