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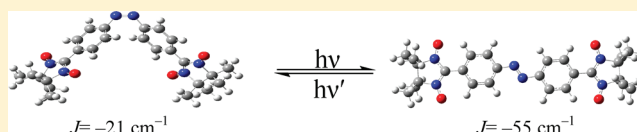
# On the Photomagnetism of Nitronyl Nitroxide, Imino Nitroxide, and Verdazyl-Substituted Azobenzene

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## S Supporting Information

**ABSTRACT:** The *cis*- and *trans*-azobenzenes are known as photochromic isomers with the *trans*- converting into the *cis*-form and vice versa upon irradiation with specific wavelengths. We have quantum chemically investigated the *cis*- and *trans*-forms of substituted azobenzene diradicals, with two nitronyl nitroxides, imino nitroxides, or verdazyls at para positions and serving as monoradical centers, to determine whether they can exhibit a photoassisted magnetic crossover. Geometries of both substituted and unsubstituted molecules have been optimized by density functional (DF) method UB3LYP using the 6-311G(d,p) basis set. Optimization of the geometry of the *cis* isomers has required special care. Single point singlet, triplet, and broken symmetry calculations have been done using 6-311++G(3df, 3pd) basis set. The magnetic exchange coupling constants have been estimated from the broken symmetry calculations. Absorption wavelengths have been estimated for both substituted and unsubstituted species from time-dependent DF treatment using restricted spin-polarized methodology RB3LYP and 6-311++G(3df, 3pd) basis set. From the similarity in the calculated absorption wavelengths for the unsubstituted and substituted azobenzenes, and the increased oscillator strengths (*f*) for the substituted species, we predict that the diradical isomers would be strongly photochromic. From our triplet state and broken symmetry calculations, we predict that both the *cis*- and the *trans*-diradicals are antiferromagnetically coupled. This prediction is consistent with the spin alternation rule, and the possibility of a magnetic crossover is nonexistent for these species.

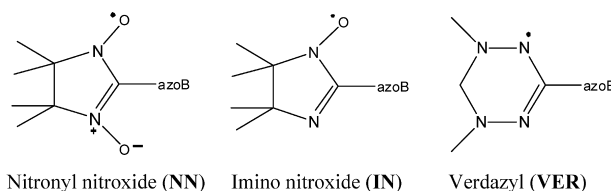


## 1. INTRODUCTION

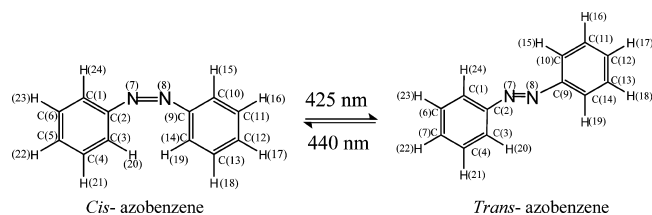
The reversible transformation of a chemical species between two isomeric forms by photoexcitation is called photochromism. By irradiating photochromic materials, geometries and physical properties can be changed.<sup>1</sup> This is important for designing photoswitchable species. If a photoswitchable molecule is used as a spin coupler between two magnetic units, then the magnetic characteristics of the species can change upon irradiation. At present, either a high magnetic field or a radiofrequency field in combination with a static field is required to reverse the magnetization.<sup>2</sup> Matsuda and co-workers have isolated and examined various photochromic species like azobenzene and diarylethene.<sup>1</sup> *trans*-Azobenzene converts into *cis*-form when exposed to light.<sup>3</sup> It is known that out of all types of allowed transitions,  $n-\pi^*$ ,  $\pi-\pi^*$ , and  $\varphi-\varphi^*$ , the first two types lead to the interconversion.<sup>4</sup> Because the  $\pi-\pi^*$  transitions are at the edge of visible range,  $n-\pi^*$  transitions are mainly responsible for photoconversion by visible light; see Figure 1. *trans*-Azobenzene is

more stable than *cis*-azobenzene, and, consequently, it is easier to isolate.

Shil and Mishra theoretically investigated the photomagnetic behavior of bis-nitronylnitroxide (bis-NN), bis-iminonitroxide (bis-IN), and bis-verdazyl (bis-VER) derivatives of *cis*- and *trans*-azobenzenes and reported photoinduced ferromagnetic to antiferromagnetic crossover and vice versa.<sup>5</sup> This was, in fact, the first prediction of a photomagnetic crossover. The monoradical centers are shown in Figure 2. These are known for their stability.<sup>6–9</sup>



