

## Difficulties in Building Radiation-Generated Three-Spin Systems Using Spin-Labeled Luminophores

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Aromatic compounds are well-known acceptors of primary radical ions that are formed under high-energy irradiation of nonpolar systems. Thus formed radical ion pairs recombine and produce magnetosensitive fluorescence, which helps study the short-lived radical ions. It was initially suggested that a simple introduction of a spin label into the original arene would allow an easy transition from two-spin to three-spin systems, retaining the experimental techniques available for radical pairs. However, it turned out that spin-labeled arenes often do not produce magnetosensitive fluorescence in the conditions of a conventional radiochemical experiment. To understand the effect of the introduced spin label, we synthesized a series of compounds with the general structure “stable 3-imidazoline radical–two-carbon bridge–naphthalene” as well as their diamagnetic analogues. By use of this set of acceptors, we determined the processes that ruin the observed signal and established their connection with the chemical structure of the compound. We found that the compounds with flexible (saturated) two-carbon bridges between the luminophore and the stable radical moieties exist in solution in folded conformation, which leads to suppression of luminescence from naphthalene due to efficient through-space exchange quenching of the excited state by the radical. Increasing the rigidity of the bridge by introducing the double bond drastically increases the reactivity of the extended  $\pi$ -system. In these compounds, the energy released upon recombination is spent in radiationless processes of chemical transformations both at the stage of the radical ion and at the stage of the electronically excited molecule.

### 1. Introduction

Observation and explanation of the effects of electron and spin polarization in 1960s had led to inception of spin chemistry as a new field of study into the nature of chemical reactivity.<sup>1–3</sup> Traditionally spin chemistry was done with reactions proceeding via formation of spin-correlated radical pairs. Despite the rather short lifetimes of the transient radicals in a typical system, these reactions have been fairly well understood, owing mostly to their specific properties of spin-selective recombination and sensitivity to an external magnetic field.<sup>4</sup> In particular, it was found that even relatively weak magnetic fields can substantially alter the rates of chemical reactions proceeding via the formation of a spin-correlated radical pair.<sup>5–17</sup> Furthermore, it was shown that the spin-selective recombination of the pair can be controlled by an “external” paramagnetic particle—a third spin magnetically coupled to the pair partners.<sup>18,19</sup>

This phenomenon is now commonly referred to as “spin catalysis” and has been experimentally verified for several photochemical, biochemical and radiochemical systems.<sup>20–22</sup> However, convenient model objects and experimental techniques for in-depth study of this phenomenon are not so easy to find. This problem has three main aspects. First, the lifetime of such

a three-spin system is generally rather short, down into the micro- and nanosecond time scale, and their stationary concentrations are pretty low as well, which severely limits the range of applicable spin-sensitive methods, most notably ruling out the conventional ESR. Second, it turned out to be not so straightforward to provide the controllable coupling of the third spin to the pair partners, both in terms of the magnitude and the modulation depth of the coupling. It is generally desirable to have the third spin permanently linked with one or both pair partners so as to have the coupling of the order of the inverse of the characteristic lifetime of the system and as static as possible, which has led to strategies based on chemical modifications of the precursors of the pair partners by introduction of spin labels via some sort of rigid bridges, by no means a trivial chemical endeavor. The third problem is the elimination or at least maximal suppression of other than magnetic consequences of having the “spin catalyst” in the system. The introduction of the third spin via chemical modification of the initial molecules can lead to rather drastic and often unexpected changes in the properties of the molecules used as “carriers” for the spins in a three-spin system and thus completely bury the subtle magnetic effects under the overwhelming consequences of changing chemical reactivity, relaxivity, or optical properties.

It should be stressed that the sought systems cannot be just stable polyradicals in thermal equilibrium as all the coherent effects would be washed away; it is crucial to have a pair of coherently created spins that have a magnetic coupling to an

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“external” spin, which leads to photochemically or radiochemically generated short-lived systems. The experimental methods for the studies of these three-spin systems are thus based on the known techniques for observation of short-lived radical pairs, which rely heavily on such properties of the pair partners as their relative chemical stability and the propensity to form luminescing electronically excited species upon recombination. Since such pairs have been studied for quite awhile now, these properties have come to be taken for granted. However, in this work we show that seemingly transparent chemical modifications of the well-established systems for radiochemical generation of spin-correlated radical ion pairs<sup>23</sup> can be very consequential to the point of rendering the desired experiment completely impossible.

## 2. Background

Spin catalytic effects have been in the focus of researchers' interest for a number of years,<sup>18–22,24–30</sup> starting with a theoretical prediction<sup>29</sup> in 1980 and supported by first experiments in 1983, which demonstrated the increased rates of chemical reactions due to spin–orbit coupling induced acceleration of singlet–triplet conversion in the transition state.<sup>18</sup> A typical hyperfine-induced spin catalytic effect is given by the recently reported reaction of ATP synthesis in mitochondria proceeding via the formation of radical pairs and catalyzed by <sup>25</sup>Mg<sup>2+</sup>.<sup>22</sup> The general principle of spin catalysis can thus be seen as an acceleration of singlet–triplet transitions in the radical pair by an additional interaction with a magnetic particle. In the system where the “catalyst” is not fixed with respect to the pair partners, it can be difficult to tell how strong, and to which partner, does the external spin couple, and the effect is evaluated indirectly by observing the macroscopic changes in the rates of reaction. Spin catalysis for nonbound stable radicals has been realized and theoretically described in several publications.<sup>27,28,31,32</sup>

A currently active line of research is linking a stable radical into a molecule to modify spin evolution of a radical pair, typically the dynamics of intramolecular electron transfer in systems with the general structure “donor–bridge–acceptor–stable radical”. A representative example would be a system from work<sup>33</sup> having *p*-methoxyphenyl piperidine as the electron donor, naphthyl biscarboxyimide as the electron acceptor, naphthylcarboxydiimide as the bridge, and a TEMPO-type radical linked to the electron acceptor via four  $\sigma$ -bonds. Here either the lifetime of the charge transfer state or the magnitude of the magnetic field effect on the yield of its decomposition<sup>20</sup> are observed depending on the actual system. However, a general feature of the spin triads of this type is strong exchange coupling of all three spins in the system, so that the doublet and quartet states of the entire triad should be invoked when describing its spin state, rather than the singlet/triplet state of the pair and an external spin.

In our earlier works<sup>21,34</sup> we suggested forming the desired spin triad in liquid solution based on a radical ion pair generated by X-irradiation of nonpolar solutions. Here the partners are always at a substantial (above 15 Å) distance from each other, and the exchange coupling between them can be neglected. Thus if a stable radical moiety is introduced in one of the precursors of the pair partners, its spin will be exchange coupled with only one partner of the forming radical ion–biradical ion triad. Its effect on the singlet–triplet conversion of the pair can be observed by monitoring the intensity of the recombination fluorescence of the triad using such methods for radical ion pairs as optically detected electron spin resonance (OD ESR),<sup>35</sup> time-resolved magnetic field effect,<sup>36</sup> and level-crossing (MARY)

spectroscopy.<sup>37</sup> A theoretical analysis of such a system<sup>38</sup> predicted that three-spin effects can be indeed observed by the pair-oriented techniques and furthermore suggested the presence of an additional feature, the so-called J-resonance, in the field close to the magnitude of the exchange coupling *J* in the biradical ion. Thus it becomes feasible to correlate the magnitude of the exchange interaction in the short-lived biradical ion with the structure of its molecular precursor—the types of the stable radical and acceptor moieties, the length and the structure of the bridge, etc. To this end in the work,<sup>21</sup> we prepared and studied a set of *p*-terphenyls substituted with 2-imidazoline-type radicals.

However, the MARY and OD ESR signals there could be detected only in the system with the least interfragment conjugation in the biradical ion,<sup>21</sup> with the estimated magnitude of the exchange coupling about 1 kG. Presumably, the reason was too strong and/or heavily modulated exchange interaction between the two spins in the biradical in the systems with stronger conjugation. To reduce the conjugation, we later tried to use 3-imidazoline radicals as the third-spin moieties, which have broken conjugation from the radical spin location to the bridge insertion point inside the ring itself and thus should keep the spin population inside the stable radical moiety.<sup>39</sup> This would furthermore allow using a rigid unsaturated bridge to avoid the effects of spin exchange modulation by the mutual rotation of the paramagnetic fragments in the biradical. As the luminophore/electron acceptor naphthalene was used, which, besides being an effective charge acceptor and a sufficiently good luminophore, is much more convenient synthetically than *p*-terphenyl.

However, it was found that 3-imidazoline-based spin-labeled acceptors would give no magnetic field-sensitive signal at all. Of all the naphthalene derivatives synthesized, which included both radicals and their diamagnetic analogues, only the diamagnetic compounds gave magnetic field effects, which were similar or close to those observed for the systems with unsubstituted naphthalene. The purpose of this work was thus to prepare a representative set of the spin-labeled naphthalenes, to find out the reasons why these seemingly more promising spin-labeled electron acceptors did not work, and to suggest a synthetic direction for further studies into the spin catalysis in a radiation-generated three-spin system.

