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Peculiarities of Spin Exchange in Nitroxide Biradicals Containing Two para-Phenylene Groups in the Bridge. EPR Investigation and DFT Calculations --Manuscript Draft--

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Abstract:	Two nitroxide biradicals of similar composition: R5-CC-Ph-Ph-CC-R5 (B3a) and R6-CC-Ph-Ph-CC-R6 (B3b), where Ph = p-C6H4, and R6 is 2,6,6-tetramethyl-5,6-dihydropyridin-1(2H)-yloxyl, and R5 is 2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrol-1-yloxyl nitroxide rings, have been studied by electron paramagnetic resonance (EPR) spectroscopy. Variations of the intramolecular electron spin exchange in the biradicals, dissolved in toluene, as a function of temperature were characterized by changes in the isotropic ¹⁴ N hyperfine splitting (hfs) constant a, values of the exchange integral J , and compared with the data obtained by DFT calculations. Thermodynamic parameters of the conformational rearrangements were calculated. Geometries of nitroxide biradicals in PES local minima and transition states in the triplet state were calculated at UDFT/B3LYP level with split-valence basis set cc-pVTZ [43]. Probable differences in biradicals behavior are discussed.
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Peculiarities of Spin Exchange in Nitroxide Biradicals Containing Two *para*-Phenylene Groups in the Bridge. EPR Investigation and DFT Calculations

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Abstract Two nitroxide biradicals of similar composition: $R_5-C\equiv C-Ph-Ph-C\equiv C-R_5$ (**B3a**) and $R_6-C\equiv C-Ph-Ph-C\equiv C-R_6$ (**B3b**), where $Ph = p-C_6H_4$, and R_6 is 2,6,6-tetramethyl-5,6-dihydropyridin-1(2*H*)-yloxyl, and R_5 is 2,2,5,5-tetramethyl-2,5-dihydro-1*H*-pyrrol-1-yloxyl nitroxide rings, have been studied by electron paramagnetic resonance (EPR) spectroscopy. Variations of the intramolecular electron spin exchange in the biradicals, dissolved in toluene, as a function of temperature were characterized by changes in the isotropic ^{14}N hyperfine splitting (hfs) constant a , values of the exchange integral $|J|$, and compared with the data obtained by DFT calculations. Thermodynamic parameters of the conformational rearrangements were calculated. Geometries of nitroxide biradicals in PES local minima and transition states in the triplet state were calculated at UDFT/B3LYP level with split-valence basis set cc-PVTZ [43]. Probable differences in biradicals behavior are discussed.

Key words: EPR spectroscopy, nitroxide biradical, spin density distribution, DFT calculations

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1 Introduction

During last fifty years, stable nitroxide biradicals became routine subjects of numerous investigations. Many hundreds of them have been synthesized, studied and utilized in different applications as spin probes, as polarizing agents for dynamic nuclear polarization, etc. [1-10], and in Refs. therein. Among these hundreds of various structures, there is a special group of chemically rigid biradicals, which contain several acetylene groups in the bridge connecting two paramagnetic nitroxide rings [1, 3, 5, 11-20]. In such biradicals intramolecular spin exchange is realized by the indirect mechanism, i.e., by the spin coupling via the chain of atoms and bonds [3, 5]. Temperature dependence of $|J|$ in liquid solutions of such biradicals is not so much as in the case of flexible biradicals and only slightly depends on the solvent nature [21-25]. It was recently shown [19, 20, 26] that in such biradicals as $R_6-(C\equiv C)_2-R_6$ (**B1**) and $R_6-C\equiv C-Ph-C\equiv C-R_6$ (**B2**), where $Ph = p-C_6H_4$, and R_6 is 2,2,6,6-tetramethyl-5,6-dihydropyridin-1(2*H*)-yloxyl nitroxide ring, which look like chemically rigid structures with high degree of conjugation between two unpaired electrons locating in paramagnetic $>N-O$ groups [11-15, 17] are not really rigid. These biradicals are characterized by a very slight dependence of the exchange integral $|J|$ on temperature, similar in different molecular solvents. Values of $|J|$ can be easily measured from their EPR spectra with high accuracy, and biradicals structure can be determined with high precision by quantum-chemical calculations based on density functional theory (DFT).