**Figure 2.** Monoradicals used in this work. The link with azobenzene is indicated.

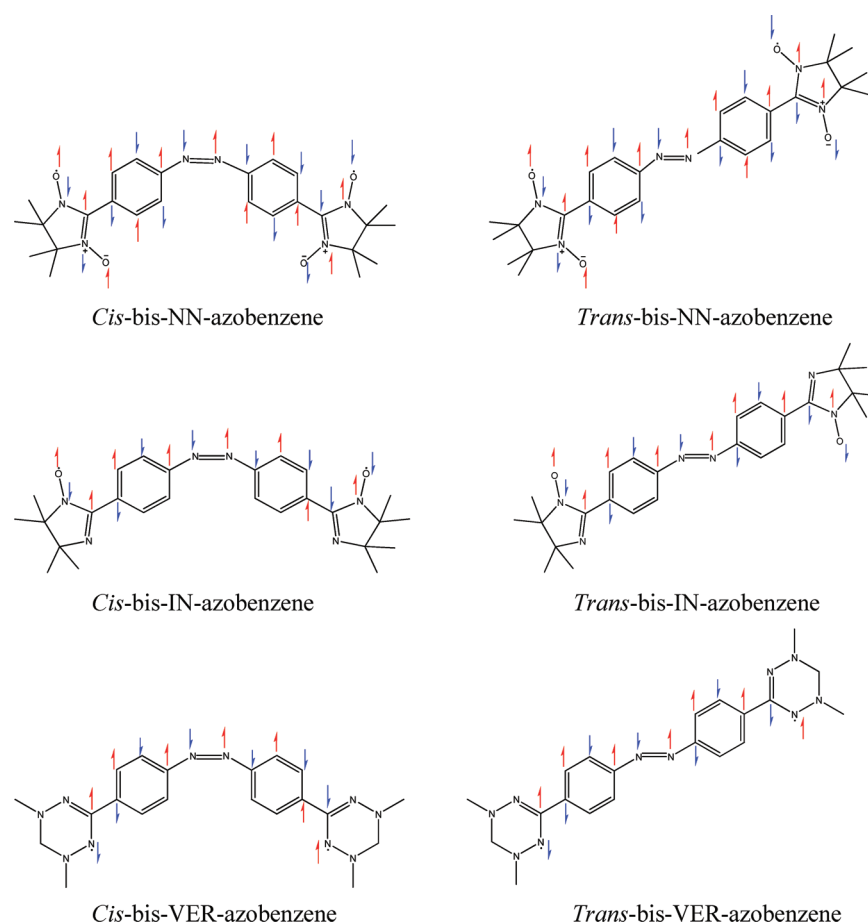


**Figure 1.** Photoconversion of azobenzene isomers. Numbering of the atoms is explicitly shown. The data are from ref 4.

Nevertheless, the spin alternation rule<sup>10</sup> for unrestricted treatments indicates that a photoinduced crossover in these systems is not possible, as both of the isomers would have intramolecular antiferromagnetic coupling (Figure 3). This contradiction has led

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**Figure 3.** Illustration of spin alternation rule. All diradicals can be predicted to have intramolecular antiferromagnetic coupling.

us to investigate the photomagnetism of substituted azobenzene diradicals by quantum chemical methods.

We have used large basis sets and took care to optimize the molecular geometries. For all three diradicals, we have determined spectroscopic transition energies and oscillator strengths for both *cis*- and *trans*-isomers, and these are generally comparable to the spectral features of *cis*- and *trans*-azobenzenes. In all three cases, we calculated negative  $J$  values for both *cis*- and *trans*-isomers, in agreement with spin alternation rule. Therefore, although we predict that the diradicals would be strongly photochromic, we also predict that both the *cis*- and *trans*-forms of each diradical would have intramolecular antiferromagnetic coupling and a spin crossover is not possible. This is discussed in the following.

## 2. METHODOLOGY

The Heisenberg effective spin Hamiltonian:

$$H_{\text{ex}} = -2JS_1 \cdot S_2 \quad (1)$$

constitutes an approximate description of the magnetic exchange interaction in a diradical. A positive sign of  $J$  indicates a ferromagnetic interaction, and a negative sign is the signature for antiferromagnetic coupling. As  $H_{\text{ex}}$  commutes with the spin operators  $S^2$  and  $S_z$ , where  $S$  is the total spin angular momentum, they have common eigenfunctions. For a diradical:

$$E(S = 1) - E(S = 0) = -2J \quad (2)$$

The diradical triplet can be described by a single determinant, but the diradical singlet must be a two-determinant function.

Borden, Davidson, and Feller have shown that the restricted open-shell Hartree–Fock [R(O)HF] fails to produce the correct relative energies and geometries, although they may provide qualitatively correct molecular orbitals for the two open-shell electrons in diradicals.<sup>11</sup> It is well-known that the unrestricted methodology leads to a good molecular geometry with less computational effort,<sup>11</sup> and also spin polarization.<sup>12</sup> Unfortunately, conventional unrestricted methodologies are based on a single determinant treatment. Therefore, the diradical singlet wave function cannot be translated in the unrestricted framework. This difficulty led Noodleman<sup>13</sup> to construct the so-called broken symmetry (BS) methodology. The average value of  $S^2$  is ideally 1 for a BS wave function that is generated from an equal admixture of singlet and triplet determinants. The magnetic exchange coupling constant is given by:

$$J = \frac{(E_{\text{BS}} - E_{\text{T}})}{1 + S_{ab}^2} \quad (3)$$

where  $S_{ab}$  is the overlap integral between the two magnetically active orbitals  $a$  and  $b$ . This overlap is notoriously difficult to calculate. Also, an unrestricted calculation rarely gives the ideal values of  $\langle S^2 \rangle$ , that is, 2 and 1 for triplet and BS states, respectively.

This problem was side-stepped by Yamaguchi et al.<sup>14</sup> who showed that the magnetic exchange coupling constant for a diradical can be calculated as:

$$J = \frac{E_{\text{BS}} - E_{\text{T}}}{\langle S^2 \rangle_{\text{T}} - \langle S^2 \rangle_{\text{BS}}} \quad (4)$$

where  $E_{\text{BS}}$ ,  $E_{\text{T}}$  and  $\langle S^2 \rangle_{\text{BS}}$ ,  $\langle S^2 \rangle_{\text{T}}$  are the energy and average spin square values for corresponding BS and triplet states. In our work, we use the Yamaguchi expression to estimate  $J$ .