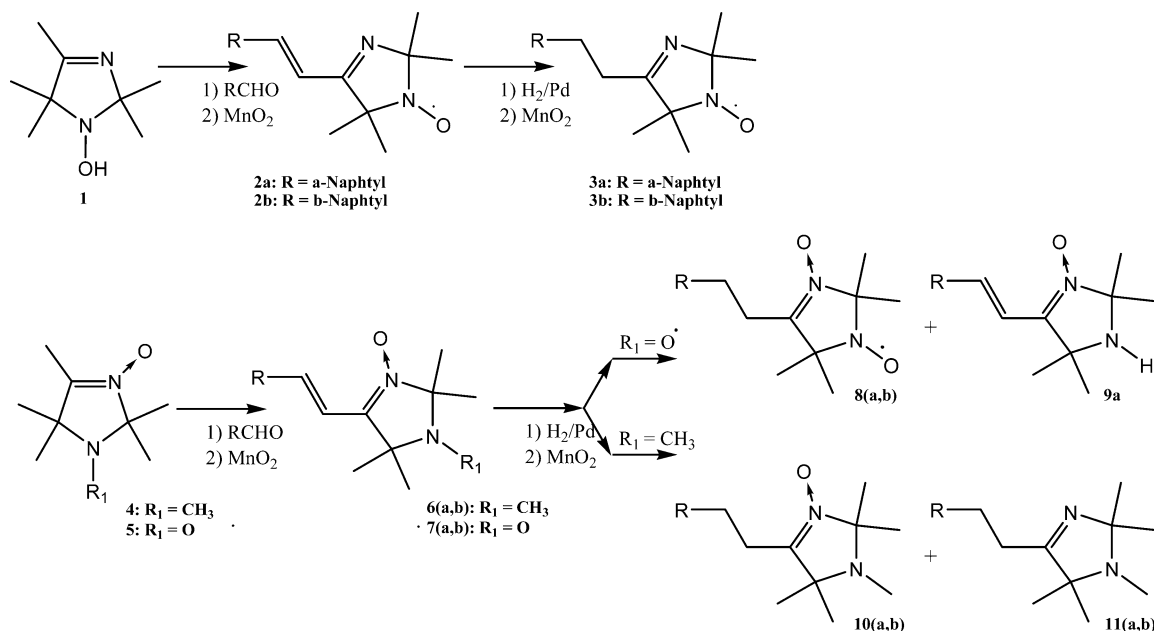
## 3. Experimental

### 3.1. Synthesis and Characterization of Target Compounds.

The target compounds were prepared using condensation of naphthaldehydes with imidazolines **1**, **4**, and **5** followed by hydrogenation of the C=C bond as shown in Scheme 1.

**2,2,5,5-Tetramethyl-4-[(E)-2-(1-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-1-oxyl (2a)**. Diisopropylamine, 2.7 mL, was added dropwise upon stirring to a solution of phenyl lithium, prepared from 2 mL of phenyl bromide and 0.27 g of lithium in 50 mL of anhydrous ether in an argon atmosphere. After stirring for 15 min, a solution of 1 g of imidazoline **1** in 15 mL of ether was added dropwise, and stirring was continued for more 15 min. The reaction mixture was cooled to 0 °C, and a solution of 2 g of  $\alpha$ -naphthaldehyde in 5 mL of ether was added in one portion, and the stirring was continued for 30 min. After that, 15 mL of water was added to the reaction mixture, ether solution was separated, the water solution was extracted with ether (3  $\times$  15 mL), the combined organic extract was dried with anhydrous MgSO<sub>4</sub>, the desiccant was filtered off, and the filtrate was stirred with 3 g of manganese dioxide for 15 min. Oxidant excess was filtered off, the solvent was removed in vacuum, and **2a** was isolated chromatographically on silica gel using 40:1

## SCHEME 1: Synthesis of 3-Imidazoline-Type Spin-Labeled Naphthalenes



chloroform–methanol mixture as eluent. Yield: 790 mg (42%), mp 114–115 °C (from hexane). Found, %: C 77.78, H 7.25, N 9.51; calculated for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O, %: C 77.78, H 7.21, N 9.55. UV (EtOH):  $\epsilon$  ( $\lambda$  = 226 nm) =  $3.0 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 252 nm) =  $1.73 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 334 nm) =  $1.44 \times 10^4$ . IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3079–2855;  $\nu$  (C=C) 1634;  $\nu$  (C=N) 1573. ESR (hexane):  $a_N$  = 13.86 G;  $a_H$  = 0.22 G;  $a_{13C}$  = 5.99 G;  $g$  = 2.0059.

**2,2,5,5-Tetramethyl-4-[(E)-2-(2-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-1-oxyl (2b).** **2b** was synthesized similarly, using  $\beta$ -naphthaldehyde with the same yield, mp 89 °C (hexane). Calculated for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O, %: C 77.78, H 7.21, N 9.55. IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3056–2867;  $\nu$  (C=C) 1634;  $\nu$  (C=N) 1586. UV (cyclohexane):  $\epsilon$  ( $\lambda$  = 219 nm) = 4448;  $\epsilon$  ( $\lambda$  = 265 nm) = 1992;  $\epsilon$  ( $\lambda$  = 275 nm) = 2215;  $\epsilon$  ( $\lambda$  = 305 nm) = 1485. ESR (hexane):  $a_N$  = 13.84 G;  $a_H$  = 0.23 G;  $a_{13C}$  = 6.00 G;  $g$  = 2.0058.

**2,2,5,5-Tetramethyl-4-[2-(1-naphthyl)ethyl]-2,5-dihydro-1H-imidazole-1-oxyl (3a).** A solution of 50 mg of **2a** in 10 mL of ethyl acetate was stirred in a hydrogen atmosphere in the presence of Pd/C catalyst for 3 h; the catalyst was then filtered off, and the filtrate was stirred with 1 g of manganese dioxide for 15 min, the oxidant excess was filtered off, and the solvent was removed in vacuum. Compound **3a** was purified by chromatography on alumina with benzene as eluent. Yield: 30 mg (58%), mp 104–106 °C. Found, %: C 77.23, H 8.14, N 9.39. Calculated for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O, %: C 77.25, H 7.85, N 9.48. UV (EtOH):  $\epsilon$  ( $\lambda$  = 272 nm) = 1065;  $\epsilon$  ( $\lambda$  = 283 nm) = 1985;  $\epsilon$  ( $\lambda$  = 293 nm) = 165. IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3060–2936;  $\nu$  (C=N) 1636. ESR (hexane):  $a_N$  = 13.86 G;  $a_H$  = 0.22 G;  $a_{13C}$  = 5.22 G;  $g$  = 2.0059.

**1,2,2,5,5-Pentamethyl-4-[(E)-2-(1-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-3-oxide (6a).** A solution of 0.85 g of imidazoline **4**, 1.85 g of  $\alpha$ -naphthaldehyde, and 0.54 g of sodium methylate in 15 mL of methanol was boiled for 6 h; then the solvent was removed in vacuum, and the residue was dissolved in 10 mL of water. The mixture was extracted with chloroform (3  $\times$  20 mL), the combined extract was dried with MgSO<sub>4</sub>, the solution was evaporated, and compound **6a** was isolated by chromatography of the residue on alumina using 4:1 hexane–ethyl acetate mixture as eluent. Yield: 0.5 g (32%), mp 92.5–94 °C (from hexane). Found, %: C 77.78, H 7.89, N 9.11.

Calculated for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O, %: C 77.89, H 7.84, N 9.0. UV (EtOH):  $\epsilon$  ( $\lambda$  = 250 nm) =  $1.39 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 356 nm) =  $2.78 \times 10^4$ . IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3059–2817;  $\nu$  (C=C) 1605;  $\nu$  (C=N) 1546. <sup>1</sup>H NMR ( $\delta$ , ppm): 1.39 (s, 6H); 1.45 (s, 6H, 2,5-(CH<sub>3</sub>)<sub>2</sub>); 2.41 (s, 3H, N–CH<sub>3</sub>); 6.51 (d,  $J$  = 15.8 Hz, 1H); 7.3–7.55 (m, 3H); 7.65–7.8 (m, 3H); 8.2–8.3 (m, 1H,  $\alpha$ -naphthyl); 9.40 (d,  $J$  = 15.8 Hz, 1H).

**1,2,2,5,5-Pentamethyl-4-[(E)-2-(2-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-3-oxide (6b).** **6b** was synthesized similarly, using  $\beta$ -naphthaldehyde with the same yield, mp = 116 °C (hexane). Found, %: C 77.78, H 7.78, N 8.95. Calculated for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O, %: C 77.89, H 7.84, N 9.0. UV (EtOH):  $\epsilon$  ( $\lambda$  = 210 nm) =  $3.40 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 230 nm) =  $2.31 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 248 nm) =  $1.74 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 257 nm) =  $0.29 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 280 nm) =  $1.48 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 290 nm) =  $1.54 \times 10^4$ ;  $\epsilon$  ( $\lambda$  = 343 nm) =  $2.97 \times 10^4$ . IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3050–2810;  $\nu$  (C=C) 1609;  $\nu$  (C=N) 1528. <sup>1</sup>H NMR ( $\delta$ , ppm): 1.08 (s, 6H); 1.45 (s, 6H, 2,5-(CH<sub>3</sub>)<sub>2</sub>); 1.95 (s, 3H, N–CH<sub>3</sub>); 6.91 (d,  $J$  = 16.2 Hz, 1H); 7.19–7.23 (m, 3H); 7.52–7.68 (m, 4H,  $\beta$ -naphthyl); 9.14 (d,  $J$  = 16.2 Hz, 1H).

**2,2,5,5-Tetramethyl-4-[(E)-2-(1-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-1-oxyl-3-oxide (7a), (Method A).** A solution of 0.5 g of **5** and 0.66 g of  $\alpha$ -naphthaldehyde in 10 mL of anhydrous dioxane was added dropwise for 30 min to a suspension of 0.45 g of sodium hydride in 10 mL of anhydrous dioxane under an argon atmosphere on cooling to 0 to –5 °C upon stirring. The mixture was stirred for 40 min at 0 °C and for 24 h at room temperature. Half of the solvent was removed in vacuum, the residue was diluted with 50 mL water, and the resulted mixture was extracted with chloroform (3  $\times$  15 mL). The combined extract was dried with MgSO<sub>4</sub>, the solvent was removed in vacuum, and compound **7a** was purified by chromatography on alumina with chloroform as eluent. Yield: 0.52 g (58%), mp 173–174 °C (from hexane–ethyl acetate mixture). Found, %: C 73.55, H 6.84, N 8.85. Calculated for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>, %: C 73.76, H 6.84, N 9.05. IR (cm<sup>-1</sup>):  $\nu$  (C–H) 3053–2857;  $\nu$  (C=C) 1599;  $\nu$  (C=N) 1527. ESR (dodecane):  $a_N$  = 13.77 G;  $a_H$  = 0.22 G;  $a_{13C}$  = 5.59 G;  $g$  = 2.0060.

