

Optically Detected ESR and Low Magnetic Field Signals from Spin Triads: 2-Imidazoline-1-Oxyl Derivatives in X-irradiated Alkane Liquids as a Method to Study Three-Spin Systems

Fyodor B. Sviridenko,^{*,†} Dmitri V. Stass,^{†,‡} Tatyana V. Kobzeva,[†]
Evgeny V. Tretyakov,^{†,§} Svetlana V. Klyatskaya,[†] Elena V. Mshvidobadze,[†]
Sergey F. Vasilevsky,[†] and Yuri N. Molin^{†,‡}

Contribution from the Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, Novosibirsk 630090, Russia, Novosibirsk State University, Pirogova 2, Novosibirsk 630090, Russia, and International Tomography Center, Institutskaya 3a, Novosibirsk 630090, Russia

Received July 9, 2003; E-mail: fyodor@ns.kinetics.nsc.ru

Abstract: This contribution reports the design and synthesis of a series of spin-labeled charge acceptors to produce three-spin systems of “radical ion/biradical ion” type in X-irradiated alkane liquids. This opens the way to study spin triads in experimental conditions, in which short-lived radical ion pairs are conventionally studied, thus offering optically detected techniques such as magneto-resonance OD ESR and level-crossing MARY spectroscopy. The structure of the synthesized 2-imidazoline-1-oxyl derivatives is **A-Sp-R**, where **A** is a positive or negative charge acceptor, **R** is a stable radical, and **Sp** is a hydrocarbon bridge. The set of 20+ compounds represent a convenient tool to construct experimental three-spin systems with various properties, e.g. with the “third” spin introduced into one or the other partner of the radical ion pair. The degree of exchange coupling between the two paramagnetic fragments in the biradical ion has been demonstrated to strongly depend on the type of the radical fragment **R** and the structure of the bridge **Sp**. As a result, a series of acceptors with systematically reduced exchange interaction has been synthesized, and optimal systems for the observation of low magnetic field effect have been found. In the most favorable case, an OD ESR signal from a spin triad living as short as ca. 100 ns has been registered as a single unresolved line. The exchange integral for this biradical anion (**9**) was estimated from OD ESR and ESR experiments to be ca. 10^3 G by the order of magnitude, which is much greater than the hyperfine couplings in the biradical ion but much smaller than the thermal energy kT .

Introduction

One of the recent trends in modern spin chemistry is a progressively growing interest toward higher spin systems, including pairs with particles having spin higher than 1/2, and/or systems of more than two paramagnetic species that have to be treated as a coherent whole. Besides sheer curiosity, the attention to this line of research is explained by the observation that many naturally occurring paramagnetic systems are more complex than the model spin one-half pair. Some examples would include interaction of excited triplet molecules or localized biradicals with radicals (triplet–doublet pairs), biochemical reactions catalyzed by ferments, prosthetic groups of which often contain paramagnetic ions, and interaction of conventional geminate radical pairs with ubiquitous molecular oxygen, the ground state of which is paramagnetic. This class of processes has been formalized as the phenomenon of “spin catalysis”, or the effect of the third, “external”, spin on the evolution of a pair of spins, and has been recently attended to in the works of several groups.¹

Studying three-spin systems in liquid solution at room temperature requires special experimental techniques, which can in certain conditions provide information on the physical (e.g., paramagnetic relaxation) and chemical (e.g., monomolecular decay) processes involving short-lived radicals that practically cannot be obtained in a more conventional experiment. Certain advance in the study of short-lived radical ion pairs has recently been achieved using MARY spectroscopy,² which, although not always as informative as other registration techniques, is good for qualitative experiment. In this work we used MARY spectroscopy to make the first step toward more complex systems built on the base of the conventional radical ion pairs.

- (1) (a) Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 5041; *J. Am. Chem. Soc.* **1996**, *118*, 9552; Anderson, M. A.; Xu, Y.; Grissom, C. B. *J. Am. Chem. Soc.* **2001**, *123*, 6720. (b) Buchachenko, A. L.; Berdinsky, V. L. *J. Phys. Chem.* **1996**, *100*, 18292; *Chem. Phys. Lett.* **1998**, *298*, 279; *J. Phys. Chem. A* **1999**, *103*, 865; *Chem. Rev.* **2002**, *102*, 603. (c) Wakasa, M.; Hayashi, H.; Mikami, Y.; Takeo, T. *J. Phys. Chem.* **1995**, *99*, 13181; Werner, U.; Sakaguchi, Y.; Hayashi, H.; Nohya, G.; Yonoshima, R.; Nakajima, S.; Osuka, A. *J. Phys. Chem.* **1995**, *99*, 13930; Mori, Y.; Sakaguchi, Y.; Hayashi, H. *Chem. Phys. Lett.* **1999**, *301*, 365; *J. Phys. Chem. A* **2000**, *104*, 4896. (d) Minaev, B. V. *J. Mol. Catal.: A* **2001**, *171*, 53. (e) Turro, N. J.; Khudyakov, I. V. *J. Phys. Chem.* **1995**, *99*, 7654; *Res. Chem. Intermed.* **1999**, *25*, 505. (f) Salikhov, K. M.; van der Est, A. J.; Stehlik, D. *Appl. Magn. Reson.* **1999**, *16*, 101. (g) Magin, I. M.; Shevel'kov, V. S.; Obynochny, A. A.; Kruppa, A. I.; Leshina, T. V. *Chem. Phys. Lett.* **2002**, *357*, 351.

[†] Institute of Chemical Kinetics and Combustion SB RAS.

[‡] Novosibirsk State University.

[§] Current affiliation: International Tomography Center.

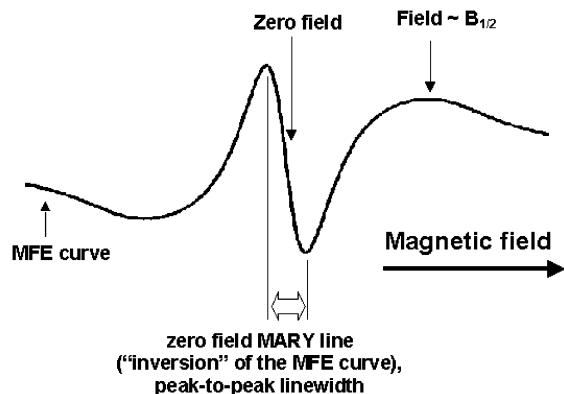


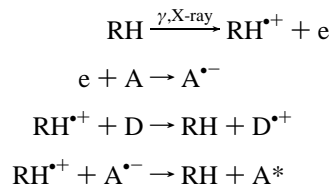
Figure 1. General look of the magnetic field effect curve (first derivative, as usually registered in experiment) with the inversion (MARY line) in the vicinity of zero field.

MARY spectrum consists of sharp lines in zero and low field that develop against the background of the conventional stationary magnetic field effect (MFE) curve—dependence of the yield of recombination fluorescence from radical ion pairs in irradiated solutions on external static magnetic field—due to degeneracy of the spin energy levels of the pair. The physical background of the effect and the necessary conditions for its observation have been discussed elsewhere,³ and the detailed description of the technique as applied in this work has recently been published.^{2a} Usually only the strongest MARY line in zero field is experimentally studied, and so the spectra are taken and presented in the vicinity of the zero field. The general look of the MARY spectrum is schematically shown in Figure 1. The width of the zero field MARY line is determined by the lifetime of the spin-correlated system of the two geminate radical ions, thus giving a good instrument to detect its decay through either chemical or relaxational processes, without complications from the unknown hyperfine structure of the pair partners. The best MARY spectra are produced by systems with substantial hyperfine interaction (HFI) concentrated in one of the partners of a relatively long-lived radical ion pair. On the other hand, the background of the MARY spectrum, i.e., the conventional MFE curve, bears information about the ESR parameters of the partners of the radical ion pair that yields fluorescence upon recombination. The maximum of its first derivative is located in the field close and proportional to the value⁴ $B_{1/2} = 2(A_1^2 + A_2^2/A_1 + A_2)$, where A_1 and A_2 are effective HFI constants of the partners: $A_{\text{eff}} = (\sum_i a_i^2 I_i(I_i + 1))^{1/2}$. Together, the MARY line and the MFE background constitute a flexible qualitative tool to estimate important properties of the radical ion pair and register processes involving its partners.

It should be stressed that a conventional spectroscopic technique, *when applicable*, can surely provide more complete and detailed information about the species under study, and it is the extreme situations of very short lifetimes, very high

reaction and relaxation rates, very low stationary concentration, which nevertheless are so common for paramagnetic intermediates of chemical reactions in solutions, when the specialized low-field techniques, often requiring specially tailored chemical systems, can be used to advantage.

A convenient way to modify the properties of the system under study is adding electron or hole acceptors (typical concentration being 10^{-4} and 10^{-2} M, respectively) to the solution to capture the partners of the radical ion pair and form a secondary pair with different properties (lifetime, relaxation or decay rate, etc.). The simplified pattern of chemical processes in irradiated alkane solutions of charge acceptors/luminophores relevant for this study is shown below.⁵



Here RH is the solvent molecule, A is the electron acceptor, and D is the positive charge acceptor (electron donor). Either A or D can also be the luminophore (A in this scheme).