For biradicals **B1** and **B2** expected to be rigid because of conjugation of double bonds in the nitroxide ring with triple bonds in the bridge, we showed using the UDFT/B3LYP/cc-pVDZ calculations that the rotation barriers for **B1** and **B2** biradicals do not exceed a value of 1.0 kJ mol^{-1} and $\sim 8 \text{ kJ mol}^{-1}$ respectively, therefore, the internal rotation around the main axis in both biradicals is practically free at ambient temperatures. It was also published that for a short acetylene biradical, $R_6-C\equiv C-R_6$, the barrier of the internal rotation is also very low and equal to 4.0 kJ/mol . It is of scientific interest to proceed such DFT calculations and to compare them with EPR measurements for similar biradicals of bigger size.

In this paper we report our experimental and theoretical results about the structure and EPR spectra peculiarities of two nitroxide biradicals with similar structures with two acetylene and two *para*-phenylene groups in the spacer. $R-C\equiv C-Ph-Ph-C\equiv C-R$, in which R depicts five or six-membered nitroxide ring.

2. Experimental

2.1 Synthesis of the biradicals

In our work, biradicals **B3a** and **B3b** were synthesized by the procedure which is shown in Fig. 1 and described below in details from compounds **2a** [27] and **2b** [28], which were prepared according to published procedures. 4,4'-diethynylbifenil was purchased from TCI, other reagents

were purchased from Aldrich or Alfa Aesar. Anhydrous THF was used and Et₃N was distilled from CaH₂ prior to use. Melting points were determined with a Boetius micro melting point apparatus and are uncorrected. Elemental analyses (C, H, N, S) were performed on Fisons EA 1110 CHNS elemental analyzer. Mass spectra were recorded on a Thermoquest Automass Multi. Flash column chromatography was performed on Merck Kieselgel 60 (0.040-0.063 mm). Qualitative TLC was carried out on commercially available plates (20 x 20 x 0.02 cm) coated with Merck Kieselgel GF₂₅₄.

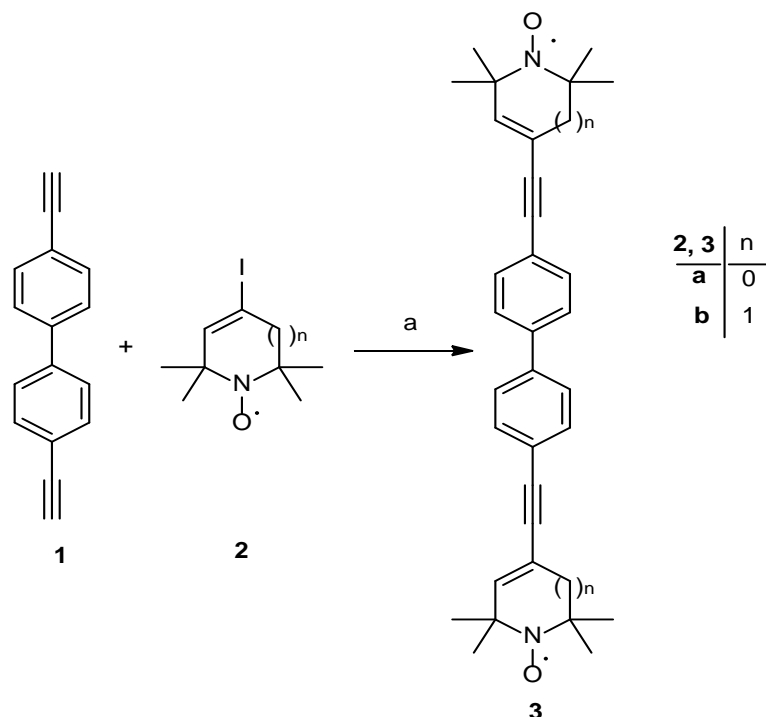


Fig. 1 Scheme of the synthetic procedure for biradicals **B3a** and **B3b**. Details see in the text

To a degassed solution of **2a** or **2b** (2.0 mmol) in THF (20 mL) and Et₃N (2.5 mL), CuI (20 mg, 0.1 mmol) and Pd(PPh₃)₄ (50 mg, 0.04 mmol) was added under N₂ and after stirring for 15 min. compound **1** (202 mg, 1.0 mmol) in THF (5 mL) was added dropwise. After stirring the mixture overnight at rt., it was filtered through Celite, the solvent was evaporated and the residue was dissolved in CH₂Cl₂ (15 mL) washed with brine (10 mL), the organic phase was separated, dried (MgSO₄), activated MnO₂ (86 mg, 1.0 mmol) was added and O₂ was bubbled through 15 min. The mixture was set aside for 6h, then filtered, evaporated and the residue was purified by flash column chromatography (hexane/CH₂Cl₂) to yield compound **B3a** or **B3b**.