**(Method B).** A solution of 0.86 g of 2,2,4,4,5,5-pentamethyl-2,5-dihydro-1H-imidazol-1-ol 3-oxide and 1.2 g of  $\alpha$ -naphthaldehyde in 15 mL of isopropanol was added dropwise upon

stirring to a suspension of sodium isopropoxide, prepared from 0.12 g of sodium and 15 mL of isopropanol during 20 min. The mixture was stirred for 24 h; after that the main part of solvent was removed in vacuum, and the residue was diluted with 50 mL of water. The sticky precipitate was filtered off, washed with water, dried on air, and then dissolved in 30 mL of chloroform; the solution was stirred with 3 g of manganese dioxide for 15 min. Oxidant excess was filtered off, filtrate was evaporated, and compound **7a** (yield 0.23 g, 15%) and **2,2,5,5-tetramethyl-4-[(E)-2-(1-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-3-oxide (9a)** were isolated by chromatography on alumina with chloroform as eluent. Yield of **9a**: 0.15 g (10%). Found, %: C 77.82, H 7.53, N 9.55. Calculated for  $C_{19}H_{22}N_2O$ , %: C 77.52, H 7.53, N 9.52. IR ( $cm^{-1}$ ):  $\nu$  (N—H) 3262;  $\nu$  (C—H) 3055–2932;  $\nu$  (C=C, C=N) 1519.  $^1H$  NMR ( $\delta$ , ppm): 1.54 (s, 6H); 1.65 (s, 6H, 2,5-(CH<sub>3</sub>)<sub>2</sub>); 2.02 (broad s., 1H, N—H), 6.78 (d,  $J = 16.0$  Hz, 1H); 7.4–7.55 (m, 3H); 7.76–7.85 (m, 3H); 8.2–8.25 (m, 1H,  $\alpha$ -naphthyl); 9.25 (d,  $J = 16.0$  Hz, 1H).

**2,2,5,5-Tetramethyl-4-[(E)-2-(2-naphthyl)vinyl]-2,5-dihydro-1H-imidazole-1-oxyl-3-oxide (7b)**. **7b** was synthesized according to method **A** from  $\beta$ -naphthaldehyde with the same yield, mp 172–173 °C (hexane–ethyl acetate). Found, %: C 74.09, H 6.80, N 9.01. Calculated for  $C_{19}H_{21}N_2O_2$ , %: H 73.76, H 6.84, N 9.05. UV (EtOH):  $\epsilon$  ( $\lambda = 211$  nm) =  $3.39 \times 10^4$ ;  $\epsilon$  ( $\lambda = 232$  nm) =  $2.20 \times 10^4$ ;  $\epsilon$  ( $\lambda = 281$  nm) =  $1.30 \times 10^4$ ;  $\epsilon$  ( $\lambda = 292$  nm) =  $1.33 \times 10^4$ ;  $\epsilon$  ( $\lambda = 348$  nm) =  $2.63 \times 10^4$ . IR ( $cm^{-1}$ ):  $\nu$  (C—H) 3019–2935;  $\nu$  (C=C) 1604;  $\nu$  (C=N) 1522. ESR (hexane):  $a_N = 13.85$  G;  $a_H = 0.23$  G;  $a_{13C} = 5.64$  G;  $g = 2.0061$ .

**2,2,5,5-Tetramethyl-4-[2-(1-naphthyl)ethyl]-2,5-dihydro-1H-imidazole-1-oxyl-3-oxide (8a)**. A solution of 80 mg of **7a** in 10 mL of ethyl acetate was stirred in a hydrogen atmosphere for 5 h with Pd/C catalyst, the catalyst was then filtered off, and the filtrate was stirred with 1 g of manganese dioxide for 20 min. Oxidant excess was filtered off, and the solvent was removed at reduced pressure. Nitroxide **8a** was isolated from the residue by chromatography on silica gel using a 50:1 chloroform–methanol mixture as eluent. Yield: 14 mg (17%), mp 102–106.5 °C (hexane). Found, %: C 73.25, H 7.51, N 8.98. Calculated for  $C_{19}H_{23}N_2O_2$ , %: C 73.28, H 7.44, N 9.00. UV (EtOH):  $\epsilon$  ( $\lambda = 224$  nm) =  $6.75 \times 10^4$ ;  $\epsilon$  ( $\lambda = 273$  nm) =  $2155$ ;  $\epsilon$  ( $\lambda = 283$  nm) =  $3375$ ;  $\epsilon$  ( $\lambda = 294$  nm) =  $1190$ . IR ( $cm^{-1}$ ):  $\nu$  (C—H) 3060–2936;  $\nu$  (C=N) 1596. ESR (dodecane):  $a_N = 13.91$  G;  $a_H = 0.22$  G;  $a_{13C} = 5.68$  G;  $g = 2.0059$ .

**2,2,5,5-Tetramethyl-4-[2-(2-naphthyl)ethyl]-2,5-dihydro-1H-imidazole-1-oxyl-3-oxide (8b)**. **8b** was synthesized similarly with the yield 50%, mp 79–80 °C. Found, %: C 73.25, H 7.59, N 8.98. Calculated for  $C_{19}H_{23}N_2O_2$ , %: C 73.28, H 7.44, N 9.00. UV (EtOH):  $\epsilon$  ( $\lambda = 224$  nm) =  $5.37 \times 10^4$ ;  $\epsilon$  ( $\lambda = 276$  nm) =  $0.52 \times 10^4$ ;  $\epsilon$  ( $\lambda = 304$  nm) =  $0.06 \times 10^4$ ;  $\epsilon$  ( $\lambda = 319$  nm) =  $0.04 \times 10^4$ . IR ( $cm^{-1}$ ):  $\nu$  (C—H) 3047–2863;  $\nu$  (C=N) 1598. ESR (hexane):  $a_N = 13.97$  G;  $a_H = 0.23$  G;  $a_{13C} = 5.67$  G;  $g = 2.0060$ .

**1,2,2,5,5-Pentamethyl-4-[2-(1-naphthyl)ethyl]-2,5-dihydro-1H-imidazole-3-oxide (10a)** and **1,2,2,5,5-Pentamethyl-4-[2-(1-naphthyl)ethyl]-2,5-dihydro-1H-imidazole (11a)**. A solution of 0.3 g of **6a** in ethyl acetate was stirred in a hydrogen atmosphere with Pd/C catalyst for 5 h, the catalyst was then filtered off, and the solvent was removed at reduced pressure. Compounds **10a** and **11a** were separated by chromatography on alumina using 4:1 hexane–ethyl acetate mixture as eluent.

**10a**. Yield: 210 mg (70%), mp 102–103 °C (hexane). Found, %: C 77.11, H 8.43, N 9.01. Calculated for  $C_{20}H_{26}N_2O$ , %: C

77.38; H 8.44; N 9.02. IR ( $cm^{-1}$ ):  $\nu$  (C—H) 3066–2814;  $\nu$  (C=N) 1602.  $^1H$  NMR ( $\delta$ , ppm): 0.84 (s, 6H); 1.35 (s, 6H, 2,5-(CH<sub>3</sub>)<sub>2</sub>); 2.23 (s, 3H, N—CH<sub>3</sub>); 2.63 (m, 2H); 3.49 (m, 2H); 7.2–7.8 (m, 7H,  $\alpha$ -naphthyl).

**11a**. Mp about room temperature. Found  $m/z = 294.20972$ , calcd for  $C_{20}H_{26}N_2$   $m/z = 294.20757$ . IR ( $cm^{-1}$ ):  $\nu$  (C—H) 3065–2796;  $\nu$  (C=N) 1651.  $^1H$  NMR ( $\delta$ , ppm): 0.97 (s, 6H); 1.23 (s, 6H, 2,5-(CH<sub>3</sub>)<sub>2</sub>); 2.25 (s, 3H, N—CH<sub>3</sub>); 2.50 (m, 2H); 3.42 (m, 2H, CH<sub>2</sub>—CH<sub>2</sub>); 7.55–7.65 (m, 3H); 7.71–7.8 (m, 3H); 8.00–8.09 (m, 1H,  $\alpha$ -naphthyl).

**1,2,2,5,5-Pentamethyl-4-[2-(2-naphthyl)ethyl]-2,5-dihydro-1H-imidazole-3-oxide (10b)** and **1,2,2,5,5-tetramethyl-4-[2-(2-naphthyl)ethyl]-2,5-dihydro-1H-imidazole (11b)** were synthesized and separated similarly.

**10b**. Yield: 15%, turns crystalline below 0 °C.  $^1H$  NMR ( $\delta$ , ppm): 0.6 (s, 6H); 1.4 (s, 6H); 1.65 (s, 3H); 2.5 (t,  $J = 7.8$  Hz, 2H); 3.3 (t, 2H); 7.6–7.7 (m, 7H).

**11b**. Yield: 25%, turns crystalline below 0 °C.  $^1H$  NMR ( $\delta$ , ppm): 0.8 (s, 6H); 1.4 (s, 6H); 2.1 (s, 3H); 2.4 (t, 2H); 3.3 (t,  $J = 7.5$  Hz, 2H); 7.5–7.6 (m, 7H).

A total of 14 target compounds were synthesized that covered most of the 16 possible combinations of 4 structural elements:  $\alpha$ -naphthyl vs  $\beta$ -naphthyl, saturated vs unsaturated two-carbon bridge, imino vs nitronyl radical, and paramagnetic RNO' vs diamagnetic RCH<sub>3</sub> imidazoline moiety. Although we failed to obtain two compounds, **1,2,2,5,5-pentamethyl-4-[(E)-2-(1-naphthyl)vinyl]-2,5-dihydro-1H-imidazole** and **1,2,2,5,5-pentamethyl-4-[(E)-2-(2-naphthyl)vinyl]-2,5-dihydro-1H-imidazole**, the available set of model objects proved sufficient.