This work reports the synthesis and results of the first qualitative MARY spectroscopy study of a class of spin-labeled charge acceptors of the type **A-Sp-R**, containing in one molecule an aromatic or heteroaromatic acceptor fragment **A** and a stable 2-imidazoline radical **R** connected via a hydrocarbon bridge **Sp**, whose structure determines the degree of exchange coupling between the two paramagnetic moieties of the biradical ion which can form upon X irradiation of alkane solutions of such compounds. The other radical ion partner of the triad in this situation is supplied by a conventional charge acceptor added to the solution. High-field studies of similar photogenerated systems have recently been reported by Mori et al.^{1c}

The idea of this work is to expand the experimental study of X-ray irradiation-generated radical ion pairs to systems with a nonzero exchange interaction with a third spin. In literature there are examples of introduction of exchange interaction into radical-ion pair using micellized systems,⁶ photogenerated covalently linked biradicals⁷ and “electron donor”/“electron acceptor” pairs connected with a hydrocarbon bridge.⁸ However, this method is only feasible when the pairs are generated photochemically,

- (5) Werst, D. W.; Trifunac, A. D. *J. Phys. Chem.* **1988**, *92*, 1093.
 (6) (a) Zimmt, M. B.; Doubleday, C. E.; Turro, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3363. (b) Closs, G. E.; Forbes, M. D. E.; Norris, J., Jr. *J. Phys. Chem.* **1987**, *91*, 3592. (c) Shkrob, I. A.; Tarasov, V. F.; Bagryanskaya E. G. *Chem. Phys.* **1991**, *153*, 427. (d) Wu, J. Q.; Baumann, D.; Steiner, U. *Mol. Phys.* **1995**, *84*, 981. (e) Scaiano, J. C.; Jovanovic, S. V.; Morris, D. G. *J. Photochem. Photobiol., A* **1998**, *113*, 197. (f) Eveson, R. W.; Timmel, C. R.; Brocklehurst, B.; Hore, P. J.; McLauchlan, K. A. *Int. J. Radiat. Biol.* **2000**, *76*, 1509. (g) Chaney, E. E.; Forbes, M. D. E. *J. Phys. Chem. B* **2003**, *107*, 4464.
 (7) (a) Doubleday, C., Jr.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199. (b) Johnson, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521. (c) Mukai, M.; Fujiwara, Y.; Tanimoto, Y.; Okazaki, M. *J. Phys. Chem.* **1993**, *97*, 12660. (d) Wakasa, M.; Hayashi, H. *J. Phys. Chem.* **1995**, *99*, 17074. (e) Forbes, M. D. E.; Avdievich, N. I.; Ball, J. D.; Schulz, G. R. *J. Phys. Chem.* **1996**, *100*, 13887. (f) Dvinskikh, S. V.; Yurkovskaya, A. V.; Vieth, H.-M. *J. Phys. Chem.* **1996**, *100*, 8125. (g) Maeda, K.; Araki, Y.; Kamata, Y.; Enjo, E.; Murai, M.; Azumi, T. *Chem. Phys. Lett.* **1996**, *262*, 110.
 (8) (a) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (b) Werner, U.; Kuhnle, W.; Staerk, H. *J. Phys. Chem.* **1993**, *97*, 9280. (c) Klumpp, T.; Linsenmann, M.; Larson, S. L.; Limoges, B. L.; Bürsner, D.; Krissinel, E. B.; Elliott, C. M.; Steiner, U. *E. J. Am. Chem. Soc.* **1999**, *121*, 1076. (d) Miller, S. E.; Lukas, A. S.; Marsh, E.; Bushard, P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7802.

- (2) (a) Sviridenko, F. B.; Stass, D. V.; Molin, Yu. N. *Chem. Phys. Lett.* **1998**, *297*, 343. (b) Sviridenko, F. B.; Stass, D. V.; Molin, Yu. N. *Mol. Phys.* **2003**, *101*, 1839. (c) Verkhovlyuk, V. N.; Morozov, V. A.; Stass, D. V.; Doktorov, A. B.; Molin, Yu. N. *Chem. Phys. Lett.* **2003**, *378*, 567. (d) Grigoryants, V. M.; McGrane, S. D.; Lipsky, S. *J. Chem. Phys.* **1998**, *109*, 7354. (e) Batchelor, S. N.; Kay, C. W. M.; McLauchlan, K. A.; Shkrob, I. A. *J. Phys. Chem.* **1993**, *97*, 13250. (f) Sacher, M.; Grampp, G. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 971.
 (3) (a) Stass, D. V.; Lukzen, N. N.; Tadjikov, B. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *233*, 444. (b) Timmel, C. R.; Till, U.; Brocklehurst, B.; McLauchlan, K. A.; Hore, P. *J. Mol. Phys.* **1998**, *95*, 71. (c) Bagryansky, V. A.; Borovkov, V. I.; Molin, Yu. N. *Mol. Phys.* **2002**, *100*, 1071.
 (4) Weller, A.; Nolting, F.; Staerk, H. *Chem. Phys. Lett.* **1983**, *96*, 16.

so that the probe molecule can be selectively excited, and cannot be applied when nonselective radiation generation of the pairs is used. In this report another way to introduce a controlled exchange interaction into the system is discussed: introduction of a paramagnetic center (a stable radical) into the precursor of one of the pair partners. Thus, a three-spin system, or a triad (radical anion/radical cation/stable radical) appears, in which there is a nonzero exchange interaction only between the radical ion and the stable radical that form one of the pair partners. On one hand, such a system retains the properties of the radical-ion pair and can therefore be registered with MARY and OD ESR techniques. On the other hand, it can be considered as an elementary model system realizing the effect of spin catalysis, as one of the pair partners is affected by the third spin.

Similar triads with neutral radicals were described in the literature,⁹ and model triads were studied theoretically.¹⁰ The results of the first experiments using compounds of the structure discussed, obtained using the technique of time-resolved magnetic field effect in recombination fluorescence in the field of 9600 G, can be found in ref 11. The authors point to a fast (in a few nanoseconds) decay of spin correlation in radical ion pair with a strong exchange interaction between the electron captured at the acceptor fragment of the luminophore and the spin of the stable radical, and also mention the prohibiting difficulties of accumulating the experimental fluorescence kinetics with acceptable signal-to-noise ratio. Another problem that makes the triads a complicated object of study was the low solubility of most spin-labeled acceptors in alkanes used as solvents. Thus, there arose a problem of creating acceptors with systematically impeded exchange interaction, along with searching for other, less demanding spin-sensitive techniques and experimental conditions to study three-spin systems. In this work, this was realized through using the stationary MARY spectroscopy technique, an experimental method specifically designed for investigation of short-lived paramagnetic species, and through systematically varying the structure of the spin-labeled acceptor, sometimes taking a nonstandard solvent.

Experimental Section

MARY/OD ESR Equipment. The design of the experimental setup for the registration of MARY and OD ESR spectra, the procedures of solvent purification, sample preparation and measurement were described elsewhere.² About 1 mL of degassed sample solution in a quartz cuvette is irradiated with an X-ray tube (BSV-27Mo, 40 kV × 20 mA) in the field of the electromagnet of Bruker ER200D EPR spectrometer equipped with an auxiliary coil shifting the field by −50 G. The fluorescence is registered with a FEU-130 photomultiplier tube using external field modulation at a frequency of 12.5 kHz and lock-in amplification (Stanford SR810 Lock-In Amplifier) with signal accumulation in computer. OD ESR spectra were taken in X-band (3400 G) in a regular rectangular cavity, MW power 700 mW. MARY spectra were taken in the vicinity of zero field (−50 to +50 G), no MW power applied to the sample. All presented OD ESR and MARY spectra were obtained by averaging over 10 to 20 scans 200–500 s each, modulation amplitude 1–10 G. All experiments were carried out in liquid solution at room temperature unless indicated otherwise.

Analytical Techniques. CW ESR spectra were registered on a Bruker EMX CW ESR spectrometer in similar experimental conditions

(solvent, sample preparation, temperature). ¹H NMR spectra were recorded on a Bruker Avance-300 spectrometer. IR spectra were taken on a Bruker IFS-66 spectrometer in KBr pellets. Electron impact mass spectra were taken on a Finnigan SSQ-710 instrument with direct sample inlet, temperature of ionization chamber 220–270 °C, ionization voltage 70 eV. Column chromatography was carried out using KSK 60/200 μm silica gel. The course of the reactions and the purity of the compounds were monitored by TLC on Silufol UV-254 plates.