3,3'-([1,1'-Biphenyl]-4,4'-diylbis(ethyn-2,1-diyl))bis(2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrol-1-yloxy) Biradical (**B3a**): 215 mg (45%), pale yellow solid, mp 228-230°C, R_f: 0.54 (hexane/EtOAc, 2:1). MS (70eV): m/z = 478 (M⁺, 20), 448 (8), 418 (100), 403 (8). Anal calcd for C₃₂H₃₄N₂O₂: C, 80.30; H, 7.16; N, 5.85; found: C, 80.21; H 7.02; N, 5.74.

4,4'-([1,1'-Biphenyl]-4,4'-diylbis(ethyn-2,1-diyl))bis(2,2,6,6-tetramethyl-5,6-dihydropyridin-1(2*H*)-yloxy) Biradical (**B3b**): 116 mg (23%), deep yellow solid, mp230-233°C, *R*_f: 0.60 (hexane/EtOAc, 2:1). MS (70eV): *m/z* = 506 (*M*⁺, 32), 491 (45), 476 (58), 461 (85), 446 (75), 165 (100). Anal calcd for C₃₄H₃₈N₂O₂: C, 80.60; H,7.56; N, 5.53; found: C, 80.42; H 7.46; N, 5.48.

2.2 EPR measurements

Toluene was selected as a solvent and was carefully purified according to literature procedure [29]. Solutions were prepared, bubbled with nitrogen for 20-25 min. 0.5 ml of a solution was taken into a thin capillary and degassed by frieze-pump circle to remove oxygen, and sealed off under vacuum. Radical concentrations were sufficiently low ($\leq 4 \times 10^{-4}$ mol l⁻¹) to eliminate intermolecular exchange broadening of EPR lines [30].

EPR spectra were recorded at X-band on a Bruker EMX-8 spectrometer with a modulation frequency of 100 kHz. Temperatures were controlled with accuracy $\pm 0.5^\circ\text{C}$ at temperatures between 298 and 368 K by means of a JEOL JNM-VT-30 temperature control system. EPR parameters: the hyperfine splitting, hfs, constant on nitrogen ¹⁴N atom, *a*, and a value of the exchange integral $|J/a|$, which is sensitive to any changes of the spin density distribution of the unpaired electron in the system. The exchange integral values $|J/a|$ were calculated in accordance with [3, 31]. EPR spectra of biradicals were simulated with the computer program package created by Dr. A. A. Shubin (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences) and described in details in Ref. [31]. For our calculations, we used spin-Hamiltonian parameters of similar nitroxide radicals collected in [32].

In liquid solutions with rather low viscosity, the spin Hamiltonian \hat{H} comprises the isotropic hyperfine, the Zeeman interactions and the exchange coupling. In the case when both radical fragments are identical and each carries only one nucleus with a nonzero nuclear spin *I* the following equation is valid [33, 34]:

$$\hat{H} = g\beta_e H_0 (S_z^{(1)} + S_z^{(2)}) + a(S_z^{(1)}I_z^{(1)} + S_z^{(2)}I_z^{(2)}) + JS^{(1)}S^{(2)} \quad (1)$$

The spin Hamiltonian is here written in frequency units; superscripts 1 and 2 denote different radical fragments; $S^{(k)}$ are electron spin operators; $S_z^{(k)}$ and $I_z^{(m)}$ are projections of the electron and nuclear spins to the *Z*-axis, respectively; *g* is the isotropic *g*-factor of the radical fragments; β_e is the Bohr magneton; H_0 is the external magnetic field; $a \approx 3 \cdot 10^8$ rad/s denotes the ¹⁴N isotropic hyperfine splitting (hfs) constant, and *J* is the exchange integral. In low-viscous solvents, the tensor of the dipole-dipole coupling is averaged to zero by fast rotation of the

biradical molecule [32, 33]. For any individual conformation, the one value of $|J|$ should correctly describe the position and integral intensities of all lines in the EPR spectrum. Values of $|J|$ are usually measured in units of the hfs constant a , i.e. as $|J/a|$, with an accuracy of $\pm 2-3\%$.