IR spectra were taken in KBr pellets (concentration 0.25%, pellet thickness 1 mm) on a Bruker IFS-66 spectrometer. UV spectra were taken in ethanol and methanol solutions on a Specord M-40 spectrometer. NMR  $^1H$  and  $^{13}C$  spectra were taken using Bruker WP 200SY, Bruker AC 200, and Bruker AV 300 spectrometers for 5–10% solution in CDCl<sub>3</sub>, (CD<sub>3</sub>)<sub>2</sub>CO, C<sub>6</sub>D<sub>6</sub>, and CCl<sub>4</sub> using HMDS as the internal standard. Melting points were determined using a Boetius melting point apparatus. ESR spectra were taken in dilute degassed alkane solutions on a Bruker EMX spectrometer.

The reactions were monitored using thin-layer chromatography on Silufol UV-254 sheets. Preparative chromatography was performed using silica gel 0.005–0.04 mm; column chromatography was performed using silica gel 0.063–0.200 mm "Merck" as well as neutral Al<sub>2</sub>O<sub>3</sub>, Brockman activity II. The solvent was removed under reduced pressure using a water-jet pump.

**3.2. Radiofluorescence: MARY and OD ESR.** Radiofluorescence experiments were performed on the experimental setup for taking magnetic field effects in the recombination fluorescence of a nonpolar solution under X-irradiation described elsewhere for MARY<sup>37</sup> and OD ESR<sup>35</sup> modes of operation. The setup is based around a Bruker ER-200D ESR spectrometer, equipped with an X-ray tube BSV-27Mo (40 kV  $\times$  20 mA) for sample irradiation and a PMT (FEU-130) for light detection. The sample, about 1 mL of degassed (3–5 freeze–pump–thaw cycles) alkane solution in a quartz cuvette, is put inside the resonator of the spectrometer, standing on the top end of a quartz light guide passing the light to the PMT. The applied static magnetic and (for OD ESR) MW fields are controlled from the Bruker ER-200D spectrometer; the static field is modulated at 12.5 kHz with an amplitude of up to 10 G and (for MARY) shifted to "negative" values by 50 G using a separate coil with a dedicated power supply. The PMT signal is fed into a Stanford Research System SRS-810 Lock-in Amplifier; its output is

stored into a computer that sweeps the static field and performs statistical averaging. A typical spectrum takes 10–20 scans with sweep time of 200–500 s. The sensitivity of the setup with respect to average concentration of radical pairs/triads is down to 100 species per sample; the sensitivity of the methods with respect to lifetime of the radical ions is down to nanoseconds for MARY and down to 100 ns for OD ESR in a stationary experiment.

**3.3. Chromato-Mass-Spectrometric Analysis (CMSA).** The samples for CMSA were prepared and irradiated as for the radiofluorescence experiments; the solution was sampled and measured on an Agilent Technologies 6890N/5973N GC-MS System operated in the gradient temperature increase mode with starting temperature 50 °C, ending temperature 250 °C, and with helium as the carrier gas. The products of photodecomposition were analyzed in a similar manner.

**3.4. Photochemical Measurements.** Photochemical measurements were performed using stationary photolysis of liquid solution at room temperature with spectrophotometric registration. Stationary photolysis was carried out using a high-pressure mercury lamp DRSH 500 with a combination of high-pass and low-pass glass filters to select the line at 313 nm. Optical absorption spectra were taken on a Hewlett-Packard HP 8354 spectrophotometer. The solutions were prepared using analytical grade solvents after additional purification. When required, the samples were bubbled with argon to remove oxygen. The intensity of the mercury line at 313 nm needed for calculation of quantum yields was determined in a standard way using a potassium ferrioxalate ( $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ ) actinometer.

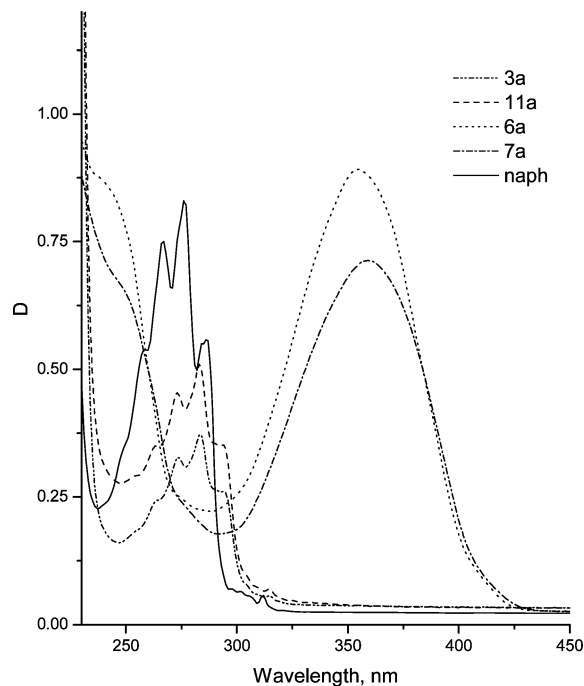
**3.5. Fluorescence.** Fluorescence measurements were taken on a stationary setup at room temperature. The fluorescence was excited with the line  $\lambda = 313$  nm of a DRSH 500 mercury lamp using frontal illumination of the sample. Fluorescence spectra were recorded in the region 320–700 nm using a FEU-119 photomultiplier tube and an H-307/1 XY recorder. Fluorescence lifetimes were estimated by comparing quantum yields from air-saturated and argon-bubbled samples.

**3.6. Cyclic Voltammetry (CVA).** Cyclic voltammograms were measured on a CVA-1  $\mu_B$  electrochemical system (Bulgaria) equipped with a LAB-MASTER polyfunctional interface (Budker Institute of Nuclear Physics, Novosibirsk, Russia) providing complete digital control of the system. The measurements were carried out in the mode of triangular pulse potential sweep in the range of sweep rates  $100 \text{ mV s}^{-1} < \nu < 20000 \text{ mV s}^{-1}$ . A standard three-electrode electrochemical cell for CV with a working volume of 5 mL was used, equipped with a salt bridge filled with a supporting electrolyte solution in MeCN to connect the working volume and the reference electrode. The working electrode was a stationary spherical Pt electrode with a surface area of 8 mm<sup>2</sup>, a Pt spiral was used as the auxiliary electrode, and a saturated aqueous calomel electrode (SCE) served as the reference electrode. The supporting electrolyte was  $Et_4NClO_4$  (0.1 mol L<sup>-1</sup>). Oxygen was removed by bubbling argon through the working solution. The concentration of depolarizer was  $1 \times 10^{-3}$  mol L<sup>-1</sup>.

## 4. Results and Discussion

### 4.1. General Characteristics of the Target Compounds.

**4.1.1. Optical Absorption.** As recombination of the radical ion pairs in the described experimental setting is monitored by optical detection, the optical characteristics of the target compounds are very important. Unfavorable optical absorption spectra could lead to internal absorption of light in the sample and render an otherwise acceptable system useless.

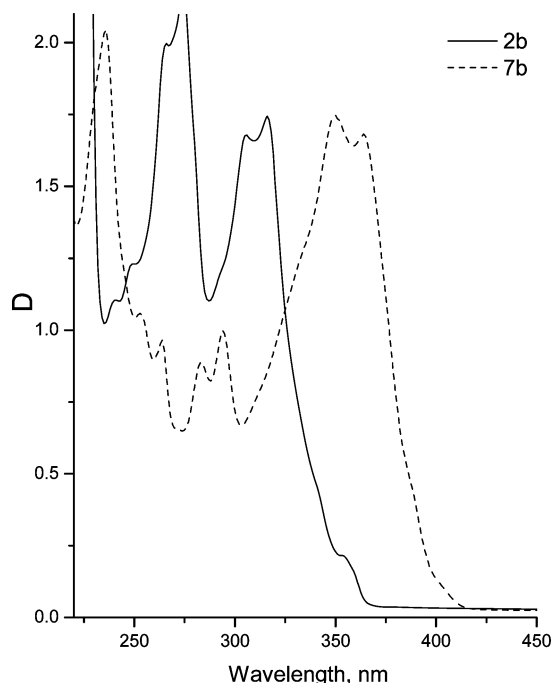


**Figure 1.** Optical absorption spectra of the representative radicals **3a** and **7a** vs their diamagnetic analogues **11a** and **6a** and naphthalene, respectively, cyclohexane solution, concentration  $5 \times 10^{-4} \text{ M}^{-1}$ .

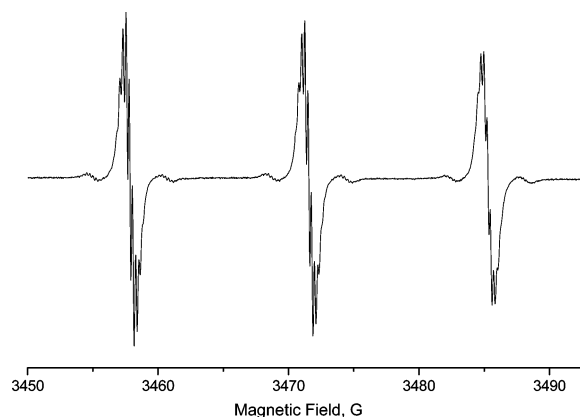
Radicals of the 3-imidazoline family RNO and their diamagnetic counterparts RCH<sub>3</sub> have an isolated nitroxyl or amine group that does not produce pronounced specific absorption bands.<sup>39</sup> For this reason UV–vis spectra of radicals A-Sp-RNO' and their diamagnetic analogues A-Sp-RCH<sub>3</sub> looked identical for all available pairs "A-Sp-RNO'/A-Sp-RCH<sub>3</sub>" of the prepared compounds (see Figure 1).