Synthetic Strategies and Procedures. Earlier developed procedures originally aimed at preparation of paramagnetic ligands for molecular magnetics¹² have been employed to synthesize a series of spin-labeled compounds containing heteroaromatic (π-electron-rich pyrazole) residues linked with 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (nitronyl nitroxyl radicals, NNR) or 4,4,5,5-tetramethylimidazoline-1-oxyl (iminonitroxyl radicals, INR) unit. In this work the methods of synthesis of heterocyclic (including benzo-crown ether) and linear polyaromatic compounds containing fragments of nitroxyl radicals of the imidazoline series connected to the charge acceptor moiety via saturated or unsaturated bridge are further developed to extend the range of spin-labeled charge acceptors available for physicochemical studies.

Three synthetic strategies were employed to prepare the target substances. The first one, the traditional Ullman approach, included condensation of formylarenes or hetarenes with 2,3-bis(hydroxylamine)-2,3-dimethylbutane or its monosulfate followed by oxidation of the adducts with sodium periodate and was used for synthesis of spin-labeled pyrazoles. The second one, applied to prepare radicals with both unsaturated and saturated bridges, was based on cross-coupling of aryl(hetaryl)iodides with propargyl alcohol followed by oxidation with pyridinium chlorochromate into aldehydes, which then were transformed into paramagnetic compounds by the above-mentioned scheme used in the Ullman approach. To obtain aromatic radicals with a saturated bridge, prior to oxidation into aldehydes the resulting propargyl alcohols were reduced to aliphatic alcohols by hydrogen over Pd/C. Other aromatic mono- and biradicals were prepared using the third strategy, Pd–Cu-catalyzed cross-coupling of the relevant aryl-iodides with separately synthesized terminal spin-labeled acetylenes. Below, the individual syntheses will be described in more detail.

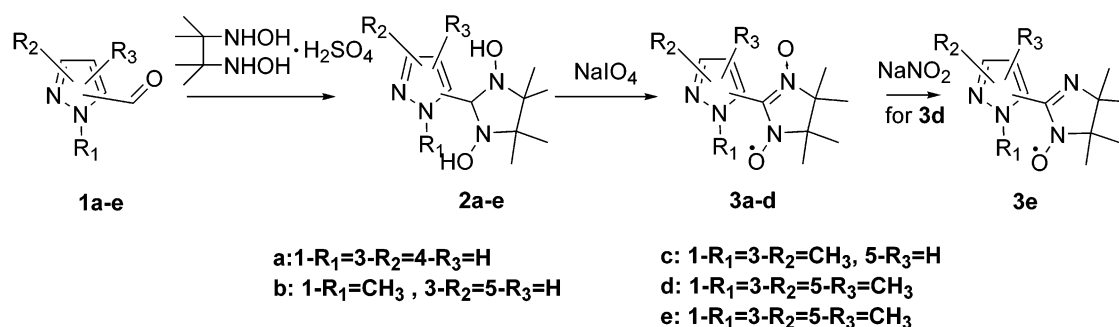
2-(Pyrazolyl)imidazoline derivatives (nitronyl nitroxyls (**3b–d**) and iminonitroxyls (**3e**)¹²), 4,4,5,5-tetramethyl-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecen-15-yl)-2-imidazoline-1-oxyl-3-oxide (**17**), 2-(arylethynylphenyl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxides (**13a,b,d–f**, **14a,b**, **15a**), 4,4,5,5-tetramethyl-2-(4-ethynylphenyl)-2-imidazoline-1-oxyl-3-oxides (**11**) and 4,4,5,5-tetramethyl-2-(3-ethynylphenyl)-2-imidazoline-1-oxyl-3-oxides (**12**),¹³ 4,4,5,5-tetramethyl-2-[4-(2-[1,1',4',1'']terphenyl-4-ylethyl)phenyl]-2-imidazoline-1-oxyl (**16a**),¹¹ 2,3-bis(hydroxyamino)-2,3-dimethylbutane and its monosulfate,¹⁴ and pyridinium chlorochromate (PCC)¹⁵ were prepared according to published procedures. CuI, PPh₃, Pd(OAc)₂, Pd-[PPh₃]₂Cl₂ (“Lancaster”) were used without additional purification. Other reagents and organic solvents were prepared according to standard procedures.

Nitroxide **3a**, in which the pyrazole moiety is linked directly to the radical fragment (see Scheme 1), and nitroxyls **8**, **9**, in which the terphenyl and the radical moieties are connected via a short ethane bridge (see Scheme 2) were prepared by a classical procedure for the synthesis¹⁶ of substituted imidazoline-derived nitroxides: condensation

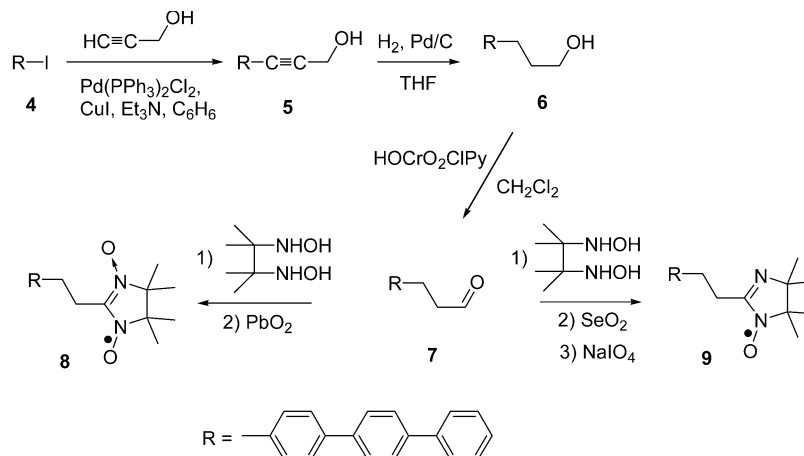
- (9) Step, E. N.; Buchachenko, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1994**, *116*, 5462.
 (10) Lukzen, N. N.; Usov, O. M.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5249.
 (11) Tretyakov, E. V.; Novikova, T. V.; Korolev, V. V.; Usov, O. M.; Vasilevsky, S. F.; Molin, Yu. N. *Russ. Chem. Bull.* **2000**, *49*, 1409.

- (12) (a) Romanenko, G. V.; Fokin, S. V.; Vasilevsky, S. F.; Tretyakov, E. V.; Shvedenkov, Yu. G.; Ovcharenko, V. I. *Russ. J. Coord. Chem.* **2001**, *27*, 360. (b) Vasilevsky, S. F.; Tretyakov, E. V.; Ikorskii, V. N.; Romanenko, G. V.; Fokin, S. V.; Shvedenkov, Yu. G.; Ovcharenko, V. I. *Arkhivoc* **2001**, *IX*, 55. (c) Ovcharenko, V. I.; Fokin, S. V.; Romanenko, G. V.; Ikorskii, V. N.; Tretyakov, E. V.; Vasilevsky, S. F.; Sardeev, R. Z. *Mol. Phys.* **2002**, *100*, 1107.
 (13) Klyatskaya, S. V.; Tretyakov, E. V.; Vasilevsky, S. F. *Russ. Chem. Bull.* **2002**, *51*, 128.
 (14) Ovcharenko, V. I.; Fokin, S. V.; Romanenko, G. V.; Korbkov, I. V.; Rey, P. *Russ. Chem. Bull.* **1999**, *48*, 1519.
 (15) Corey, E. J.; Sugg, J. W. *Tetrahedron Lett.* **1975**, *31*, 2647.

Scheme 1



Scheme 2



of aldehydes with 2,3-bis(hydroxyamino)-2,3-dimethylbutane followed by oxidation of the cyclic adducts with sodium periodate or lead dioxide. This procedure, however, did not work for the preparation of polyaromatic imidazoline nitroxides with “heavy” phenylethynyl bridge. Benzene, tetrahydrofuran, 1,4-dioxane, and methanol were tried as solvents, and temperature and reaction time were varied, but all attempts to prepare the target derivatives by condensation of aldehydes, such as biphenyl-4-ylbenzaldehyde or [1,1';4',1'']terphenyl-4-ylethynylbenzaldehyde, with 2,3-bis(hydroxyamino)-2,3-dimethylbutane were unsuccessful.

The synthesis of 4,4,5,5-tetramethyl-2-(2*H*-pyrazol-3-yl)-2-imidazoline-1-oxyl-3-oxide (**3a**) is given in Scheme 1.

4,4,5,5-Tetramethyl-2-(2*H*-pyrazol-3-yl)-2-imidazoline-1-oxyl-3-oxide (**3a**).

1. A mixture of aldehyde **1a**¹⁷ (0.50 g, 5.21 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane monosulfate monohydrate (1.38 g, 5.23 mmol) in H₂O (10 mL) and MeOH (3 mL) was stirred at room temperature until **1a** was consumed (monitored by TLC). NaHCO₃ (0.44 g, 5.24 mmol) was then added to the reaction mixture, and the precipitate was filtered off and recrystallized from ethyl acetate. The yield of 4,4,5,5-tetramethyl-2-(2*H*-pyrazol-3-yl)-imidazolidine-1,3-diol (**2a**) was 1.17 g (99%). IR, ν (cm⁻¹) 790, 848, 916, 989, 1055, 1088, 1107, 1146, 1286, 1367, 1460, 1544, 2981, 3258 (br). ¹H NMR (DMSO-*d*₆) δ 0.94 (s, 12 H, 4 CH₃); 4.56 (br s, 1 H, 2-H_{im}); 6.10 (s, 1 H, 4-H_{pz}); 7.33 (s c, 0.4 H); 7.58 (s, 1.4 H); 7.81 (s, 0.8 H).