For the two-conformational model [3, 33, 34], the Arrhenius plot of $|J/a|$ should be linear for any biradical, and this allow determining the differences in enthalpies, ΔH , and entropies, ΔS , of these two conformations:

$$\ln|J/a| = \Delta S/R - \Delta H/RT, \quad (2)$$

The experimental observation of such plot may confirm the validity of the two-conformational model for a biradical.

2.3 Calculation Details

Geometries of nitroxide biradicals in PES local minima and transition states in the triplet state were calculated at UDFT/B3LYP level with split-valence basis set cc-PVTZ [43]. Stationary point achievement was verified by calculation of normal mode frequencies. Open-shell singlet state geometries were calculated using Broken Symmetry approximation [44, 45] at the same level of theory and were found to match triplet state equilibrium geometries. Distances $R_{\text{NO-NO}}$ were taken as a distances between centers of N–O bonds. Zero field splitting values D were also calculated at UDFT/PBE0/cc-PVTZ level neglecting a spin-orbit part. Spin-spin part was calculated on the basis of unrestricted natural orbitals [46].

3. Results and Discussion

Typical EPR spectra of biradicals **B3a** and **B3b** at 338 K are shown in Fig. 2. The comparison of simulated (*open circles*) and experimental (*solid lines*) spectra shows that they are in a good agreement, positions of all “exchange” lines in the magnetic field are practically coincide (Fig. 2), therefore, the exchange integral values are measured with high precision.

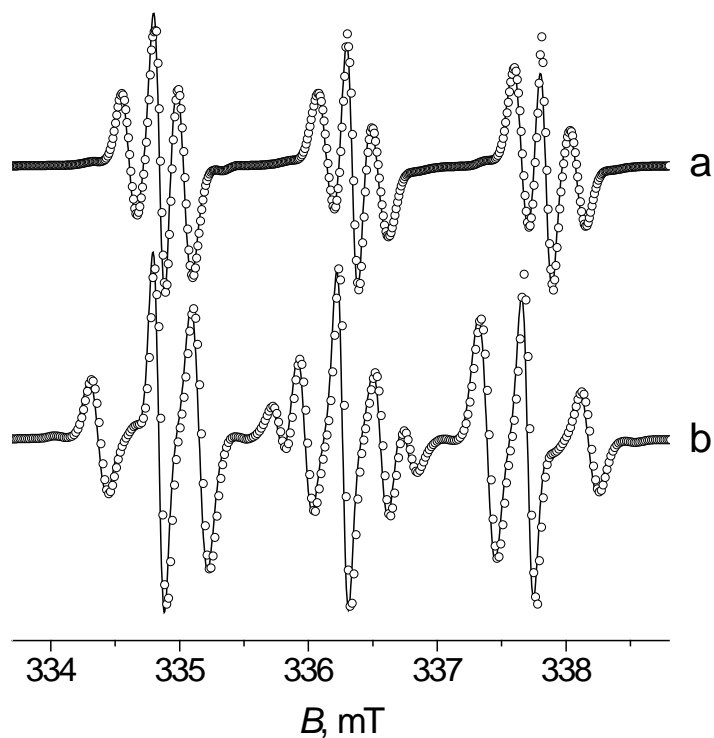


Fig. 2 Experimental (*solid lines*) and calculated (*open circles*) EPR spectra of biradicals **B3b** (a) and **B3a** (b) in toluene at 338 K

One can see from Fig. 2 that amplitudes of the central and high-field simulated main “radical” lines are bigger than those of experimental ones. This is caused by the “stick-shape” of both molecules, that is realized in the anisotropic rotation of both biradicals performed in the experimental spectrum, while spectra simulations have been done for the case of the isotropic rotation [31]. Positions of all lines for both spectra are coincide. Measured from spectra simulation values of the exchange integral $|J|$ at 338 K are equal to 7.6 ± 0.3 G ($a = 14.32$ G) and 4.35 ± 0.2 G ($a = 15.0$ G) for **B3a** and **B3b** respectively. Temperature changes of the hfs constant $a' = da/dT$ are equal to $-7.2 \cdot 10^{-4}$ and $3.4 \cdot 10^{-3}$ G·K⁻¹ for **B3b** and **B3a**, which are comparable with data published in [5].