When compared to the unsubstituted naphthalene, the compounds with single-bond bridge Sp (corresponding to aliphatic substitution of the aromatic nucleus) have a slight long-wave shift (about 10 nm for the pair naphthalene/**3a**). The compounds with double bond C=C in the bridge Sp, as expected, have absorption spectra that are substantially shifted to longer wavelengths, with the band having no characteristic vibrational structure. The shift is different for the nitron and imine systems (long-wave maxima at 364 nm for **7b** and 314 nm at **2b** as compared to 280 nm for naphthalene; the spectra are shown in Figure 2) and reflects the gradual extension of the  $\pi$ -system upon moving from the unsubstituted naphthalene to the imine and then nitron-type system. The extinction coefficients for the shorter wavelength band for all compounds are of the order of  $10^4$  and do not differ significantly from the extinction of naphthalene. The actual numbers are given in the Experimental section.

As optical absorption spectra directly reflect the electronic structure of the compounds, it can be expected that compounds with saturated bridge **3**, **8**, **9**, **10**, and **11ab** will indeed have the properties of the  $\pi$ -systems (where the charge and spin is delocalized upon charge capture in the course of radiolysis) similar to the properties of the  $\pi$ -system of naphthalene, a commonly used acceptor and luminophore for spin chemistry under X-irradiation. Compounds **2**, **6**, and **7ab** would probably show delocalization of the charge over the extended system of unsaturated bonds involving the naphthalene, bridge, and imidazoline moieties. In both cases the nitroxyl group is not included into conjugation, as can be seen from the characteristic ESR spectra of all the paramagnetic compounds (Figure 3). All spectra show the dominant triplet with a splitting of about 14



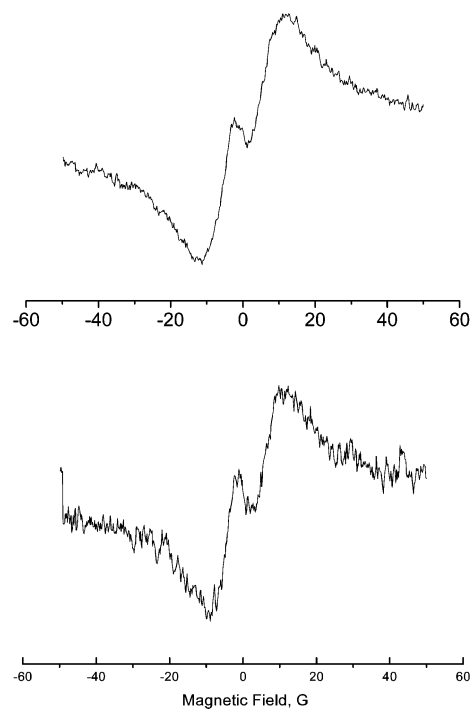
**Figure 2.** Optical absorption spectra of radicals **7b** and **2b** with and without oxygen at third position of imidazoline ring–nitrone–imine-type system, respectively, cyclohexane solution.



**Figure 3.** Typical ESR spectrum of obtained radicals, the spectrum of compound **2a**, hexane solution.

G from the coupling with the  $^{14}\text{N}$  nucleus of the nitroxyl group, additional minor splittings of 0.22 G from the 12 protons of the four guarding methyl groups in the second and fifth positions of the imidazoline cycle, and shoulders with a splitting of about 6 G from  $^{13}\text{C}$  in natural abundance in the four guarding methyls. No signs of farther delocalization can be seen in the spectra, which confirms that the unpaired electron in all our target compounds is indeed confined to the nitroxyl group as intended.

**4.1.2. Magnetic Field Effects for Diamagnetic Compounds with Saturated Bridges.** As the first step in the radiolytic creation of a three-spin system is the charge capture by a spin-labeled acceptor to form a biradical ion, it is critically important to figure out how the performed substitution in the naphthalene ring alters its charge-accepting properties. When devising the described systems, it was suggested that the electron released upon solvent ionization under X-irradiation would be captured by the naphthalene nucleus. However, the additional functional groups introduced into the molecule upon its chemical modification can compete for electrons. Thus, it is known<sup>40,41</sup> that imidazoline nitrones similar to substituents introduced into naphthalene in our compounds form rather stable radical anions. The question



**Figure 4.** MARY spectra from pairs consisting of radical anions of naphthalene (top) and **10a** (bottom) with squalane cation radical as the counterion.

as to which group in the molecule gets the electron is justified if the fragments in question are not conjugated. Among our target compounds these are the saturated bridge compounds **8–11**.

To answer this question, we compared MARY and OD ESR spectra of radical ion pairs that have as the radical anion partner the radical anion of either naphthalene or its diamagnetic derivative **10a**.

The peak-to-peak half-width of the wings of MARY spectrum reflects the average hyperfine coupling in the radical ions of the pair partners<sup>42</sup>

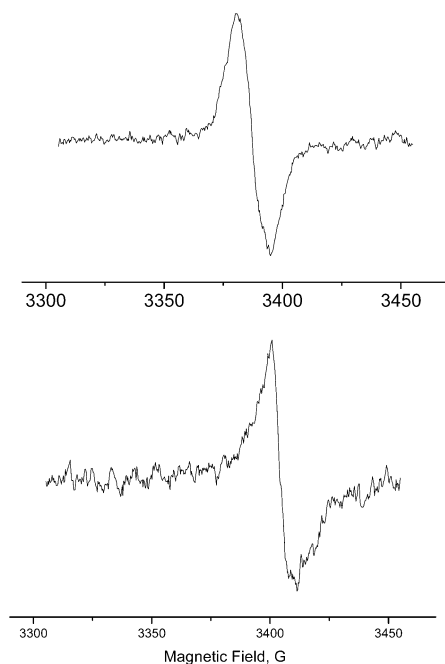
$$B_{1/2} = 2 \frac{A_1^2 + A_2^2}{A_1 + A_2}$$

where

$$A_1 = \sum_i a_i^2 I_i(I_i + 1), A_2 = \sum_j a_j^2 I_j(I_j + 1)$$

Here  $I_i$  is the spin of the  $i$ th magnetic nucleus in the first partner of the pair,  $a_i$  is the hyperfine coupling constant with this nucleus,  $I_j$ ,  $a_j$  are the corresponding values for the second partner. Figure 4 shows experimental MARY spectra for the pairs consisting of the radical anion of either naphthalene or **10a** and the radical cation of squalane used as the counterion of the pair. As can be seen, the spectra are quite similar. The measured peak-to-peak half-widths are equal to about  $B_{1/2} = 10$  G, which corresponds to the calculated width  $B_{1/2} = 9.15$  G. For the radical anion of naphthalene the effective coupling  $A_1$  was calculated using the known couplings  $a_{\text{H1}}$ ,  $a_{\text{H2}}$  with the two groups of equivalent protons:<sup>43</sup>  $a_{\text{H1}} = 4.95$  G and  $a_{\text{H2}} = 1.85$  G, for the exchange-narrowed radical cation of squalane  $A_2 \approx 0$ .<sup>44</sup>

OD ESR spectra to first approximation are a superposition of the ESR spectra of the pair partners and thus can provide the second moments of the spectra, i.e., their widths, and the



**Figure 5.** OD ESR spectra for the pairs consisting of radical anions of naphthalene (top) and **10a** (bottom) with squalane cation radical as the counterion.

individual splittings on magnetic nuclei if these can be resolved. The second moment is given by the following expression

$$\sigma^2 = \frac{1}{3} \sum_i a_i^2 I_i(I_i + 1)$$

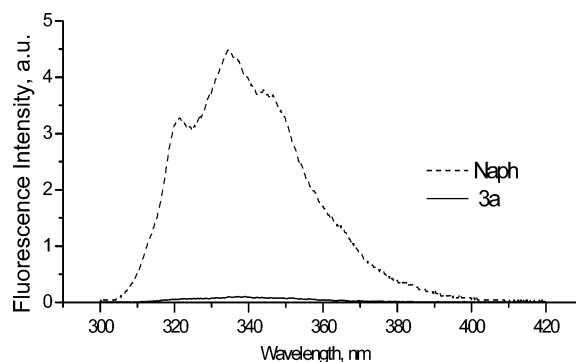
According to results of the work,<sup>40</sup> the hyperfine coupling constants for the radical anion of the corresponding nitron are  $a_N = 13.3$  G and  $a_H = 9.2$  G, producing second moment  $\sigma = 11.8$  G. By use of the reference data for the radical anion of naphthalene,<sup>43</sup> we obtain  $\sigma = 5.3$  G. The two moments can be seen to be rather different, and furthermore, had the spectrum come from the radical anion of nitron, the rather large splitting at the  $^{14}\text{N}$  nucleus would have been observed.<sup>40</sup> Experimentally for the discussed pairs of the radical anion of naphthalene or **10a** with the radical cation of squalane we see similar OD ESR spectra with the width corresponding to the naphthalene radical anion and no splitting, see Figure 5. Thus the electron is indeed captured by the naphthalene nucleus, at least for the studied systems.

#### 4.2. Paramagnetic Compounds with Saturated Bridge.

Since the diamagnetic counterparts (**10a,b**; **11a,b**) form radical anions analogous to the radical anion of naphthalene, and taking into account that the nitroxyl group bearing the unpaired electron has much poorer electron affinity than the naphthalene nucleus,<sup>39</sup> it would be expected that the paramagnetic compounds with saturated bridge also form naphthalene-centered radical anions. However, no magnetosensitive signal was observed in any of these systems, which was traced down to quenching of the fluorescence from the excited state of naphthalene presumably forming upon recombination.

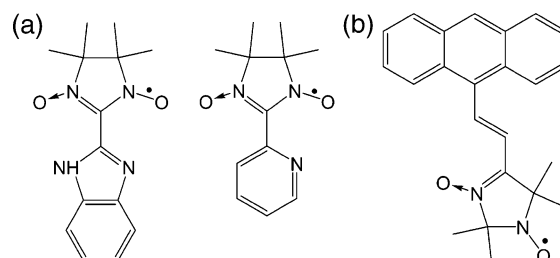
Nitroxyl radicals generally have no intrinsic fluorescence, i.e., nitroxyl group is not a luminophore per se.<sup>45</sup> Only in special cases, i.e., for several 2-imidazoline radicals directly conjugated with an aromatic system (Scheme 2a), has a very weak solid-phase fluorescence been reported.<sup>46</sup>

It is known that direct covalent bonding of a 3-imidazoline radical having an isolated nitroxyl group with anthracene



**Figure 6.** Fluorescence spectra of naphthalene and **3a**. Quenching of **3a** leads to quantum yield 45 times lower than for free naphthalene.