2. NaIO₄ (1.67 g, 7.80 mmol) was added for 30 min in small portions to a stirred mixture of adduct **2a** (1.175 g, 5.20 mmol), water (10 mL), and CH₂Cl₂ (20 mL), cooled with ice water. Stirring was continued at room temperature for 4 h. The organic phase was separated, and the aqueous layer was extracted with chloroform (3 × 3 mL). The combined organic extracts were dried over MgSO₄ and filtered through a short

plug of Al₂O₃ (2 × 5 cm). The solvent was removed, and the residue was purified by chromatography on silica gel using chloroform as eluent and crystallized from C₆H₆-CHCl₃ mixture. The yield of **3a** was 0.91 g (78%), mp 148–149 °C. IR, ν (cm⁻¹) 765, 817, 870, 901, 921, 1016, 1037, 1098, 1137, 1190, 1210, 1242, 1270, 1299, 1374, 1406, 1428, 1453, 1494, 2992, br 3283. Found (%): C, 53.90; H, 6.50; N, 24.84. C₁₀H₁₅N₄O₂. Calcd (%): C, 53.80; H, 6.77; N, 25.10.

The synthesis of 4,4,5,5-tetramethyl-2-(2-[1,1';4',1'']terphenyl-4''-ylethyl)-2-imidazoline-1-oxyls **8** and **9** was carried out according to Scheme 2.

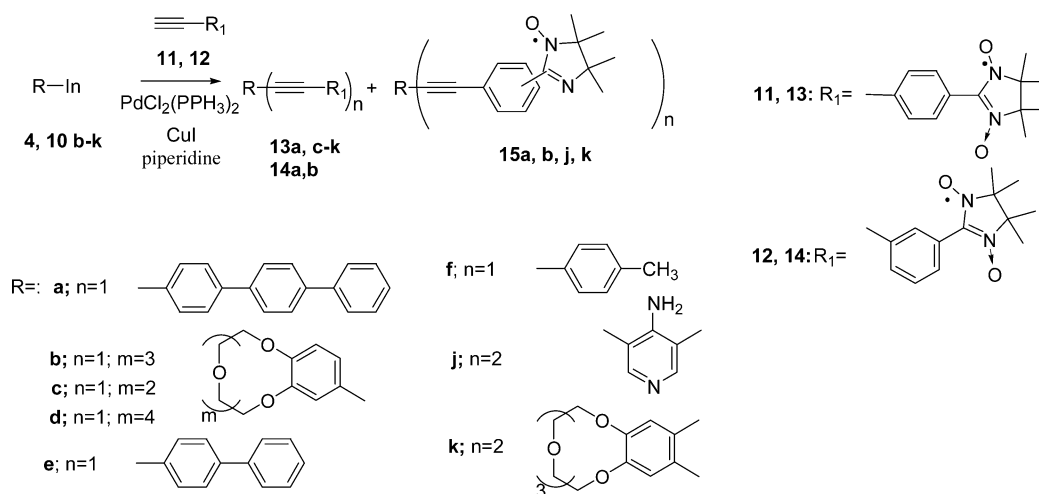
4-[1,1';4',1'']Terphenyl-4''-yl-but-3-yn-1-ol (5). A mixture of 4''-iodo[1,1';4',1'']terphenyl **4**¹¹ (1.07 g, 3 mmol), prop-2-yn-1-ol (0.6 g, 9 mmol), Pd(PPh₃)₂Cl₂ (60 mg), CuI (30 mg), PPh₃ (30 mg) in piperidine (3 mL) and benzene (8 mL) was stirred at 40 °C under argon stream for 15 min. Hexane (50 mL) was added, and the residue was filtered off and dissolved in benzene. The solution was chromatographed on silica gel using benzene as eluent. The solvent was removed, and the residue was crystallized from the benzene-hexane mixture. The yield of **5** was 0.50 g (59%), pale-yellow needles, mp 244–245 °C. IR, ν (cm⁻¹) 2215 (C≡C), 3019 (C-H), 3434 (OH). ¹H NMR (DMSO-*d*₆) δ 4.33 (d, 2 H, CH₂); 5.39 (t, 1 H, OH); 7.33–7.83 (m, 13 H, H_{ar}). MS *m/z* (*I*_{rel.} (%)) 284.1 [M]⁺ (100), 267.0 (7.30), 266.1 (1.19), 256.0 (12.64), 253.0 (6.49), 239.0 (9.84), 229.1 (2.29), 153.0 (1.30), 152.0 (3.31), 77.0 (1.77), 27.9 (6.15). Found: *m/z* 284.1190 [M]⁺. C₂₁H₁₆O. Calcd: M = 284.1201.

3-[1,1';4',1'']Terphenyl-4''-yl-propan-1-ol (6). Acetylenic alcohol **5** (1.15 g, 4 mmol) dissolved in methanol (10 mL) was hydrogenated over 4% Pd/C at room temperature until **5** was consumed (monitored by TLC). The catalyst was filtered off, and the solvent was removed. The residue was crystallized from benzene-hexane mixture. The yield of alcohol **6** was 1.0 g (86%), colorless crystals, mp 214–215 °C. IR, ν (cm⁻¹) 3300 (OH). ¹H NMR (CD₂Cl₂) δ 1.85–1.98 (m, 2 H, β H); 2.75 (t, 2 H, γ H); 3.67 (t, 2 H, α H), 7.41–7.79 (m, 13 H, H_{ar}). MS *m/z* (*I*_{rel.} (%)) 287.9 [M]⁺ (100), 270.8 (3.57), 269.8 (16.19), 256.8 (4.0),

(16) Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

(17) Hüttl, R. *Ber.* **1941**, *74*, 1680; *Ann.* **1954**, *585*, 115.

Scheme 3



244.8 (3.15), 243.8 (23.51), 242.8 (83.32), 228.8 (3.34), 152.9 (1.18), 114.9 (5.12), 76.9 (1.51), 27.9 (10.78). Found: m/z 288.1515 $[M]^+$. $C_{21}H_{20}O$. Calcd: $M = 288.1514$.

3-[1,1';4',1'']Terphenyl-4'-yl-propionaldehyde (7). A mixture of alcohol **6** (0.16 g, 0.56 mmol) and PCC (1.6 g, 7.4 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The reaction mixture was filtered through a layer of SiO_2 , the solvent was removed, and the residue was crystallized from benzene–hexane mixture. The yield of aldehyde **7** was 60 mg (38%), cream-colored crystals, mp 220.5–221.5 °C. IR, ν (cm^{-1}) 1720 (C=O). 1H NMR (CD_2Cl_2) δ 9.83 (s, 1 H_{CHO}); 3.0 (t, 2 H, αH); 2.82 (t, 2 H, βH), 7.31–7.78 (m, 13 H, H_{ar}). MS m/z ($I_{rel.}$ (%)) 285.9 $[M]^+$ (91.66), 257.9 (7.09), 256.9 (4.89), 243.9 (22.84), 242.9 (100), 229.9 (16.02), 228.9 (93.36), 164.9 (8.44), 152.9 (1.09), 114.9 (95.87), 77.0 (2.15), 28.0 (0.60). Found: m/z 286.1334 $[M]^+$. $C_{21}H_{18}O$. Calcd: $M = 286.1358$.

4,4,5,5-Tetramethyl-2-(2-[1,1';4',1'']terphenyl-4''-ylethyl)-2-imidazole-1-oxyl-3-oxide (8). A mixture of aldehyde **7** (50 mg, 0.17 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane (45 mg, 0.3 mmol) in benzene (10 mL) was stirred at room temperature for 2 days until **7** was consumed (monitored by TLC). The solvent was removed, and the residue was chromatographed on a layer of SiO_2 using ethyl acetate as eluent. The solvent was removed, and a mixture of $CHCl_3$ (10 mL), H_2O (10 mL), and $NaHCO_3$ (0.1 g) was added to the residue and stirred for 30 min with $NaIO_4$ (100 mg). The organic layer was separated and filtered through a layer of Al_2O_3 , the solvent was removed, and the residue was chromatographed on silica gel using benzene as eluent. The yield of **8** was 35 mg (48%), crimson needles, mp 204–205 °C (benzene–hexane). MS m/z ($I_{rel.}$ (%)) 413.3 $[M]^+$ (1.83), 382.3 (23.72), 302.2 (12.09), 284.2 (20.18), 274.2 (44.80), 269.2 (19.17), 258.2 (34.83), 257.2 (63.46), 256.2 (27.64), 243.1 (100), 239.2 (11.1), 229.2 (15.13), 228.2 (23.05), 149.1 (23.79), 125.1 (11.27), 113.1 (12.63), 111.1 (15.89), 101.1 (10.14), 99.1 (12.35), 97.1 (22.46), 85.1 (18.69), 84.1 (17.15), 83.1 (26.04), 82.1 (17.85), 71.1 (29.46), 70.1 (11.13), 69.1 (31.92), 58.1 (18.37), 57.1 (40.69), 55.1 (25.1), 43.1 (24.65), 41.1 (17.95), 28.0 (12.68). Found: m/z 413.2218 $[M]^+$. $C_{27}H_{29}N_2O_2$. Calcd: $M = 413.2229$.