Quantum chemical calculations have been performed on different spin states of substituted and unsubstituted azobenzenes by following the density functional (DF), unrestricted Becke 3-parameter exchange<sup>15a</sup> and Lee, Yang, and Parr correlational functional<sup>15b</sup> (UB3LYP) methodology. Gaussian 09 (G09)<sup>16</sup> code has been used for all of these calculations. It is possible to calculate  $J$  by employing other methods such as CASSCF, CASPT2, MRCI, etc. However, the present systems are so large that their investigation by these methodologies is currently beyond our computational capabilities.

Another critical issue in this investigation is to ascertain whether the substituted azobenzenes would be photochromic. The  $\pi-\pi^*$  transition of the azo group wipes out the N–N  $\pi$  bond order and makes the rotation around the N–N  $\sigma$  bond almost free, with a very low activation barrier, thereby aiding the interconversion of the geometrical isomers. The  $n-\pi^*$  transition certainly weakens the  $\pi$ -bond and has a similar effect, although to a much lesser extent. Therefore, the key to the understanding of photochromism is to identify whether the  $n-\pi^*$  and  $\pi-\pi^*$  transitions in the substituted azobenzenes have peak frequencies and oscillator strengths similar to those for the unsubstituted species. The excitation wavelengths and oscillator strengths have been obtained from time-dependent density functional theory (TDDFT) and, more specifically, by using the RB3LYP methodology.

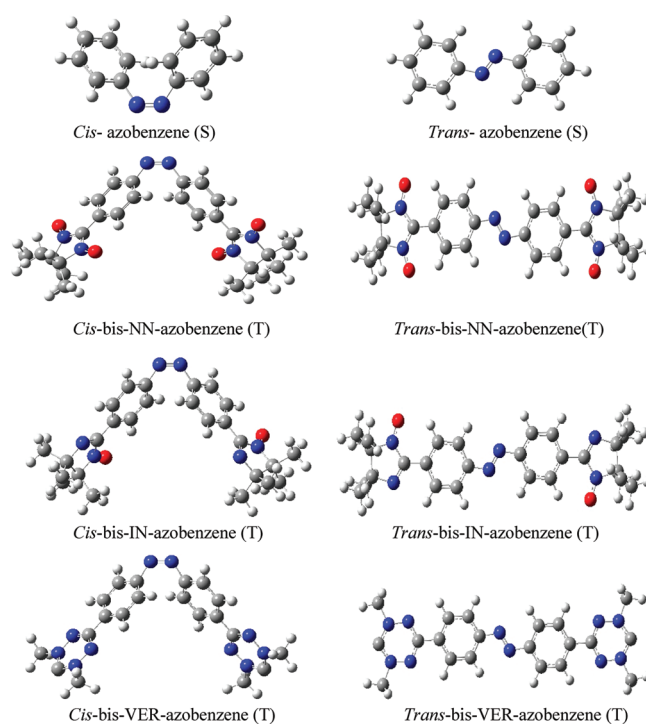
### 3. RESULTS AND DISCUSSION

**Geometry Optimization.** All of the molecular geometries have been optimized using the 6-311G(d,p) basis set. We have done single point calculations with the 6-311++G(3df,3pd) basis set using these geometries. The diradicals are (1) *cis*- and *trans*-forms of bis-NN-azobenzene, (2) *cis*- and *trans*-forms of bis-IN-azobenzene, and (3) *cis*- and *trans*-forms of bis-VER-azobenzene. The optimized molecular geometries calculated using the 6-311G(d,p) basis set are illustrated in Figure 4. Computed total energy and  $\langle S^2 \rangle$  values are given in Table 1.

We emphasize here the need for optimizing the molecular geometry in a rigorous way, especially for the *cis*-isomers. In the latter case, it is possible to end up with a local minimum as there is a crowding effect. A wrongly optimized geometry may give a wrong estimate of  $J$  for the diradical. We found that a default calculation leads to a local minimum for the *cis*-structure. We also found that the DF optimized geometries due to Fliegl et al.<sup>17</sup> as well as the experimental geometries<sup>18,19</sup> are good starting points for the optimization of the structures of azobenzene isomers. The optimized azobenzene structures are in turn good starting points for optimizing the diradical structures.

The optimized structure of *cis*-azobenzene is approximately planar. The calculated dihedral angle around  $-\text{N}=\text{N}-$  of *cis*-azobenzene is  $9.4^\circ$ , as compared to the crystallographic value  $8.0^\circ$ .<sup>18</sup> The point group is  $C_2$ . This is basically a stereoelectronic effect. The optimized geometry of *trans*-azobenzene is completely planar (Table 3), with  $C_{2h}$  point group symmetry. The two phenyl rings and the nitrogen atoms are all in the same plane. The non-bonding orbitals of the nitrogen atoms are also in the molecular plane. The single-determinant singlet state becomes the ground state for both isomers (Table 1). The *trans*-form is about  $15.7 \text{ kcal mol}^{-1}$  more stable than the *cis*-form.

Optimized bond lengths, bond angles, and dihedral angles are given for *cis*-azobenzene in Table 2 and *trans*-azobenzene in



**Figure 4.** Optimized molecular geometries for unsubstituted and substituted azobenzenes, found from UB3LYP calculations with the 6-311G(d,p) basis set. The spin states are indicated by S for singlet and T for triplet.