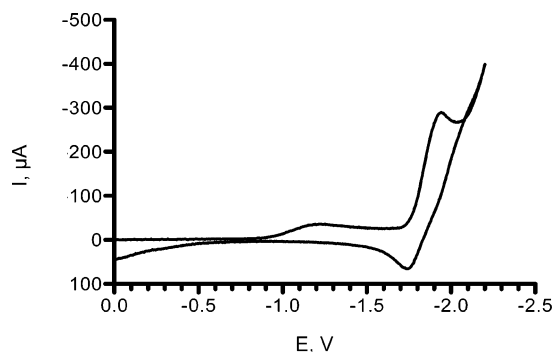
#### SCHEME 2: (a) Stable 2-Imidazoline Radicals; (b) Stable 3-Imidazoline Radical



(Scheme 2b) leads to substantial, by a factor of about 50, quenching of fluorescence from anthracene.<sup>34</sup> The diamagnetic analogues ( $>\text{N}-\text{O}^{\cdot-} \rightarrow >\text{N}-\text{OH}$ ) have absorption spectra similar to their paramagnetic counterparts but do not produce such a quenching. This rules out the effective mechanism of intramolecular dipole-dipole quenching caused by overlapping emission bands of the emitter and absorption bands of the quencher. A quenching mechanism has been suggested<sup>47</sup> specifically related to paramagnetism of the dihydroimidazoline moiety, the so-called distant electron-exchange quenching, leading to local relaxation of the excited singlet state of the emitter into its ground state without the actual energy transfer.

Fluorescence of luminophores with exceptionally long fluorescence lifetimes, i.e., pyrene, can be completely quenched by the nitroxyl group, which is used in biochemical studies. When the nitroxyl moiety of the corresponding spin-labeled luminophore reacts with antioxidants (ascorbic acid, quercetin) or traps active free radicals ( $\text{NO}$ ,  $\text{O}_2^{\cdot-}$ ), its ESR spectrum disappears with a parallel rise in fluorescence, which can be measured with higher sensitivity as compared to ESR.<sup>48</sup> A reciprocal process of using fluorescing nitrones as spin traps and trading fluorescence for ESR signal has also been recently described.<sup>49</sup> The paramagnetic quenching of luminescence was also demonstrated for transition metal complexes. Thus, the work<sup>50</sup> studied the efficiency of quenching the luminescence from a free porphyrin half of a porphyrin dimer with one site occupied by a paramagnetic  $\text{Cu}^{2+}$  ion as a function of the length of the connecting bridge and suggested the quenching of the singlet excited state due to increased rate of intersystem crossing in the presence of the paramagnetic center.

In our systems we did not find magnetic field effects from the pairs "solvent radical cation/radical anion of the paramagnetic compound" from all available stable radicals with saturated bridge, compounds **3ab**, **8ab**, **10ab**, and decided to directly check the availability of fluorescence by comparing the compound **3a** with its diamagnetic counterparts **11ab** and free naphthalene. As Figure 6 shows, the fluorescence is indeed substantially quenched in the paramagnetic target compounds.



**Figure 7.** CVA curve for electrochemical reduction of **10b** in acetonitrile, ramp rate 5 V/s rel. SCE.

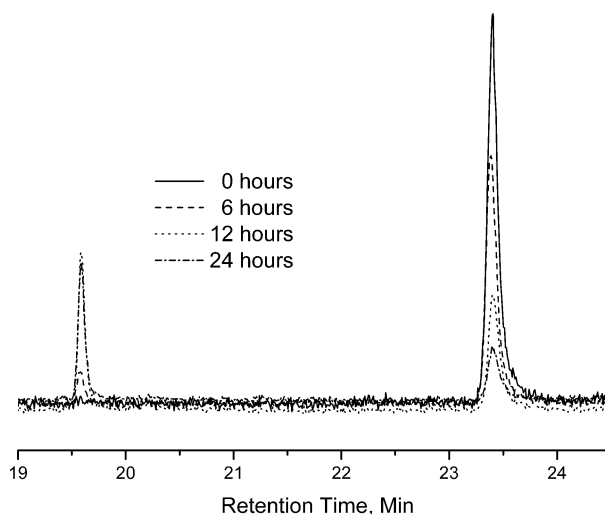
The measured fluorescence quantum yield  $\varphi(\mathbf{3a}) = 0.005$ , which is 45 times lower than that for naphthalene,  $\varphi(\text{C}_{10}\text{H}_8) = 0.23$ , and the fluorescence lifetime  $\tau(\mathbf{3A}) = 2.3$  ns is shorter than for naphthalene,  $\tau(\text{C}_{10}\text{H}_8) = 100$  ns, by about the same factor, which points to an intramolecular mechanism of the quenching.

Following the authors of the ref 47, paramagnetic quenching should be explained by exchange interaction of the excited state of naphthalene with the nitroxyl group. However, the through-bond exchange in this case is not expected to be effective, as the two fragments are separated by five  $\sigma$ -bonds C–C. Another possibility is a through-space exchange, which requires close approach of the two fragments. Apparently, this is geometrically allowed by the combination of a C–C bridge and 3-imidazoline structure of the radical. The favorability of such folded conformation was verified by NMR spectra of the diamagnetic analogues that show differences abnormal for imidazolines in chemical shifts of the two groups of nonequivalent methyl protons in the second and fifth positions of the imidazoline ring. While typical values are  $\delta_1 = 1.39$ ;  $\delta_2 = 1.45$ , we observed shifts  $\delta_1 = 0.7$  and  $\delta_2 = 1.3$  for **10b**. Such a large difference in chemical shifts can be explained by an asymmetric shielding provided by the naphthalene nucleus as it folds toward one of the methyl groups, that is, toward the nitroxyl fragment.

Thus the absence of magnetic field effect in the pairs (solvent<sup>+</sup> / <sup>-</sup>**3a**) should be explained not by the lower quantum yield of **3a** (this is sufficient to be registered at our setup) but rather by a strong direct (contact) exchange interaction in the forming biradical anion, washing away the spin correlation between the “radical ionic” electrons in the triad. This is an unwelcome feature that was not encountered in the 2-imidazoline radicals studied in ref 21, apparently resulting from the unfavorable combination of the structures of the bridge and the radical.

**4.3. Compounds with Unsaturated Bridge.** Compounds with double bond in the bridge C=C have rigid structures that block the direct contact exchange quenching discussed earlier. Nevertheless, in the studied systems no magnetosensitive signal was observed even for the diamagnetic compounds. To figure out at what stage of the radiation chemical experiment things go wrong, we checked them in sequence: electron capture, recombination (back electron transfer), and emitting the excess energy from the product of recombination.

The first stage that the system has to pass is electron capture. Figure 7 shows CVA of the diamagnetic **10b** in acetonitrile at negative, i.e., reduction, potentials. The direct wave (top curve in the figure) corresponds to electron transfer from anode to the molecule; the back wave (lower trace) shows the return of the electron to anode. The reversible wave indicates that the compound forms stable enough radical anions, and from the



**Figure 8.** Consecutive chromatograms of X-irradiated cyclohexane solution of **6b**. The 23.5-min peak and the 19.5-min peak correspond to the initial compound and the reaction product, respectively.

used sweep rates of 5 V/s, we can estimate the lifetime of the radical anions in these conditions as at least several milliseconds.

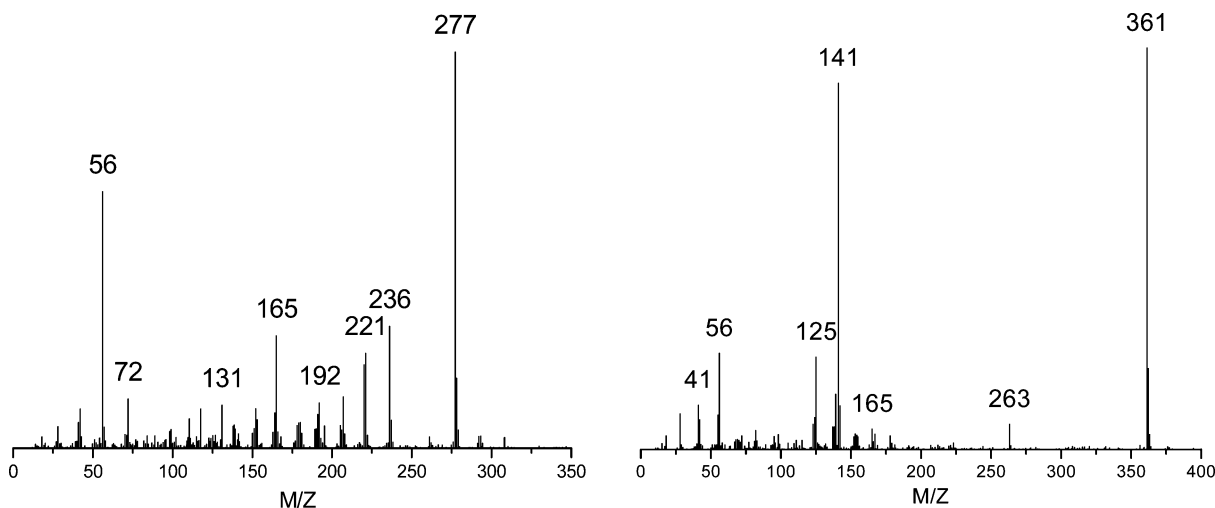
As typical recombination time in the systems under study is nanoseconds, we can state that these compounds capture electrons to form stable enough radical anions. Thus, the absence of luminescence should be traced to channels of energy release other than emitting light. The most probable candidate for this is a chemical reaction. As this would probably give some specific products, we analyzed the samples after irradiation by chromato-mass-spectrometry.