4,4,5,5-Tetramethyl-2-(2-[1,1';4',1'']terphenyl-4''-ylethyl)-2-imidazole-1-oxyl (9). A mixture of aldehyde **7** (150 mg, 0.52 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane (80 mg, 0.54 mmol) in benzene (4 mL) and MeOH (4 mL) was stirred at room temperature for 2 h. The solvent was removed, and SeO_2 (20 mg, 0.18 mmol) in MeOH (5 mL) was added to the residue. The solvent was distilled off, and the residue was stirred with $NaIO_4$ (200 mg, 0.93 mmol) in $CHCl_3$ (10 mL) and H_2O (10 mL) for 2 h at 20 °C. The organic phase was separated and filtered through a layer of Al_2O_3 , the solvent was removed, and the residue was chromatographed on silica gel using a

mixture of $CHCl_3:CH_3COOC_2H_5$ (10:1, v/v) as eluent. The yield of compound **9** was 60 mg (32%), pale-yellow powder, mp 175–177 °C (benzene–hexane). IR, ν (cm^{-1}) 694, 734, 764, 820, 1004, 1076, 1143, 1368, 1449, 1486, 1598, 1631, 2926, 2978, 3031. MS m/z ($I_{rel.}$ (%)) 397.2 $[M]^+$ (4.76), 382.2 (16.94), 324.2 (4.68), 288.2 (8.74), 284.1 (23.90), 283.1 (100.0), 270.2 (8.81), 269.1 (30.18), 268.1 (8.40), 258.1 (4.02), 257.1 (5.66), 256.1 (5.54), 244.1 (17.50), 243.1 (77.45), 241.1 (8.88), 239.1 (6.95), 165.1 (8.99), 114.1 (20.72), 84.1 (84.13). Found: m/z 397.2265 $[M]^+$. $C_{27}H_{29}N_2O$. Calcd: $M = 397.22798$.

As noted earlier, the Ullman procedure did not work for the preparation of polyaromatic imidazoline nitroxyls with “heavy” phenylethynyl bridge. Cross-coupling of aryl halides with terminal acetylenes¹⁸ catalyzed by complex palladium or copper salts made it possible to perform an alternative synthesis of 2-(arylethynylphenyl)imidazole-1-oxyl-3-oxides. The paramagnetic molecules were synthesized by condensation of aryl halides with paramagnetic 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-imidazole-1-oxyl-3-oxide (**11**) and 2-(3-ethynylphenyl)-4,4,5,5-tetramethyl-imidazole-1-oxyl-3-oxide (**12**). It should be stressed here that attempts to introduce spin-labeled acetylene into the reaction with 4-iodoarenes under standard conditions ($PdCl_2(PPh_3)_2$, CuI, NEt_3 , benzene (55–80 °C)) were unsuccessful, and the reaction gave rise only to the products of homo-coupling. Nevertheless, the use of piperidine, which is a stronger base than triethylamine, made it possible to carry out the reaction at room temperature, suppressing, to some extent, side processes. Cross-coupling of the iodoarene **10a** with alkyne **11** under the above-mentioned conditions (Scheme 3) produced a mixture of 4,4,5,5-tetramethyl-2-(4-[1,1';4',1'']terphenyl-4-ylethynylphenyl)imidazole-1-oxyl-3-oxide (**13a**) (yield 20%), 4,4,5,5-tetramethyl-2-(4-[1,1';4',1'']terphenyl-4-ylethynylphenyl)imidazole-1-oxyl, 4,4,5,5-tetra-methyl-2-(4-[1,1';4',1'']terphenyl-4-ylethynylphenyl)imidazole-1-oxyl, terphenyl, and the products of homo-coupling of alkyne **11**.

Hydrogenation of nitronyl nitroxide **15a** over Pd/C followed by oxidation with $NaIO_4$ yielded 4,4,5,5-tetramethyl-2-[4-(2-[1,1';4',1'']terphenyl-4-ylethyl)phenyl]imidazole-1-oxyl (**16a**).

The synthesis of mono- (**13c**, **15b**) and biradicals (**13j**, **15j**, **15k**) based on cross-coupling of aryl iodides with spin-labeled acetylenes is shown in Scheme 3.

4,4,5,5-Tetramethyl-2-[4-(6,7,9,10,12,13-hexahydro-5,8,11,14-tetraoxa-benzocyclododecen-2-ylethynyl)-phenyl]-2-imidazole-1-oxyl-3-oxide (13c). Alkyne **11** (70 mg, 0.27 mmol) was added in small portions to a mixture of iodide **10c**¹⁹ (80 mg, 0.25 mmol), $PdCl_2(PPh_3)_2$ (20 mg), and CuI (10 mg) in piperidine (10 mL) under argon flow at 20 °C for 3 h. The solvent was removed in vacuo with an oil pump

(18) (a) Dieck, H. A.; Heck, F. P. *J. Organomet. Chem.* **1975**, *93*, 259. (b) Sonogashira, K.; Tohda, Y.; Hagihara, N. A. *Tetrahedron Lett.* **1975**, *50*, 4467.

(0.1 Torr) at 20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al₂O₃, and the solvent was distilled off. The residue was then dissolved in benzene and twice chromatographed on silica gel. Elution with benzene yielded 40 mg (41%) of compound **13c**, mp 125–126 °C (hexane–benzene mixture). IR, ν (cm⁻¹) 2200 (C≡C); 2980 (CH₃); 2958, 2988 (C–H_{ar}). Found (%): C, 67.74; H, 6.34; N, 5.66. C₂₇H₃₁N₂O₆. Calcd (%): C, 67.62; H, 6.52; N, 5.84.

4,4,5,5-Tetramethy-2-[3-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaaza-benzocyclododecen-15-ylethynyl)phenyl]-2-imidazoline-1-oxyl (15b). A mixture of iodide **10b**¹⁹ (100 mg, 0.25 mmol), alkyne **12** (70 mg, 0.27 mmol), PdCl₂(PPh₃)₂ (20 mg), and CuI (10 mg) in piperidine (10 mL) was stirred under argon flow at 20 °C for 3 h. The solvent was removed in vacuo with an oil pump (0.1 Torr) at 20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al₂O₃, and the solvent was distilled off. The residue was dissolved in benzene and twice chromatographed on silica gel. Elution with chloroform yielded 50 mg (41%) of compound **15b**, mp 93–95 °C (benzene). IR, ν (cm⁻¹) 2195 (C≡C); 2988 (CH₃); 2945, 2988 (C–H_{ar}). Found (%): C, 68.55; H, 7.58; N, 5.66. C₂₉H₃₇N₂O₆. Calcd (%): C, 68.35; H, 7.32; N, 5.50.

1,5-Bis-(4-(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide)-phenylethynyl)-4-amine-pyridine (13j) and 1,5-Bis-(4-(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl)-phenylethynyl)-4-amine-pyridine (15j). A mixture of iodide **10j** (200 mg, 0.57 mmol) and compound **11** (300 mg, 1.2 mmol) was stirred in piperidine (3 mL) in the presence of PdCl₂(PPh₃)₂ (20 mg) and CuI (10 mg) under argon flow at 20 °C for 3 h. The solvent was removed in vacuo with an oil pump (0.1 Torr) at 20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al₂O₃, and the solvent was distilled off. The residue was dissolved in benzene and twice chromatographed on silica gel.

13j. Elution with chloroform yielded 40 mg (11.7%) of compound **13j**, mp 226–227 °C (benzene). IR, ν (cm⁻¹) 2205 (C≡C); 2988 (CH₃); 3455 (NH₂); 2938, 2988 (C–H_{ar}). Found (%): C, 69.74; H, 6.34; N, 13.66. C₃₅H₃₆N₆O₄. Calcd (%): C, 69.52; H, 6.0; N, 13.9.

15j. Elution with benzene yielded 40 mg (14.1%) of compound **15j**, mp 226–227 °C (benzene). IR, ν (cm⁻¹) 2200 (C≡C); 2978 (CH₃); 3475 (NH₂); 2938, 2988 (C–H_{ar}). Found (%): C, 73.74; H, 6.61; N, 13.99. C₃₅H₃₆N₆O₂. Calcd (%): C, 73.40; H, 6.34; N, 14.67.