Table 3. These quantities are compared to the DF values calculated by Fliegl et al.<sup>17</sup> as well as the experimental values from refs 18 and 19. The geometries obtained in this work compare well with those in ref 17. In a few cases, the data here are closer to the observed data, and in some other cases the data in ref 17 are closer. The only noteworthy point is that for the *cis*-isomer, the dihedral angles calculated in this work are closer to the experimental angles (Table 2).

All three diradicals, in *cis*- as well as *trans*-isomeric forms, have triplets as single-determinant ground states of proper spin, although the BS calculations show that the actual ground states are (two-determinant) spin-singlets; see Table 1. The methyl groups in NN have almost free rotation. The local symmetry of the *cis*- and *trans*-forms of bis-NN-azobenzene is  $C_2$  and  $C_{2h}$ , respectively, with  $\text{C}^{(2)}-\text{N}^{(7)}-\text{N}^{(8)}-\text{C}^{(9)}$  dihedral angles of  $10.9^\circ$  and  $180^\circ$ . The  $\text{C}^{(2)}-\text{N}^{(7)}-\text{N}^{(8)}-\text{C}^{(9)}$  dihedral angles of the *cis*- and *trans*-forms of bis-IN-azobenzene and bis-VER-azobenzene are  $10.7^\circ$  and  $180^\circ$ , and  $10.4^\circ$  and  $180^\circ$ , respectively.

**Coupling Constant.** The singlet geometry optimization (with declared multiplicity equal to 1) for the substituted azobenzenes led to BS solutions in every case, thereby indicating that the single-determinant singlet lies much higher in energy. Single point calculations using the 6-311++G(3df,3pd) basis set have been done with the optimized molecular geometries from calculations involving the 6-311G(d,p) basis. The calculated  $J$  values are all negative as shown in Table 4.

All of the diradicals are antiferromagnetically coupled, and the spin alternation rule in unrestricted methodology remains vindicated. The obtained coupling constants for *cis*-bis-IN-azobenzene and *cis*-bis-VER-azobenzene are small, but they always remain small and unchanged in sign by changing the functionals used in the DF method. For example, the UB3PW91 functional using 6-311G(d,p) basis gives a  $J$  value

Table 1. Optimized Energies and  $\langle S^2 \rangle$  in atomic units for the Species under Investigation<sup>a</sup>

molecule	multiplicity	6-311G(d,p)	6-311++G(3df, 3pd) <sup>b</sup>
<i>cis</i> -azobenzene	1	−572.8754752 (0.00000)	−572.9272234 (0.000009)
	3	−572.8552710 (2.041892)	−572.8627259 (2.018124)
<i>trans</i> -azobenzene	1	−572.9005047 (0.000000)	−572.9310844 (0.000184)
	3	−572.8462370 (2.024728)	−572.8967776 (2.025128)
<i>cis</i> -bis-NN-azobenzene	1 <sup>c</sup>	−1639.5758339 (1.137869)	−1639.7160870 (1.128850)
	3	−1639.5757226 (2.128791)	−1639.7159910 (2.123273)
<i>trans</i> -bis-NN-azobenzene	1 <sup>c</sup>	−1639.6003520 (1.146642)	−1639.7390553 (1.137721)
	3	−1639.6000888 (2.130614)	−1639.7388059 (2.125219)
<i>cis</i> -bis-IN-azobenzene	1 <sup>c</sup>	−1489.1884503 (1.035629)	−1489.3130404 (1.038971)
	3	−1489.1884475 (2.037233)	−1489.3130255 (2.037898)
<i>trans</i> -bis-IN-azobenzene	1 <sup>c</sup>	−1489.2126067 (1.039367)	−1489.3354946 (1.043705)
	3	−1489.2125667 (2.038633)	−1489.3354538 (2.039569)
<i>cis</i> -bis-VER-azobenzene	1 <sup>c</sup>	−1321.7118495 (1.041994)	−1321.8282671 (1.041088)
	3	−1321.7118300 (2.039974)	−1321.8282517 (2.040753)
<i>trans</i> -bis-VER-azobenzene	1 <sup>c</sup>	−1321.7363569 (1.042372)	−1321.8511678 (1.040603)
	3	−1321.7362937 (2.039215)	−1321.8511323 (2.040693)

<sup>a</sup>The  $\langle S^2 \rangle$  values are in parentheses. <sup>b</sup>Single point calculation using 6-311G(d,p) optimized geometry. <sup>c</sup>The optimization of molecular geometry for the single-determinant singlet calculation reduced to the optimization of the molecular geometry for the broken symmetry states.