Figure 8 shows consecutive chromatograms for irradiated **6b** in cyclohexane for 0, 6, 12, and 24 h. As can be seen, the concentration of the starting compound gradually decreases, and a (single) product of radiolysis builds up.

Figure 9 shows mass-spectra taken at the peaks of the starting compound and the product. It can be concluded that X-irradiation leads to formation of a compound with molecular ion having the mass equal to the sum of the masses of the starting compound and the solvent, cyclohexane. The corresponding optical spectra show the decrease in the intensity of the long-wave absorption band and the appearance of a new band at shorter wavelength typical for naphthalene, indicating the shortening of the  $\pi$ -system. A sensible explanation of these facts is addition of cyclohexane to the double bond of the bridge within the radical pair as shown in Scheme 3. As the partners of the radical ion pair approach each other to recombine, a proton is shot from radical cation of cyclohexane to the biradical anion instead of electron transfer. It is known that the radical cations of alkanes donate protons at diffusion-controlled rates in the presence of even such moderately strong proton acceptors as alcohols,<sup>51</sup> and the radical anions of alkenes are fairly good proton acceptors.<sup>52</sup>

In this particular case, the driving and orienting force of the proton transfer is the stability of the naphthyl-type radical forming upon transfer of proton to the farthest from the naphthalene nucleus carbon atom of the C=C bridge. The formation of the product observed in mass spectra then proceeds as a covalent bonding of the two neutral radicals that happen to be next to each other. This harpooning mechanism explains the formation of a single product as revealed by the chromatogram: presumably selective addition of cyclohexane to the closest to the naphthalene nucleus carbon atom of the C=C bridge.

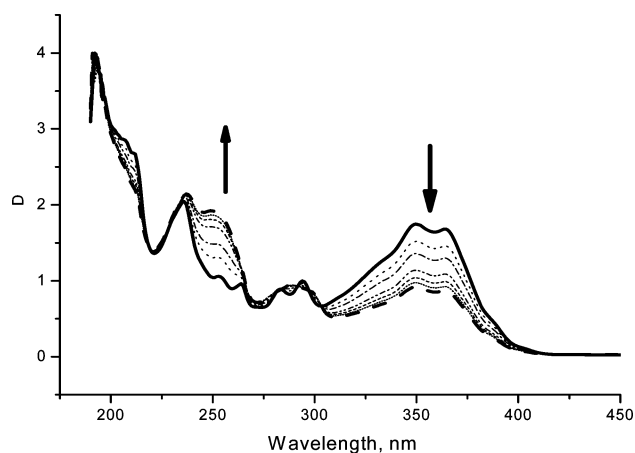




**Figure 9.** Mass spectrum of **6b** (left) and the product of its radiolysis (right). The observed shift of the main mass ( $361 - 277 = 84$ ) is equal to molecular weight of cyclohexane.

It is known that the efficiency of electron capture for the used concentrations of acceptor ( $10^{-4}$  M) is about 10%. The remaining primary pairs “electron/solvent radical cation” recombine to form electronically excited molecules of cyclohexane that are prone to decay forming neutral alkyl radicals.<sup>53–60</sup> An irradiated alkane solution thus always contains a certain stationary concentration of alkyl radicals. It can be thought that our compound in its initial neutral state can trap these radicals to form the observed product, which is thus formed outside the radical pair. However, this route would produce a complex mixture of the products of addition of various alkyl radicals at both atoms of the bridge. Experimentally we observed the products of solvent radiolysis (hexyl-cyclohexane, bicyclohexane, cyclohexyl-cyclohexene, dodecane, cyclohexanone, etc.) and separately a single product of radiolysis of the target compound. This fact strongly supports the suggested explanation of the reaction inside the radical ion pair.

However, recombination with the radical anions of the target compounds would not always proceed as a process with formation of a new C–C bond. For example, a radical cation can be taken that will not release proton as readily, so harpooning will become impossible. Thus we checked the next stage of the radiation process: the formation of an electronically excited molecule of the target compound, the expected product of normal recombination. The question is whether this system luminesces or not. To answer it, we performed stationary photolysis of **6b** (irradiation at 313 nm in 5 s intervals) with results partially shown in Figure 10. It can be seen that the system indeed undergoes photochemical transformations, and

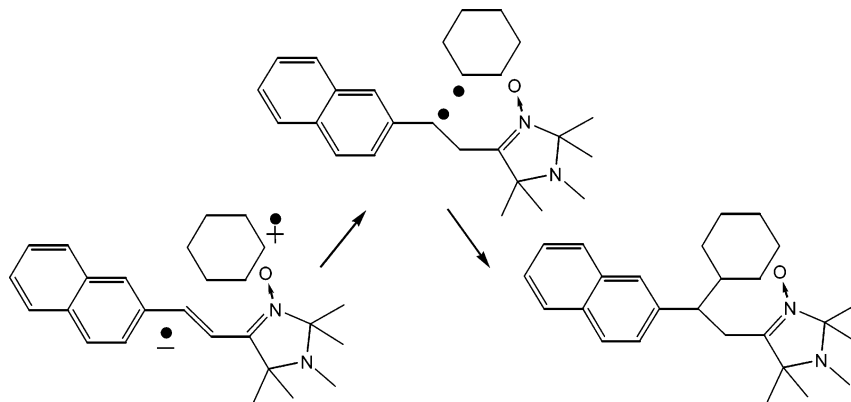


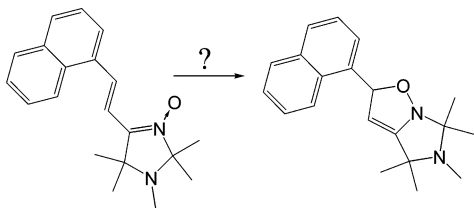
**Figure 10.** Consecutive optical absorption spectra of **6b** under irradiation by 313 nm light. Only the first (primary) stage of photodecomposition is shown. Arrows indicate falling and rising absorption bands.

analyses of optical absorption spectra and CMSA of photolysate show that at least two intermediates are formed. The quantum yield of the first stage (the primary photochemical process, the corresponding spectral transformations shown in Figure 10) was found to be  $\varphi = 0.21 \pm 0.04$ .

Mass spectra of the intermediates show the same molecular ion as the starting compound ( $m/z = 308$ ;  $M(\mathbf{6b}) = 308$  g/mol), which suggests an intramolecular rearrangement. A chemically sensible route of rearrangement with formation of isoxazoline

### SCHEME 3: Suggested Route for Formation of the Product of Radiolysis from **6b**



**SCHEME 4: Suggested Route of Direct Photochemical Transformations of 6b**

cycle is shown in Scheme 4. The suggested scheme is in agreement with the observed reduction of long-wave absorption in optical spectra and the observed reduction of intensities of signals corresponding to fragmentation of the N→O bond in mass spectra.

**5. Conclusions and Outlook**

To understand the difficulties in building radiation-generated spin triads from 3-imidazoline-substituted luminophores, we synthesized a set of 14 target compounds with general structure “stable 3-imidazoline radical—two-carbon bridge—naphthalene” with different combinations of structural elements, including the diamagnetic analogues. It was found that, for this particular combination of the luminophore, bridge, and radical, the flexibility of the saturated bridge leads to quenching of fluorescence from the luminophore moiety, presumably due to folding of the molecule into a conformation favoring effective through-space exchange quenching of the excited-state by the radical. Increasing the rigidity of the bridge by changing it to a double bond increases the chemical lability of the molecule to such a degree that chemical transformations are observed both at the stage of the radical ion pair and the excited molecule. Further search for the three-spin systems based on radical ion pairs generated by X-irradiation of nonpolar solutions should move in the direction of structurally more rigid systems with the rigidity provided by saturated skeleton structures such as cyclohexane,<sup>61</sup> decalin,<sup>62</sup> or piperidine<sup>63</sup> acting as the spacer linking the luminophoric and the stable radical moieties of the molecule. The already obtained systems however can be quite promising for photochemical generation of spin triads, as naphthalene and some of its derivatives are known to form exciplexes<sup>64–72</sup> required for photo-MARY.<sup>73–79</sup>