2,3-Bis-(4-(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide)phenylethynyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaazabenzocyclododecene (13k) and 2,3-Bis-(4-(4,4,5,5-tetramethyl-2-imidazoline-1-oxyl)-phenylethynyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaazabenzocyclododecene (15k). A mixture of iodide **10k** (500 mg, 0.96 mmol)²⁰ and alkyne **11** (620 mg, 2.4 mmol) was stirred in piperidine (10 mL) in the presence of PdCl₂(PPh₃)₂ (50 mg) and CuI (25 mg) under argon flow at 20 °C for 5 h. The solvent was removed in vacuo with an oil pump (0.1 Torr) at 20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al₂O₃, and the solvent was distilled off. The residue was dissolved in benzene and twice chromatographed on silica gel.

13k. Elution with chloroform yielded 90 mg (12.6%) of compound **13k**, mp 128–130 °C (benzene). IR, ν (cm⁻¹) 2207 (C≡C); 2978 (CH₃); 28748, 2929 (C–H_{ar}). Found (%): C, 67.34; H, 6.51; N, 7.04. C₄₀H₅₀N₄O₉. Calcd (%): C, 67.85; H, 6.47; N, 7.09.

15k. Elution with benzene yielded 80 mg (13.2%) of compound **15k**, mp 82–84 °C (benzene–hexane 1:3, v/v). IR, ν (cm⁻¹) 2215 (C≡C); 2965 (CH₃); 2948, 2998 (C–H_{ar}). Found (%): C, 70.74; H, 6.34; N, 7.66. C₄₀H₅₀N₄O₇. Calcd (%): C, 70.76; H, 6.75; N, 7.5.

2,3-Bis-(*p*-formyl-phenylethynyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaazabenzocyclopentadecene (18). A mixture of iodide **10k** (900 mg, 1.7 mmol), 4-ethynyl-benzaldehyde (500 mg, 3.8 mmol), Pd(OAc)₂ (20 mg), CuI (10 mg), and PPh₃ (60 mg) in

triethylamine (7 mL) and benzene (15 mL) was stirred at 70–75 °C for 2.5 h. The yield of compound **18** was 690 mg (77%), mp 156–157 °C (benzene). ¹H NMR (CDCl₃) δ 3.69 (s, 8 H, 4 OCH₂); 3.86–3.95 (m, 4 H, 2 ArOCH₂CH₂); 4.15–4.22 (m, 4 H, 2 ArOCH₂CH₂); 7.08 (s, 2 H, H (1), H (4)), 7.69 (d, 4 H, 2 H (2'), H (6'), *J* = 8.2), 7.89 (d, 4 H, 2 H (3'), H (5'), *J* = 8.2), 10.05 (c, 2 H, CHO). IR, ν (cm⁻¹) 1697 (C=O), 2204 (C≡C). Found (%): C, 73.14; H, 5.45. C₃₂H₂₈O₇. Calcd (%): C, 73.27; H, 5.38.

The structure of the synthesized radicals and the parameters of their ESR spectra are given in Table 1.

Results and Discussion

Thus, a series of 2-imidazoline-1-oxyl derivatives with the general structure **A-Sp-R** were synthesized, which have in one molecule an acceptor of positive or negative charge (**A**) that can also be the luminophore, and a stable nitroxyl radical of the 2-imidazoline series (**R**) connected with a bridge (**Sp**). Having a luminophore in the radical ion pair is necessary to observe the MFE/MARY/OD ESR effect. Negative charge acceptor is required in nonpolar and nonviscous alkanes to slow the “free” electron and extend the lifetime of the pair to at least several nanoseconds so that magnetic interactions would have ample time to affect its spin state before recombination. In the case of solvent 1,4-dioxane that will also be discussed in this work, where the mobility of the “free” electron is apparently lower, an electron acceptor can still slow it down even more and thus improve the signal. A positive charge acceptor can provide some extra possibilities, e.g. to form a stable radical cation with long relaxation and decay times or to change the effective HFI in the cation partner of the pair by capturing it to an acceptor with a different HFI structure.

Since acceptors have proved to be such a convenient tool to probe the properties of the spin system, in this work they were employed to introduce the “third spin” into the pair. In the synthesized series of spin-labeled acceptors the third spin (a stable radical **R**) is present in the precursor of the (bi)radical ion to be formed. Similarly to conventional acceptors, these compounds can be used to create a system with desired properties, while the stable radical thus introduced into one of the pair partners will be involved in the exchange interaction with the accepted spin. As expected, the third constituent of the spin-labeled acceptor, the bridge **Sp**, can be used to control the extent of exchange coupling by modifying the structure of the spacer.

First, the characteristic time domain was estimated in which the third spin can affect spin dynamics of the radical ion pair. This was done using two luminescing negative charge acceptors introduced into the solution: *p*-terphenyl-*d*₁₄ (PTP-*d*₁₄) and hexafluorobenzene (HFB), forming a radical pair with a rather low or a very high HFI in the radical anion: second moment of their ESR spectra, $\sigma = (\sum_i a_i^2 I_i (I_i + 1)/3)^{1/2}$, is ca. 0.6 and 165 G,²¹ respectively. In the first case spin evolution in the pair is mostly driven by moderate (tens of gauss) HFI in the solvent hole²² or acceptor radical cation, which corresponds to a longer time of MFE/MARY formation, about 10 ns. In the second case it is strong HFI in the HFB radical anion that drives spin evolution, and the signal is formed at shorter times, about 1 ns. Providing a spin-labeled hole acceptor as counterion to these

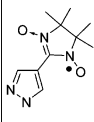
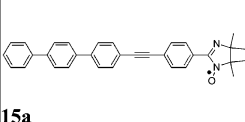
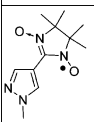
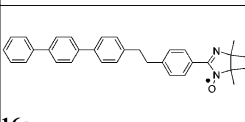
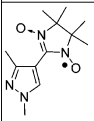
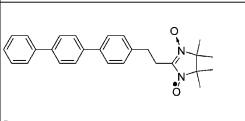
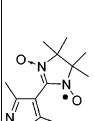
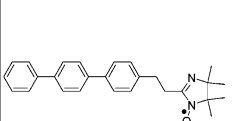
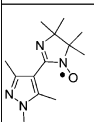
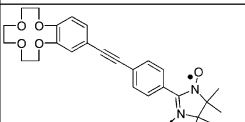
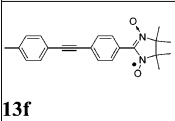
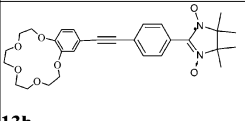
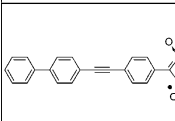
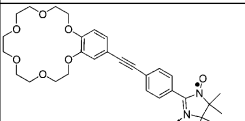
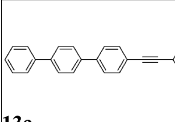
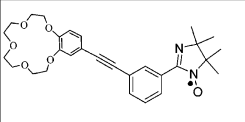
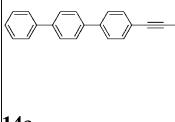
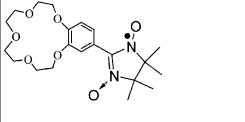
(19) Hyde, E. M.; Shaw, B. L.; Shepher, I. *J. Chem. Soc., Dalton Trans* **1978**, 1696.

(20) Klyatskaya, S. V.; Tretyakov, E. V.; Vasilevsky, S. F. *Russ. Chem. Bull.* **2001**, *50*, 868.

(21) Fischer, H., Ed. *Landolt-Börnstein, Magnetic Properties of Free Radicals*; Springer: New York, 1990; Vol. II/17f, p 185.

(22) Borovkov, V. I.; Bagryansky, V. A.; Yeletsikh, I. V.; Molin, Yu. N. *Mol. Phys.* **2002**, *100*, 1379.