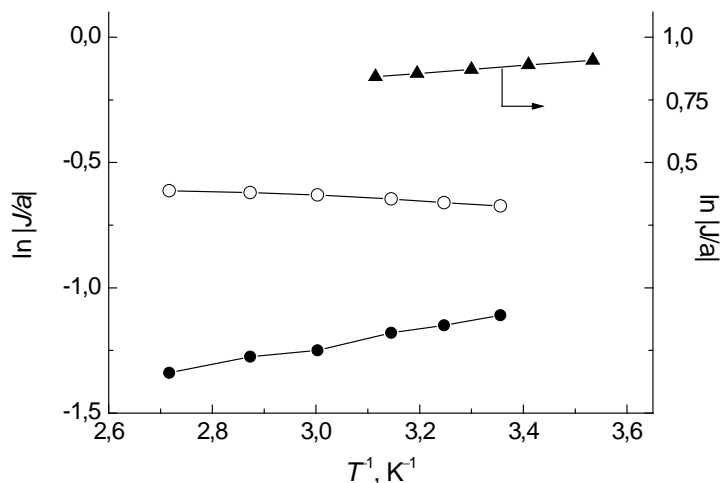


Fig. 3 $|J/a|$ as a function of temperature for biradicals **B3a** (open circle), **B3b** (filled circle) and **B2** (filled up triangle) dissolved in: toluene

Temperature dependences of $|J/a|$ values for both **B3a** and **B3b** biradicals dissolved in toluene are shown in Fig. 3. One can see slight increase of $|J/a|$ with the increase of temperature in the case of **B3a**, while in the case of **B3b** this dependence has the opposite tendency similar to that one reported for biradical **B2** (see Fig. 3) in Ref. [19] and explained in Ref. [30] for the biradical **B2**: the barrier of rotation, E_a , of piperidine rings in biradicals with acetylene groups in the bridge is rather low as results from the DFT calculations: it is not more than 8 kJ mol^{-1} for **B3**. Librations of the piperidine planes relatively the $p\text{-C}_6\text{H}_4$ plane by up to 5 degrees have a value of E_a less than 0.1 kJ mol^{-1} , i.e., negligible. These results correlate well with the experimentally measured values of enthalpy, ΔH , which are equal to -0.5 kJ mol^{-1} and close to -1.0 kJ mol^{-1} in the case of **B3** dissolved in toluene and ethanol respectively. It should be also mentioned that such small values of E_a for biradical **B3** results in rather free intramolecular rotation of the nitroxide rings even at low temperatures, i.e., the EPR spectra and measured values of $|J/a|$ do not characterize individual conformations of **B3** but an averaged pattern with very fast transitions between several rotamers, and the measured value of $|J/a|$ is averaged by all these conformations.

Formal enthalpies of conformational transitions in both biradicals **B3a** and **B3b** were calculated from linearized $|J/a|$ dependencies: $\Delta H_{\text{B3a}} = 0.8 \pm 0.2 \text{ kJ.mol}^{-1}$, and $\Delta H_{\text{B3b}} = -3.0 \pm 0.2 \text{ kJ.mol}^{-1}$. Though in the present case DFT calculation predict identical energies of all possible conformations of **B3a** and **B3b** biradicals (Fig 4). Further, **B3b** biradical has 8 energy equivalent conformations with the angle between SOMOs varying from 0° , this conformer

corresponds to the maximal J value, to $\sim 60^\circ$ at conformers with much lower $|J|$ values. It makes a simple two-conformational model inapplicable in our case.