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**References and Notes**

- Salikhov, K. M.; Molin, Y. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Field Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.
- Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.
- Dynamic Spin Chemistry*; Nagakura, S., Hayashi, H., Azumi, T., Eds.; Kodansha, Wiley: Tokyo, New York, 1998.
- Woodward, J. R. *Prog. React. Kinet. Mech.* **2002**, *27*, 165.
- Hamilton, C. A.; Hewitt, L. J. P.; McLauchlan, K. A.; Steiner, U. E. *Mol. Phys.* **1988**, *65*, 423.
- Molin, Y. N.; Anisimov, O. A.; Koptuyug, A. V.; Saik, V. O.; Antzutkin, O. N. *Physica B* **1990**, *164*, 200.
- Batchelor, S. N.; Kay, C. W.; McLauchlan, K. A.; Shkrob, I. A. *J. Phys. Chem.* **1993**, *97*, 13250.
- Stass, D. V.; Lukzen, N. N.; Tadjikov, B. M.; Molin, Y. N. *Chem. Phys. Lett.* **1995**, *233*, 444.
- Saik, V. O.; Ostafin, A. E.; Lipsky, S. *J. Chem. Phys.* **1995**, *103*, 7347.
- Grissom, C. B. *Chem. Rev.* **1995**, *95*, 3.
- Ritz, T.; Adem, S.; Schulten, K. *Biophys. J.* **2000**, *78*, 707.
- Gramp, G.; Justinek, M.; Landgraf, S. *Mol. Phys.* **2002**, *100*, 1063.
- Ponomarev, O. A.; Kubarev, S. I.; Kubareva, I. S.; Susak, I. P.; Shigaev, A. S. *Chem. Phys. Lett.* **2004**, *388*, 231.
- Timmel, C. R.; Henbest, K. B. *Phil. Trans. R. Soc. London A* **2004**, *362*, 2573.
- Vink, C. B.; Woodward, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 16731.
- Doktorov, A. B.; Hansen, M. J.; Pedersen, J. B. *Chem. Phys.* **2006**, *328*, 333.
- Miura, T.; Maeda, K.; Arai, T. *J. Phys. Chem. A* **2006**, *110*, 4151.
- Minaev, B. F. *Zh. Fiz. Khim.* **1992**, *66*, 2992 (English translation).
- Buchachenko, A. L.; Ruban, L. V.; Step, E. N.; Turro, N. J. *Chem. Phys. Lett.* **1995**, *233*, 315.
- Mori, Y.; Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem. A* **2000**, *104*, 4896.
- Sviridenko, F. B.; Stass, D. V.; Kobzeva, T. V.; Tretyakov, E. V.; Klyatskaya, S. V.; Mshvidobadze, E. V.; Vasilevsky, S. F.; Molin, Y. N. *J. Am. Chem. Soc.* **2004**, *126*, 2807.
- Buchachenko, A. L.; Kouznetsov, D. A.; Orlova, M. A.; Markarian, A. A. *PNAS* **2005**, *102*, 10793.
- Anisimov, O. A. In *Radical ionic systems. Properties in condensed phase*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991; p.285.
- Werner, U.; Sakaguchi, Y.; Hayashi, H.; Nohya, G.; Yoneshima, R.; Nakajima, S.; Osuka, A. *J. Phys. Chem.* **1995**, *99*, 13930.
- Salikhov, K. M.; van der Est, A. J.; Stehlik, D. *Appl. Magn. Reson.* **1999**, *16*, 101.
- Buchachenko, A. L.; Berdinsky, V. L. *Chem. Rev.* **2002**, *102*, 603.
- Magin, I. M.; Shevel'kov, V. S.; Obynochny, A. A.; Kruppa, A. I.; Leshina, T. V. *Chem. Phys. Lett.* **2002**, *357*, 351.
- Shakirov, S. R.; Lebedeva, N. V.; Gorelik, V. R.; Tarasov, V. F.; Bagryanskaya, E. G. *Appl. Magn. Reson.* **2006**, *30*, 535.
- Kubarev, S. I.; Shustov, A. S. *Theor. Exp. Chem.* **1981**, *16*, 418 (English translation).
- Minaev, B. F.; Agren, H. *Collect. Czech. Chem. Commun.* **1995**, *60*, 339.
- Volkova, O. S.; Taraban, M. B.; Plyusnin, V. F.; Leshina, T. V.; Egorov, M. P.; Nefedov, O. M. *J. Phys. Chem. A* **2003**, *107*, 4001.
- Magin, I. M.; Purtov, P. A.; Kruppa, A. I.; Leshina, T. V. *J. Phys. Chem. A* **2005**, *109*, 7396.
- Weiss, E. A.; Chernick, E. T.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 2326.
- Tretyakov, E. V.; Novikova, T. V.; Korolev, V. V.; Usov, O. M.; Vasilevsky, S. F.; Molin, Y. N. *Russ. Chem. Bull.* **2000**, *49*, 1409.
- Barlukova, M. M.; Beregovaya, I. V.; Vysotsky, V. P.; Shchegoleva, L. N.; Bagryansky, V. A.; Molin, Y. N. *J. Phys. Chem. A* **2005**, *109*, 4404.
- Mashnin, A. S.; Anishchik, S. V.; Borovkov, V. I.; Yeletsikh, I. V.; Anisimov, O. A.; Molin, Y. N. *Appl. Magn. Reson.* **2001**, *20*, 473.
- Kalneus, E. V.; Stass, D. V.; Molin, Y. N. *Appl. Magn. Reson.* **2005**, *28*, 213.
- Lukzen, N. N.; Usov, O. M.; Molin, Y. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5249.
- Imidazoline Nitroxides: Synthesis and Properties*; Volodarsky, L. B., Ed.; CRC: Boca Raton, Florida, 1988; Vol. I, p 222; Vol. II, p 160.
- Barlukova, M. M.; Gritsan, N. P.; Starichenko, V. F.; Grigor'ev, I. A.; Molin, Y. N. *Chem. Phys. Lett.* **2004**, *401*, 62.
- Shundrin, L. A.; Reznikov, V. A.; Irtegov, I. G.; Starichenko, V. F. *Russ. Chem. Bull.* **2003**, *52*, 939.
- Justinek, M.; Grampp, G.; Landgraf, S.; Hore, P. J.; Lukzen, N. N. *J. Am. Chem. Soc.* **2004**, *126*, 5635.
- Landolt-Bornstein. *Organic Anion Radicals*; Springer-Verlag: Berlin-Heidelberg, 1980; p 731.
- Tadjikov, B. M.; Stass, D. V.; Usov, O. M.; Molin, Y. N. *Chem. Phys. Lett.* **1997**, *273*, 25.
- Melnikov, M. Y.; Smirnov, V. A. *Handbook of Photochemistry of Organic Radicals: Absorption and Emission Properties, Mechanisms, Aging*; Begell House Publishers: New York, 1997.
- Lescop, C.; Bussiere, G.; Beaulac, R.; Belisle, H.; Belorizky, E.; Rey, P.; Reber, C.; Luneau, D. *J. Phys. Chem. Sol.* **2004**, *65*, 773.
- Green, S. A.; Simpson, D. J.; Zhou, G.; Ho, P. S.; Blough, N. V. *J. Am. Chem. Soc.* **1990**, *112*, 7337.
- Medvedeva, N.; Martin, V. V.; Weis, A. L.; Likhtenshtein, G. I. *J. Photochem. Photobiol. A* **2004**, *163*, 45.
- Hauck, S.; Schneider, M.; Trommer, W. E. *Biophys. J.* **2007**, *Suppl. S*, 339A.
- Asano, M. S.; Ishizuka, K.; Kaizu, Y. *Mol. Phys.* **2006**, *104*, 1609.
- Sviridenko, F. B.; Stass, D. V.; Molin, Y. N. *Mol. Phys.* **2003**, *101*, 1839.
- Hoenigman, R. L.; Kato, S.; Bierbaurn, V. M.; Borden, W. T. *J. Am. Chem. Soc.* **2005**, *127*, 17772.
- Brocklehurst, B. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 167.
- LaVerne, J. A.; Schuler, R. H.; Foldiak, G. J. *J. Phys. Chem.* **1992**, *96*, 2588.
- Podsoblyayev, A. P. *High Energy Chem.* **1995**, *29*, 1.

- (56) LaVerne, J. A.; Pimblott, S. M.; Wojnarovits, L. *J. Phys. Chem. A* **1997**, *101*, 1628.
- (57) Wojnarovits, L.; Schuler, R. H. *J. Phys. Chem. A* **2000**, *104*, 1346.
- (58) Feldman, V. I. In *EPR in Solids. Trends in Methods and Applications*; Lund, A., Shiotani, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; p 384.
- (59) Belevskii, V. N.; Belopushkin, S. I. *High Energy Chem.* **2005**, *39*, 1.
- (60) Borovkov, V. I.; Velizhanin, K. A. *Radiat. Phys. Chem.* **2007**, *76*, 988.
- (61) Oosterbaan, W. D.; Koper, C.; Braam, T. W.; Hoogesteger, F. J.; Piet, J. J.; Jansen, B. A. J.; van Walree, C. A.; van Ramesdonk, H. J.; Goes, M.; Verhoeven, J. W.; Schuddeboom, W.; Warman, J. M.; Jenneskens, L. W. *J. Phys. Chem. A* **2003**, *107*, 3612.
- (62) Zimmerman, H. E.; Cheng, J. J. *Org. Chem.* **2006**, *71*, 873.
- (63) Scherer, T.; Vanstokkum, I. H. M.; Brouwer, A. M.; Verhoeven, J. W. *J. Phys. Chem.* **1994**, *98*, 10539.
- (64) Matsuzawa, S.; Lamotte, M.; Garrigues, P.; Shimizu, Y. *J. Phys. Chem.* **1994**, *98*, 7832.
- (65) Chesta, C. A.; Avila, V.; Soltermann, A. T.; Previtali, C. M.; Cosa, J. J. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 2491.
- (66) Nowakowska, M.; Smoluch, M.; Petelenz, P. *Chem. Phys. Lett.* **1997**, *270*, 234.
- (67) Dogadkin, D. N.; Soboleva, I. V.; Kuz'min, M. G.; *High Energy Chem.* **2001**, *35*, 107.
- (68) Rosenblum, G.; Zaltsman, I.; Stanger, A.; Speiser, S. *J. Photochem. Photobiol. A* **2001**, *143*, 245.
- (69) Das, A.; Mahato, K. K.; Nandi, C. K.; Chakraborty, T.; Gadre, S. R.; Gokhale, N. A. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2162.
- (70) Deperasinska, I.; Prochorow, J. *Acta Phys. Pol., A* **2002**, *102*, 811.
- (71) Sebok-Nagy, K.; Biczok, L. *Photochem. Photobiol. Sci.* **2004**, *3*, 389.
- (72) Xie, G. B.; Sueishi, Y.; Yamamoto, S. *J. Fluorescence* **2005**, *15*, 475.
- (73) Bandyopadhyay, S.; Sen, K.; Choudhury, S. D.; Basu, S. *Mol. Phys.* **2002**, *100*, 1079.
- (74) Petrov, N. K.; Alfimov, M. V.; Budyka, M. F.; Gavrishova, T. N.; Staerk, H. *J. Phys. Chem. A* **1993**, *103*, 9601.
- (75) Nakai, M.; Maeda, K.; Murai, H. *Chem. Phys. Lett.* **1999**, *302*, 577.
- (76) Burshtein, A. I. *J. Chem. Phys.* **2002**, *117*, 7640.
- (77) Justinek, M.; Grampp, G.; Landgraf, S. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5550.
- (78) Das, D.; Nath, D. N.; Parui, P. P.; Chowdhury, M. *Chem. Phys. Lett.* **2006**, *424*, 300.
- (79) Rodgers, C. T.; Norman, S. A.; Henbest, K. B.; Timmel, C. R.; Hore, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 6746.