Table 1. Structural Formulas and ESR Spectrum Parameters^a of the Selection of the Synthesized Radicals

 <p>3a</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.34$ $\Delta H_{\text{pp}}=1.48$ Solvent: DD	 <p>15a</p>	$g_{\text{iso}}=2.0059$ $A_N(N_1)=9.02$ $A_N(N_2)=4.23$ $\Delta H_{\text{pp}}=1.26$ Solvent: DH
 <p>3b</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.37$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.18$ Solvent: DD	 <p>16a</p>	$g_{\text{iso}}=2.0060$ $A_N(N_1)=8.96$ $A_N(N_2)=4.14$ $\Delta H_{\text{pp}}=0.48$ Solvent: H
 <p>3c</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.42$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.21$ Solvent: DD	 <p>8</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.30$ $A_{\text{H}(\text{CH}_2)}(2\text{H})=2.14$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.22$ Solvent: H
 <p>3d</p>	$g_{\text{iso}}=2.0066$ $A_N(2N)=7.24$ $\Delta H_{\text{pp}}=0.90$ Solvent: DD	 <p>9</p>	$g_{\text{iso}}=2.0075$ $A_N(N_1)=9.03$ $A_N(N_2)=3.97$ $A_{\text{H}(\text{CH}_2)}(2\text{H})=1.54$ $A_{\text{H}(\text{CH}_3)}(6\text{H})=0.24$ $A_{\text{H}(\text{CH}_3)}(6\text{H}) < 0.1$ Solvent: H
 <p>3e</p>	$g_{\text{iso}}=2.0059$ $A_N(N_1)=9.01$ $A_N(N_2)=3.95$ $\Delta H_{\text{pp}}=0.77$ Solvent: DD	 <p>13c</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.38$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.20$ Solvent: DH
 <p>13f</p>	$g_{\text{iso}}=2.0067$ $A_N(2N)=7.34$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.24$ Solvent: DD	 <p>13b</p>	$g_{\text{iso}}=2.0066$ $A_N(2N)=7.44$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.24$ Solvent: DH
 <p>13e</p>	$g_{\text{iso}}=2.0067$ $A_N(2N)=7.34$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.24$ Solvent: H	 <p>13d</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.42$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.22$ Solvent: DH
 <p>13a</p>	$g_{\text{iso}}=2.0065$ $A_N(2N)=7.40$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.24$ Solvent: DH	 <p>15b</p>	$g_{\text{iso}}=2.0058$ $A_N(N_1)=8.99$ $A_N(N_2)=4.20$ $\Delta H_{\text{pp}}=0.97$ Solvent: DH
 <p>14a</p>	$g_{\text{iso}}=2.0066$ $A_N(2N)=7.34$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.24$ Solvent: H	 <p>17</p>	$g_{\text{iso}}=2.0064$ $A_N(2N)=7.54$ $A_{\text{H}(\text{CH}_3)}(12\text{H})=0.22$ Solvent: DH

^a All spectra were taken in liquid alkane at room temperature using solid DPPH as standard to determine g -values. The samples were degassed by repeated freeze–pump–thaw cycles prior to experiments. Concentrations of radicals 10^{-5} – 10^{-4} M. Solvents: DD: *n*-dodecane (as viscous alkane to reduce spin exchange in the case of small radicals with sufficient solubility), H: *n*-hexane (standard alkane for large radicals with sufficient solubility), DH: 20% v/v 1,4-dioxane in *n*-hexane (binary solvent for radicals with too poor solubility in alkanes). For unresolved splitting on methyl hydrogens only the width of the structureless line is given. All HFI constants and line widths are given in units of gauss.

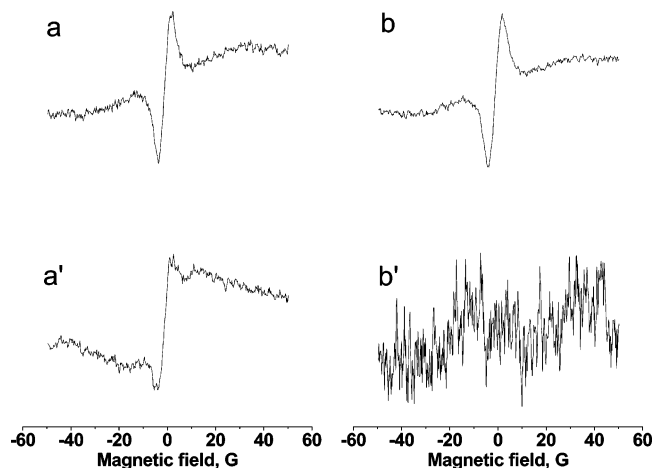


Figure 2. Experimental MARY/MFE lines in zero magnetic field for solution of 0.8×10^{-3} M (a) and 1.6×10^{-3} M (b) *p*-terphenyl- d_{14} and their transformation after addition of 2×10^{-2} M 1,3,5-trimethyl pyrazole (a') and 1.4×10^{-2} M its spin-labeled analogue **3d** (b').

two types of anions, one can compare its role on the two different time scales.

Figure 2 shows experimental MARY spectra of *n*-octane solutions of 0.8 – 1.6×10^{-3} M PTP- d_{14} (the two upper curves), which at this concentration not only acts as the electron acceptor but also captures some holes, and thus, two types of radical-ion pairs are formed, *n*-octane $^{+\bullet}$ /PTP- $d_{14}^{\bullet-}$ and PTP- $d_{14}^{\bullet+}$ /PTP- $d_{14}^{\bullet-}$. On both experimental traces there is a broad line of the normal-phase magnetic field effect produced by the former pairs, and a narrower normal-phase MFE from the latter pairs.

The width of each MFE is determined by the effective HFI in the radical ion pair, which means in this case by the effective HFI constant in the radical cation, since the radical anion is the same in both types of pairs and its ESR spectrum width is only 1.3 G. It is also important that PTP- $d_{14}^{\bullet+}$ is unlikely to deliver positive charge to another hole acceptor. In the first experiment 2×10^{-2} M of 1,3,5-trimethyl pyrazole was added to the solution (Figure 2a'). This left the narrow MFE unchanged but made the broad MFE much narrower. Such a change in the MFE signal indicates that pyrazole captures solvent hole and turns the radical ion pair *n*-octane $^{+\bullet}$ /PTP- $d_{14}^{\bullet-}$ into the pair pyrazole $^{\bullet+}$ /PTP- $d_{14}^{\bullet-}$, in which the radical cation apparently has a narrower ESR spectrum, thus giving a narrower MFE. Pyrazoles radical cations have earlier been reported in mass spectroscopic and ESR contexts,²³ and their formation in this system is not unexpected. A search through ESR and electrochemistry literature gave no indication to the existence of pyrazole radical anions in alkane liquids. However, even if present in the solution, they would form nonluminescing (and therefore unobservable) radical ion pairs with solvent radical cations. The expected narrow MARY line of inverted phase coming from the *n*-octane $^{+\bullet}$ /PTP- $d_{14}^{\bullet-}$ pair in this particular system is masked by the narrow MFE from the other pair and is not observed in experiment.

Figure 2b' shows the results of introducing a spin-labeled analogue **3d** of a similar concentration (1.4×10^{-2} M) into the solution—the signal almost completely disappears. A possible

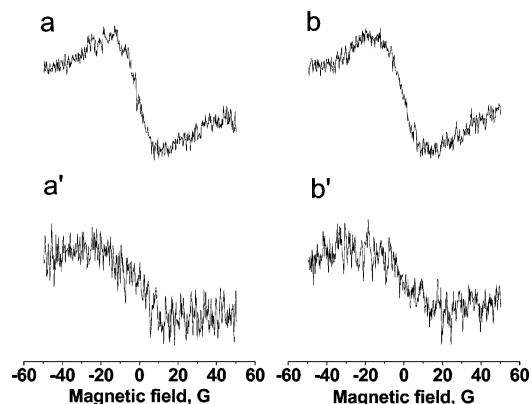


Figure 3. Experimental MARY/MFE lines in zero magnetic field for solution of 2×10^{-2} M C_6F_6 (a, b) and their transformation after addition of 2×10^{-2} M 1,3,5-trimethyl pyrazole (a') and 1.4×10^{-2} M its spin-labeled analogue **3d** (b').

explanation extrapolated from the results of ref 11 would be a similar reaction of hole capture to the pyrazole ring followed by fast paramagnetic relaxation due to the interaction between the spins of the radical cation and the stable radical. The signal formation time in this system is long enough (tens of nanoseconds) for the third spin to interfere and destroy spin coherence in the pair.

Figure 3 shows the results of a set of similar experiments with the other luminophore, hexafluorobenzene. The spectrum for solution of HFB in *n*-octane consists of the single intensive inverted MARY line in zero field due to large HFI in the HFB radical anion (Figure 3, the two upper curves). The addition of either diamagnetic (Figure 3a') or spin-labeled (Figure 3b') pyrazole led to an equal broadening of the MARY line, indicating that the added solute reduces the characteristic lifetime of the observed spin-correlated radical ion pairs. On the other hand, the fact that the signal does not disappear entirely indicates that the lifetime of the pairs still remains long enough as compared to the signal formation time, the latter being only units of nanoseconds due to strong HFI in $C_6F_6^{\bullet-}$. We believe that in the experiments shown in Figure 3b pyrazole captures the solvent hole but thus formed radical ion pairs pyrazole $^{\bullet+}$ / $C_6F_6^{\bullet-}$ produce nonluminescing molecules upon recombination, which is rather common for electron acceptors with high electron affinity such as HFB.²⁴ This means that both spin-labeled and diamagnetic pyrazole will render the pair unobservable in the experiment and broaden the MARY line. In the experiments described above it is necessary to keep in mind that hole capture to a positive charge acceptor is a diffusion-controlled process and in these systems involves normal molecular ions; therefore, other diffusion-controlled channels of interaction with the stable radical in solution should be considered as well. Those are electron transfer or formation of a bond with the radical ring and formation of a diamagnetic ion, and spin exchange between the stable radical and one of the radical ions of the pair “negative charge acceptor $^{\bullet-}$ ”/“solvent $^{\bullet+}$ ” in the bulk. All three of the possible reactions are contact processes, and therefore it is impossible to distinguish them in the described sort of experiment. As can be found from experiments with a well-known stable radical TEMPO (Figure 4), the rate constant of the reaction of a stable radical with solvent radical cation in these

(23) (a) Khmel'nitski, R. A.; Krasnoschek, A. P.; Polyakova, A. A.; Grandberg, I. I. *Zh. Obshch. Khim.* **1967**, 3, 1540/CA **1968**, 68, 34199r. (b) Elguerro, J.; Katritzky, A. R.; Denisko, O. V. *Adv. Heterocycl. Chem.* **2000**, 76, 1. (c) Neier, R., Ed. *Science of Synthesis*; Hetarenes and Related Ring Systems, Vol. 12; Georg Thieme Verlag: Stuttgart, New York, 2002.