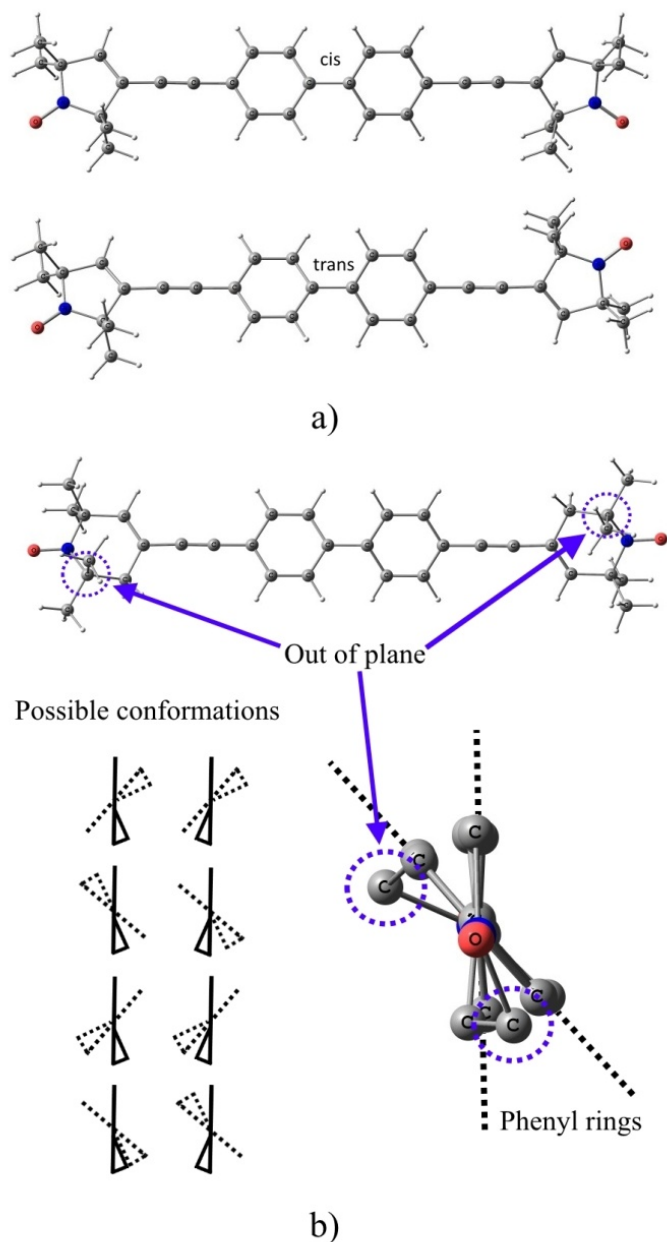


Fig. 4 Calculated geometries of biradicals **B3a** (a) in *cis*- and *trans*- configurations and **B3b** (b)

B3a and **B3b** biradicals with two acetylene and two *p*-phenylene groups in the bridge exhibit fast inversions of R_6' ring (in the case of **B3b** biradical only) and internal rotations around the axis passing through the main molecular axis of the bridge (Fig. 5) even at rather low temperatures, averaging the $|J/a|$ values. Low barriers E_a allow “mixing”, i.e., averaging the conformers spectral parameters at high temperatures effectively as have been described in Refs. [19, 20].