Table 2. Optimized Geometry of *cis*-Azobenzene

	DFT-B3LYP 6-311G(d,p)	DFT-BP86 TZVP (ref 17)	expt. (ref 18)
Bond Length, pm			
N <sup>(7)</sup> –N <sup>(8)</sup>	124.3	125.5	125.3
C <sup>(2)</sup> –N <sup>(7)</sup>	143.6	143.7	144.9
C <sup>(1)</sup> –C <sup>(2)</sup>	139.9	140.6	138.5
C <sup>(2)</sup> –C <sup>(3)</sup>	139.8	140.5	141.0
C <sup>(1)</sup> –C <sup>(6)</sup>	139.0	139.5	137.7
C <sup>(5)</sup> –C <sup>(6)</sup>	139.4	140.0	138.9
H <sup>(24)</sup> –C <sup>(1)</sup>	108.3	109.0	
H <sup>(23)</sup> –C <sup>(6)</sup>	108.4	109.2	
Angles, deg			
C <sup>(2)</sup> –N <sup>(7)</sup> –N <sup>(8)</sup>	124.2	124.1	121.9
C <sup>(3)</sup> –C <sup>(2)</sup> –N <sup>(7)</sup>	116.5	116.4	117.3
C <sup>(1)</sup> –C <sup>(2)</sup> –N <sup>(7)</sup>	122.9	122.9	122.5
C <sup>(3)</sup> –C <sup>(4)</sup> –C <sup>(5)</sup>	120.1	120.1	121.7
C <sup>(4)</sup> –C <sup>(5)</sup> –C <sup>(6)</sup>	120.0	119.8	119.0
H <sup>(24)</sup> –C <sup>(1)</sup> –C <sup>(2)</sup>	120.0	119.9	
H <sup>(20)</sup> –C <sup>(3)</sup> –C <sup>(2)</sup>	118.7	118.7	
Dihedral Angles, deg			
C <sup>(2)</sup> –N <sup>(7)</sup> –N <sup>(8)</sup> –C <sup>(9)</sup>	9.4	11.4	8.0
N <sup>(7)</sup> –N <sup>(8)</sup> –C <sup>(9)</sup> –C <sup>(14)</sup>	51.0	48.4	53.3

of  $-0.9 \text{ cm}^{-1}$  for *cis*-bis-IN-azobenzene and  $-4.1 \text{ cm}^{-1}$  for *cis*-bis-VER-azobenzene. Of course, as the calculated  $J$  is small in magnitude and it varies from one basis set to another, a small change may appear as a large multiple. As the spin alternation rule shows, the sign must remain negative, regardless of the magnitude.

We have found that the optimized structures given in ref 5 and calculated with the 6-31G(d,p) basis set are correct. They differ somewhat from our optimized geometries, because we have used a different basis set 6-311G(d,p) for optimization, and also because we have retained methyl groups while hydrogen atoms were used in ref 5. The problem arose with the single point calculations using the 6-311++G(d,p) basis set in ref 5, and especially the broken symmetry calculations. We have repeated these calculations with the same basis set using the optimized geometries in ref 5 and found different total energy

Table 3. Optimized Geometry of *trans*-Azobenzene

	DFT-B3LYP 6-311G(d,p)	DFT-BP86 TZVP (ref 17)	expt. (ref 19)
Bond Length, pm			
N <sup>(7)</sup> –N <sup>(8)</sup>	125.3	126.7	126.0(8)
C <sup>(2)</sup> –N <sup>(7)</sup>	141.8	142.0	142.7(8)
C <sup>(2)</sup> –C <sup>(3)</sup>	140.3	140.5	140.1
C <sup>(2)</sup> –C <sup>(1)</sup>	139.8	140.9	140.5
C <sup>(3)</sup> –H <sup>(15)</sup>	108.2	109.1	110.2(7)
C <sup>(1)</sup> –H <sup>(19)</sup>	108.3	109.0	110.2(7)
Angles, deg			
C <sup>(2)</sup> –N <sup>(7)</sup> –N <sup>(8)</sup>	115.2	114.8	113.6(8)
C <sup>(3)</sup> –C <sup>(2)</sup> –N <sup>(7)</sup>	115.5	115.3	
C <sup>(1)</sup> –C <sup>(2)</sup> –N <sup>(7)</sup>	124.6	124.8	
C <sup>(1)</sup> –C <sup>(2)</sup> –C <sup>(3)</sup>	119.8	119.8	
C <sup>(2)</sup> –C <sup>(1)</sup> –C <sup>(6)</sup>	120.2	119.6	
C <sup>(2)</sup> –C <sup>(3)</sup> –C <sup>(4)</sup>	119.6	120.2	
C <sup>(2)</sup> –C <sup>(3)</sup> –H <sup>(15)</sup>	118.8	118.2	
C <sup>(2)</sup> –C <sup>(3)</sup> –H <sup>(19)</sup>	118.2	118.8	
Dihedral Angles, deg			
C <sup>(2)</sup> –N <sup>(7)</sup> –N <sup>(8)</sup> –C <sup>(9)</sup>	180.0	180.0	180.0

Table 4. Coupling Constants (in  $\text{cm}^{-1}$ ) Calculated from Different Basis Sets Using Yamaguchi Formula

system	optimized molecular geometry 6-311G(d,p)	single point 6-311++G(3df,3pd)	ref 5 6-311++G(d,p)
<i>cis</i> -bis-NN-azobenzene	−24.6	−21.2	64
<i>trans</i> -bis-NN-azobenzene	−58.7	−55.4	−31
<i>cis</i> -bis-IN-azobenzene	−0.6	−3.3	15
<i>trans</i> -bis-IN-azobenzene	−8.4	−8.9	−7
<i>cis</i> -bis-VER-azobenzene	−4.3	−3.4	79
<i>trans</i> -bis-VER-azobenzene	−13.9	−7.8	−47

and  $\langle S^2 \rangle$  values. For instance, we have found (a)  $E_T = -1324.987103 \text{ au}$ ,  $E_{BS} = -1324.987206 \text{ au}$ ,  $\langle S^2 \rangle_T = 2.124114$ ,



and  $\langle S^2 \rangle_{\text{BS}} = 1.130539$  so that  $J = -22.8 \text{ cm}^{-1}$  for *cis*-bis-NN-azobenzene, and (b)  $E_{\text{T}} = -1325.010643 \text{ au}$ ,  $E_{\text{BS}} = -1325.010918 \text{ au}$ ,  $\langle S^2 \rangle_{\text{T}} = 2.126016$ , and  $\langle S^2 \rangle_{\text{BS}} = 1.144542$  so that  $J = -61.5 \text{ cm}^{-1}$  for *trans*-bis-NN-azobenzene. These  $J$  values are very comparable to the coupling constants calculated by us (Table 4), with minor differences arising from the replacement of methyl groups by hydrogen atoms.

**Spectroscopic Transitions.** A comprehensive gas-phase study of the electronic spectrum of *cis*- and *trans*-azobenzenes was carried out from flash photolysis experiments on the *cis*–*trans* isomerization by Andersson et al.<sup>4</sup> Experimental spectra with ethanol as solvent were recorded by Jaffé et al.<sup>20a</sup> and Birnbaum et al.<sup>20b</sup> Fliegl et al.<sup>17</sup> made an extensive computational study of azobenzene isomers and compared their results to those of Andersson et al. In this work, we have used the spectral data in ref 4 as our work has been on isolated species. We have calculated the transition energies for all *cis*- and *trans*-isomers in their ground states. The observed values of  $n-\pi^*$ ,  $\pi-\pi^*$ , and  $\sigma-\sigma^*$  transition energies of *cis*-azobenzene are 2.92,  $\sim 4.4$ , and 4.68 eV, and those of *trans*-azobenzene are 2.82, 4.12, and 5.64 eV.<sup>4</sup> Similar but somewhat larger values were obtained by Fliegl et al.<sup>17</sup> from their CC2 calculations. Tables 5 and 6

**Table 5. Calculated RB3LYP Vertical Excitation Energies (in eV) and Oscillator Strengths ( $f$ ) of *cis*-Azobenzene in Comparison with CCSD and Experimental Data**

this work RB3LYP 6-311G+ (3df,3pd)		CC2 Aug-cc- pVTZ (ref 17)	CCSD extrapolated (ref 21)	expt. (ref 4)
eV	$f$			
2.57	0.037	3.00	3.17	2.92 ( $n-\pi^*$ )
4.09	0.067			
4.51	0.112	4.49	4.67	$\sim 4.4$ ( $\pi-\pi^*$ )
4.89	0.046			
5.15	0.018			
5.55	0.019	4.65	4.83	4.68 ( $\sigma-\sigma^*$ )
5.90	0.121	4.79	5.02	
5.99	0.095	4.82	5.09	
6.41	0.041			
6.45	0.121			
6.46	0.067			
6.71	0.048			
6.91	0.097			
6.96	0.160			
7.02	0.132			

show the transition energies computed by RB3LYP method for *cis*- and *trans*-forms of azobenzene by using the 6-311++G(3df,3pd) basis set. From our calculation, we find  $n-\pi^*$  transitions at somewhat lower energy: 2.6 eV (*cis*-); 2.5 eV (*trans*-). These are of quite low intensity, in agreement with experiment.<sup>4</sup> There are many  $\pi-\pi^*$  transitions starting from lower energy to higher energy: 4.1–5.2 eV (*cis*-); 3.7–5.3 eV (*trans*-). These are of moderate intensity. The intense  $\sigma-\sigma^*$  transitions are found at  $\geq 5.5 \text{ eV}$  (for *cis*-) and  $\geq 5.9 \text{ eV}$  (for *trans*-). Henceforth, we will consider the shift of diradical transitions from these markers. Calculated and observed excitation energies of *cis*- and *trans*-azobenzenes are given in Tables 5 and 6.

The extensive delocalization of  $\pi$  electrons in the diradicals leads to greater stability for both  $\pi$  and  $\pi^*$  orbitals. The bandwidth increases for  $\pi$  orbitals as well as  $\pi^*$  orbitals.

**Table 6. Calculated RB3LYP Vertical Excitation Energies (in eV) and Oscillator Strengths ( $f$ ) of *trans*-Azobenzene in Comparison with CCSD and Experimental Data**

this work B3LYP 6-311G ++(3df,3pd)		CC2 Aug-cc-pVTZ (ref 17)	CCSD extrapolated (ref 21)	expt. (ref 4)
eV	$f$			
2.54	0.000	2.84	2.95	2.82 ( $n-\pi^*$ )
3.68	0.758	4.04	4.36	4.12 ( $\pi-\pi^*$ )
4.05	0.052	4.44	4.62	
4.74	0.000	4.45	4.63	
5.32	0.171	5.15	5.53	
5.90	0.022	5.79	6.13	5.64 ( $\sigma-\sigma^*$ )
6.04	0.014	5.80	6.14	
6.17	0.108	5.64	6.40	
6.27	0.035	5.78	6.49	
6.33	0.347	5.97	6.57	
6.74	0.073			
6.81	0.040			
6.87	0.007			
7.00	0.250			

In consequence, the  $\pi-\pi^*$  band gap decreases. Table 7 shows the calculated LUMO–HOMO energy difference. A similar but