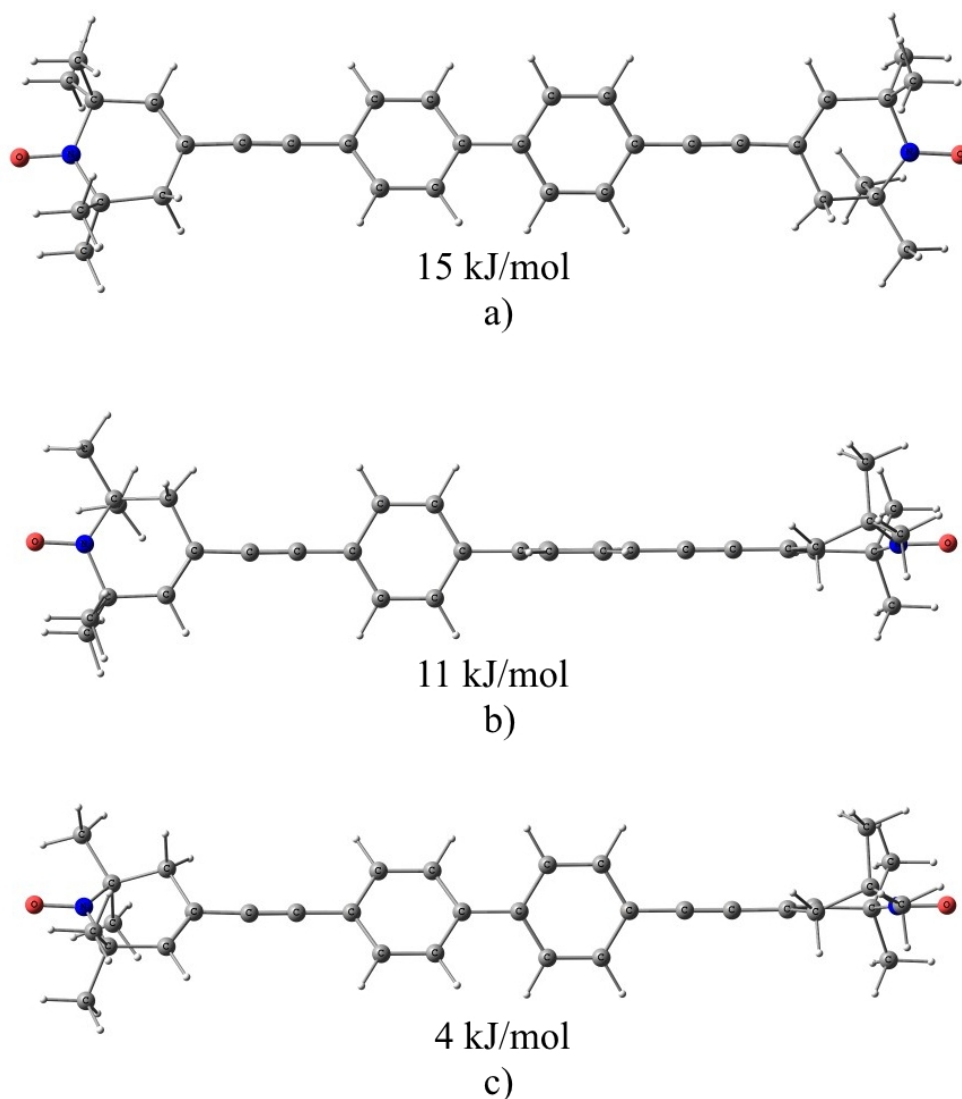


Fig. 5 Structures of the transition states of biradical **B3b** and their relative energies: plane R_6' rings (a), two perpendicular phenyl rings (b), R_6' ring is perpendicular to the nearest phenyl ring (c).

Slight decrease of $|J/a|$ values with the increase of temperature for **B3b** biradical cannot be explained by the population of distinct conformations with lower $|J|$, but rather a higher accessibility of larger deviations from equilibrium geometries leading to lowering of the exchange coupling. In the case of **B3a** biradical, there is an inverse dependence (Fig. 3): slight increase of $|J/a|$ with temperature. The idea that changes shown in Fig. 3 are caused by temperature changes of the hfs constant a are also not correct: indeed, it was shown in [5], that a values decrease with temperature in the case of all studied piperidine-type radicals and biradicals except $O=R_6$ radical [5], but a increases with temperature for five-membered pyrroline- and pyrrolidine-type nitroxides [5, 35]. Therefore, $|J/a|$ value dependences vs. temperature are similar to those of a . We assume that such differences between **B3a** and **B3b** should be connected with

structural peculiarities of these biradicals, transitions between their conformers, which are manifested in very small values of the activation energy E_a and of enthalpy ΔH . We intend to start such complex quantum chemical calculations of these systems in the future.

Important spectroscopic and structural parameters: values of the dipolar coupling constant D (a zero-field splitting) and a distance $R_{\text{NO-NO}}$ between centers of $>\text{N-O}$ groups were determined by DFT calculations (Table). This distance in the case of **B3b** is about 8% (1.6-1.7 Å) longer than for both *cis*- and *trans*- conformations of **B3a**.

Table. Zero-field splitting D parameter and $R_{\text{NO-NO}}$ in **B3a** and **B3b** biradicals

Biradical	D, cm^{-1}	$R_{\text{NO-NO}}, \text{Å}$
B3a-trans	-0.000311	20.79
B3a-cis	-0.000315	20.68
B3b	-0.000250	22.28

Studying different nitroxide biradicals with several acetylene and *p*-phenylene groups in the bridge connecting nitroxide rings [14], it was proposed that in such long stick-shape biradicals the intramolecular spin exchange can not be realized by the direct mechanism (straight overlapping of the wave functions of the unpaired electrons localized on $>\text{N-O}$ groups), and can be performed by the indirect mechanism: via spin density coupling through the bridge of atoms and bonds. EPR spectra of such biradicals are weakly temperature-dependent, and $|J/a|$ values measured for the set of them allowed authors to suggest that the efficiency of spin density delocalization of unpaired electrons should be characterized with the use of the “coefficient of attenuation” $\gamma = |J_i/J_k|$ for the biradicals with ($|J_k/a|$) and without ($|J_i/a|$) a certain group or atom in the bridge. $|J_k/a|$ and $|J_i/a|$ values should both be measured at the same temperature and in the same solvent [5]. This “attenuation coefficient” γ_k is a characteristic parameter of the functional group or atom and does not depend on other groups forming the bridge.

Knowledge of all γ_k coefficients for all groups in the bridge allows estimating the spin density ρ_s localized on the carbon atom in the fourth position of the piperidine or in the third position of the five-membered ring connected with the nearest (first) atom of the biradical bridge, or the exchange integral value $|J_{\text{RR}}|$ for a biradical $\text{R}_6\text{-R}_6$ or a hypothetical biradical $\text{R}_5\text{-R}_5$:

$$|J_{\text{RR}}| = |J_{\text{Birad}}| \cdot \gamma_i \cdot \gamma_j \cdot \gamma_k \cdot \dots, \quad (3)$$

where γ_i , γ_j , γ_k are the attenuation coefficients for i-, j- or k- atom or a group in the bridge between two R_6 or R_5 fragments in a real biradical with its $|J_{\text{Birad}}|$. Using this procedure, in the case of **B3b** ($|J_{298}/a| = 0.29$) and **B2** ($|J_{298}/a| = 2.2$ [19]), one can calculate $\gamma_{\text{Ph}} = 7.6$, which is close to the value $\gamma_{\text{Ph}} = 6.6$ obtaining from the pair **B2** and **B1**. This deviation is likely to result from the fact that in **B3b** biradical phenyl rings are not coplanar, hence, conjugation in the whole system is weaker, than in the case of **B2** biradical. This means that the electron spin exchange integral $|J|$ decreases approximately seven-fold passing through *p*-C₆H₄ group. This is in a good agreement with the result published in [3]. Using this value of γ_{Ph} and a value of $\gamma_{\text{C}\equiv\text{C}} = 2.2 \pm 0.15$ [5], one can calculate the following value: $|J_{R_6R_6}/a_{B3b}| = |J_{B3b}/a_{B3b}| \cdot \gamma_{\text{Ph}}^2 \cdot \gamma_{\text{C}\equiv\text{C}}^2 = 81$, or $|J_{R_6R_6}| \approx 1220 \text{ G} \gg a_{B3b} \approx 15.0 \text{ G}$ for biradical **B3b**. This value is in a good correlation with $|J_{R_6R_6}| \geq 0.12 \text{ cm}^{-1} \approx 1285 \text{ G}$ obtained in Ref. [20]. The same value estimated in [5] was equal to $|J_{R_6R_6}| = 1050 \text{ G}$. Similarly, for **B3a**, the value of $|J_{R_5R_5}| \approx 2220 \text{ G}$ ($|J_{298}/a| = 0.53$, $a \approx 14.3 \text{ G}$). The bigger value of $|J_{R_5R_5}|$ comparing to $|J_{R_6R_6}|$ is understandable because the C3 atom in a five-membered ring is located much closer to the paramagnetic >N-O group than the C4 atom in the six-membered ring.

Conclusions. Nature of the exchange coupling in two nitroxide biradicals $R_6\text{-C}\equiv\text{C-Ph-Ph-C}\equiv\text{C-R}_6$ (**B3b**) and $R_5\text{-C}\equiv\text{C-Ph-Ph-C}\equiv\text{C-R}_5$ (**B3a**) is discussed basing on the results obtained by DFT calculations and X-band EPR data. The attenuation coefficients of Ph group found in the work are in a good agreement with previously observed ones. Temperature dependences of the exchange couplings are explained well by the results of DFT calculations with low activation energy barriers of internal motions (rotations or librations) responsible for the averaging of the exchange coupling. Energies of transition states of these motions are found to be substantially small allowing practically free internal rotation around the main molecular axis of the biradical.

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