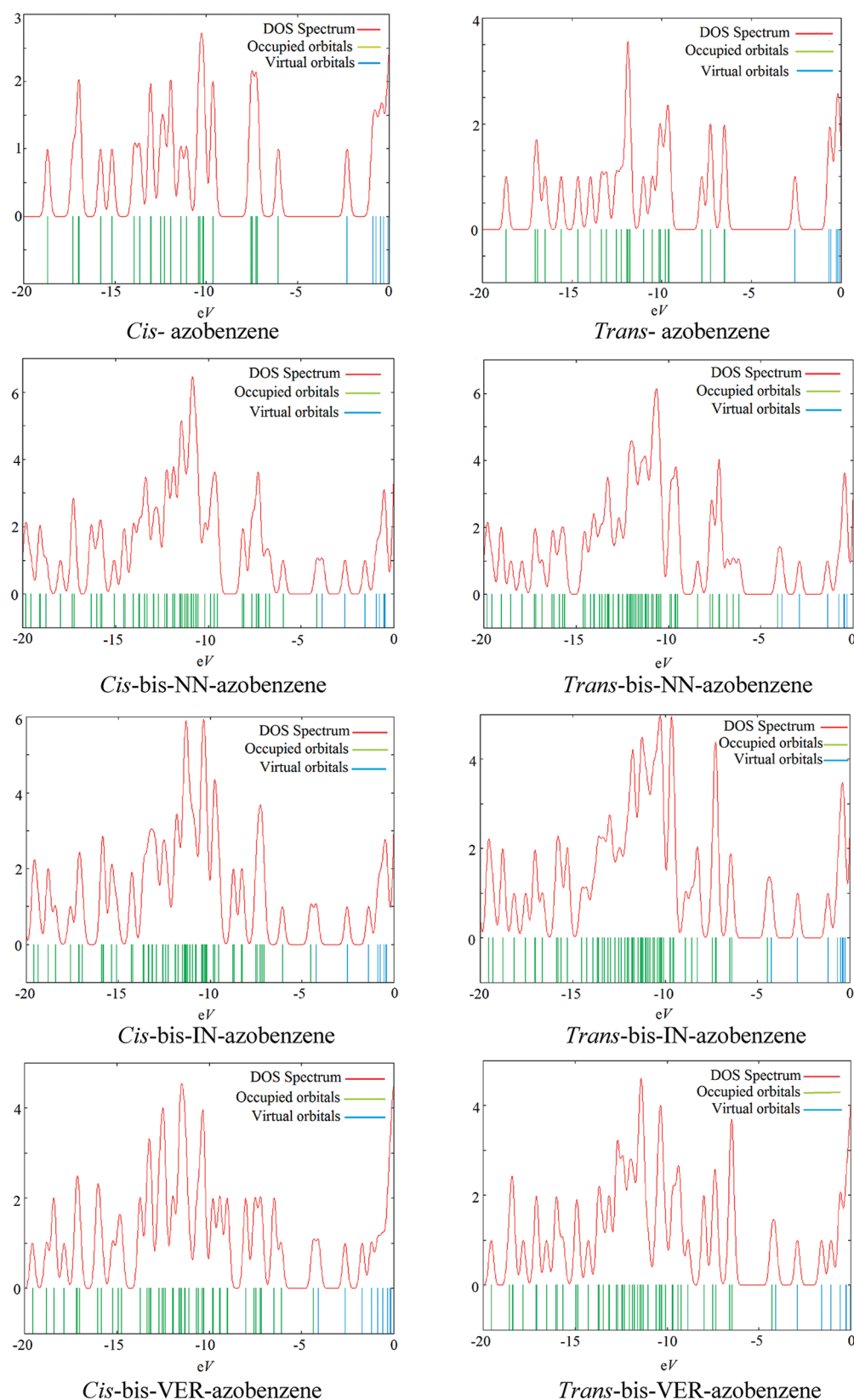
**Table 7. LUMO–HOMO Energy Differences (in eV) of Different Systems**

system	HOMO	LUMO	$\Delta E = (\text{LUMO} - \text{HOMO})$
<i>cis</i> -azobenzene	−6.49	−2.58	3.91
<i>trans</i> -azobenzene	−6.07	−2.30	3.77
<i>cis</i> -bis-NN-azobenzene	−4.15	−3.85	0.30
<i>trans</i> -bis-NN-azobenzene	−4.08	−3.87	0.21
<i>cis</i> -bis-IN-azobenzene	−4.52	−4.22	0.30
<i>trans</i> -bis-IN-azobenzene	−4.48	−4.25	0.23
<i>cis</i> -bis-VER-azobenzene	−4.31	−4.10	0.29
<i>trans</i> -bis-VER-azobenzene	−4.37	−4.08	0.21

much less prominent trend is exhibited by the  $\sigma$  and  $\sigma^*$  orbitals. Thus,  $n-\pi^*$  transitions in the diradicals are expected to start at a lower energy as compared to that for the unsubstituted azobenzenes. The  $\pi-\pi^*$  transitions are expected to start at a much lower energy as compared to the  $\pi-\pi^*$  transitions in azobenzene. The  $\sigma-\sigma^*$  transitions are expected to start at a slightly lower energy. The decrease in the transition energy can be evidenced from the decreased band gaps in the density of states plots given in Figure 5.

The  $n-\pi^*$  transitions, however, gain in oscillator strength ( $f$ ) because of the more extensive linear combination in the diradical  $\pi^*$  orbitals. Without a detailed analysis of the excited states, it is difficult to draw a simple correlation between the  $\pi-\pi^*$  and  $\sigma-\sigma^*$  oscillator strength for the diradicals and those for azobenzene. However, some of the  $\pi-\pi^*$  transitions would be intense and they would occur at lower energy (by about 0.5–0.1 eV) for *cis*-diradicals and similarly at a lower energy region (by about 0.4–0.7 eV) for *trans*-diradicals.

Tables 8–10 contain calculated energy and oscillator strength for the diradicals. The  $n-\pi^*$  transitions are found in the *cis*-diradicals at energies lower by about (i) 0.19 eV (*cis*-bis-NN-azobenzene) from Table 8, (ii) 0.12 eV (*cis*-bis-IN-azobenzene) from Table 9, and (iii) 0.13 eV (*cis*-bis-VER-azobenzene) from Table 10. These transitions gain in intensity as compared to *cis*-azobenzene.



**Figure 5.** Density of states spectrum for azobenzenes and their diradical derivatives.

The  $n-\pi^*$  transition at 2.82 eV is very weak for *trans*-azobenzene.<sup>4</sup> The calculated oscillator strength for the 2.54 eV transition is negligibly small ( $f = 0.000$ ). For the *trans*-diradicals, it is noticed from Tables 8, 9, and 10 that transitions would occur

at around 2.20 eV ( $f = 0.002$ ), 2.51 eV ( $f = 0.001$ ); 2.51 eV ( $f = 0.001$ ), 2.67 eV ( $f = 0.003$ ); and 2.78 eV ( $f = 0.006$ ), 2.79 eV ( $f = 0.009$ ). These slightly intense transitions are the outcome of the appearance of new  $\pi^*$  orbitals in the diradicals.

**Table 8. TDDFT Excitation Energies and Oscillator Strength (*f*) of bis-NN Derivative of *cis*- and *trans*-Azobenzene<sup>a</sup>**

<i>cis</i> -bis-NN-azobenzene		<i>trans</i> -bis-NN-azobenzene	
eV	<i>f</i>	eV	<i>f</i>
2.38	0.139	2.20	0.002
2.77	0.009	2.51	0.001
		2.95	1.539
3.14	0.054	3.04	0.100
3.51	0.354	3.08	0.048
3.99	0.207	3.74	0.033
4.12	0.177	3.78	0.013
4.26	0.142	3.94	0.002
4.29	0.048	4.19	0.033
4.50	0.028	4.36	0.102
		4.40	0.157
4.57	0.007		
4.62	0.005	4.82	0.011
4.64	0.203	4.84	0.117
4.70	0.004		

<sup>a</sup>The basis set used is 6-311++G(3df,3pd).**Table 9. TDDFT Excitation Energies and Oscillator Strength (*f*) of Bis-IN Derivative of *cis*- and *trans*-Azobenzene<sup>a</sup>**

<i>cis</i> -bis-IN-azobenzene		<i>trans</i> -bis-IN-azobenzene	
eV	<i>f</i>	eV	<i>f</i>
2.45	0.093	2.51	0.001
2.69	0.003	2.67	0.003
3.12	0.004	2.99	0.076
3.81	0.248	3.25	1.442
4.10	0.122	3.83	0.073
4.13	0.019	3.87	0.003
4.19	0.055	4.33	0.071
4.36	0.212		
4.43	0.147		
4.60	0.023	4.85	0.007
4.78	0.023	4.89	0.006
5.04	0.014	4.98	0.040

<sup>a</sup>The 6-311++G(3df,3pd) basis set has been used.**Table 10. TDDFT Excitation Energies and Oscillator Strength (*f*) of Bis-VER Derivative of *cis*- and *trans*-Azobenzene<sup>a</sup>**

<i>cis</i> -bis-VER-azobenzene		<i>trans</i> -bis-VER-azobenzene	
eV	<i>f</i>	eV	<i>f</i>
2.44	0.108	2.78	0.006
2.61	0.011	2.79	0.009
3.01	0.011	2.97	0.010
3.26	0.011	3.23	1.358
3.64	0.007	3.29	0.284
3.79	0.351	3.79	0.028
3.91	0.011	3.84	0.044
4.08	0.188	4.17	0.012
4.21	0.028	4.31	0.003
4.26	0.200		
4.58	0.019	4.63	0.031
4.65	0.095	4.73	0.084
4.72	0.007	4.86	0.136
4.89	0.006	4.94	0.016

<sup>a</sup>The basis set 6-311++G(3df,3pd) has been employed.

Tables 5, 6, and 8–10 demonstrate that the  $\pi$ – $\pi^*$  transitions start at considerably lower energies (about 1 eV lower for *cis*-, 0.7 eV lower for *trans*-), and some transitions gain a lot of intensity on diradical formation. Thus, the spectral features of the diradicals are similar to those of the azobenzenes, but the  $\pi$ – $\pi^*$  transitions are considerably red-shifted. The  $n$ – $\pi^*$  transitions are somewhat red-shifted for the *cis*-diradicals, but the *trans*-diradicals reveal a mixed trend. Both  $n$ – $\pi^*$  and  $\pi$ – $\pi^*$  transitions gain in intensity. In short, these diradicals would be strongly photochromic.

## 4. CONCLUSIONS

We have examined three diradicals of both *cis*- and *trans*-forms of azobenzene. These have been prepared with nitronyl nitroxide, imino nitroxide, and verdazyl radicals. From our calculations, we predict that the magnetic coupling constants (*J*) for all of the diradicals are small and negative, and there is no huge difference of *J* values between *cis*- and *trans*-forms. So, the monoradical centers in all diradicals are antiferromagnetically coupled. Spin alternation rule in the unrestricted formulation is in support of this observation. We also predict the diradical isomers to be strongly photochromic. However, the possibility of a magnetic crossover as claimed in ref 5 is nonexistent.

## ■ ASSOCIATED CONTENT

### Supporting Information

Log files of all calculations and full ref 16. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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