(24) Werst, D. W. *Chem. Phys. Lett.* **1996**, 251, 315.

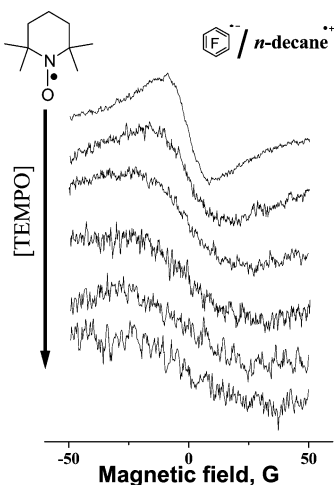


Figure 4. MARY spectrum of a solution of 10^{-2} M C_6F_6 in *n*-decane (the uppermost curve) and its broadening with addition of 3×10^{-3} , 8×10^{-3} , 1.4×10^{-2} , 1.9×10^{-2} , 2.3×10^{-2} M (from top to bottom) stable radical TEMPO. The rate constant obtained from the concentration dependence of the line width is $K \approx 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

conditions is indeed close to the diffusion-controlled limit. The rate constant here is determined through a known procedure²⁵ from a Stern–Volmer dependence of the width of the MARY line on the concentration of the radical, similar to conventional ESR. Thus, positive charge acceptors, although they have demonstrated the effect of the third spin and provided a guidance to estimating the characteristic time of its effect on the spin dynamics of the pair, appear to be a complicated way to introduce the third spin into the pair because of the diffusion character of the processes involving solvent hole.

To overcome this complication a different system was studied where a stable radical was introduced into a luminescing electron acceptor. In such a system only triads will yield magnetosensitive recombination fluorescence (the registered signal) because both luminophore/acceptor and stable radical are grouped in one molecule. The high mobility of “free” electron in alkanes will make it possible to use much lower concentrations of the spin-labeled luminophore, thus reducing the rate of the diffusion-controlled spin-exchange and other reactions in the bulk. In addition, much freedom will be available in choosing a hole acceptor with the desired properties.

To this end, a series of spin-labeled derivatives of *p*-terphenyl, an aromatic luminophore commonly used in spin chemistry studies under X irradiation, were synthesized. The experiments with these acceptors clearly demonstrated the importance of the structure of both of the functional fragments of the acceptor and the bridge, which plays an important role as it determines the degree of the exchange coupling between the two paramagnetic moieties. For example, no MARY spectra were observed with luminophore **13a**, despite its good luminescing properties. The reason is believed to be the earlier suggested¹¹ too-strong interelectron interaction in the biradical ion formed by electron capture, due to a continuous π -system from the radical center to the aromatic fragment of the luminophore. As the first step to reduce the exchange coupling, iminonitroxyl **9** was synthesized by reduction of nitronylnitroxyl **8** with NaNO_2 .

As is known from literature,²⁶ reduction of the *N*-oxide group in the third position of the 3-imidazoline-type radicals reduces

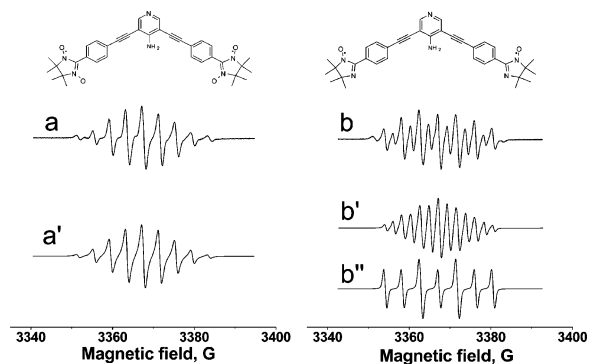


Figure 5. Experimental ESR spectra of 10^{-3} M solutions of biradicals **13j** (a) and **15j** (b) in the mixture of 20% 1,4-dioxane/80% *n*-hexane at room temperature. Below are given simulated spectra of the biradicals: (a') in the approximation of four equivalent nitrogen nuclei ($J \gg A_{\text{HFI}}$), $A_{\text{HFI}} = 3.70$ G; (b') in the approximation of two pairs of equivalent nitrogen nuclei ($J \gg A_{\text{HFI}}$), $A_{\text{HFI1}} = 4.40$ G, $A_{\text{HFI2}} = 2.41$ G; and in the approximation of $J \ll A_{\text{HFI}}$, for two nitrogen nuclei, $A_{\text{HFI1}} = 8.97$ G, $A_{\text{HFI2}} = 4.22$ G.

the exchange integral J between the two radical fragments of a stable biradical by 10–30 times per radical depending on the type of the bridge. We failed to find analogous estimates for 2-imidazoline-type radicals studied in this work, and thus several biradicals were prepared and studied by CW ESR. The results for a pair of 2-imidazoline biradicals are shown in Figure 5. The two symmetric biradicals differ only in the type of the radical fragment: nitronylnitroxyl **13j** (left) and iminonitroxyl **15j** (right). Under the structural formulas the experimental ESR spectra are shown, with the results of a simple modeling using PEST WinSim v.096. software.

The positions and intensities of the nine lines in the ESR spectrum of the nitronylnitroxyl biradical **13j** are well described under the assumption that all four nitrogen atoms of the radical fragments are equivalent. This is known to be the case for $J/A > 30$, where A is the HFI constant with the nitrogen nuclei.⁴⁴ The ESR spectrum of the iminonitroxyl biradical **15j** is more complex and can be described neither under the assumption of weak exchange (two independent radicals: the lower model spectrum; not all experimental spectrum lines are reproduced) nor under the assumption of strong exchange (two pairs of equivalent nitrogen atoms: the upper model spectrum; all lines are there but their relative magnitudes are reproduced incorrectly). The spectrum has features of both the biradical and the monoradical spectra, which means that there should be an intermediate value of the exchange integral ($J \approx A$).

The ESR parameters of the biradical ion formed from acceptor with a NNR/INR radical fragment cannot be measured directly using the ESR technique because of its too short lifetime (units to tens of nanoseconds). However, it is now reasonable to expect that in 2-imidazoline radicals as well, reduction of the *N*-oxide group should strongly decrease the conjugation between the two functional parts of the biradical ion. Nevertheless, despite sufficient luminescing properties of the INR luminophores, MARY/MFE effect could not be observed when they were used as electron acceptors (Figure 6c).

It is known that every saturated bond introduced into the bridge reduces the exchange integral J by about an order of

(25) Stass, D. V.; Lukzen, N. N.; Tadjikov, B. M.; Grigoryants, V. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *243*, 533.

(26) (a) Volodarsky, L. B.; Grigoriev, I. A.; Dikanov, S. A.; Reznikov, V. A.; Schukin, G. I. In *Imidazoline Nitroxyl Radicals*; Molin, Yu. N., Ed.; Nauka, Novosibirsk, 1988 (in Russian). (b) Volodarsky, L. B.; Reznikov, V. A. *Synthetic Chemistry of Stable Nitroxides*; CRC Press: Boca Raton, FL, 1993.

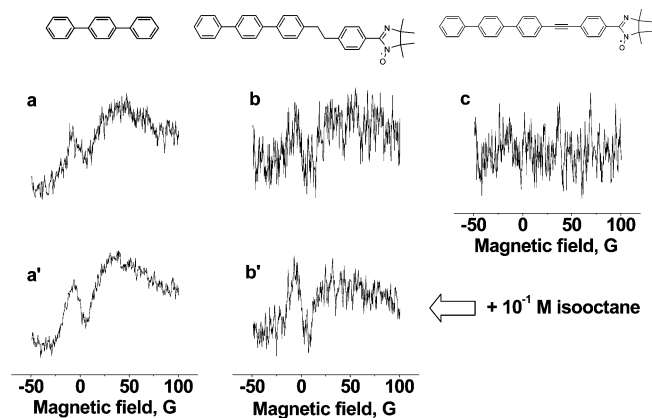


Figure 6. Experimental MARY spectra of solution of 10^{-4} M *p*-terphenyl- h_{14} (a) and its two derivatives (b, c) in *n*-hexane at room temperature. Spectra a' and b': 10^{-1} M isooctane was added to solutions a and b, respectively.

magnitude. Therefore, to further decrease J , 2-imidazoline radical **16a** with a saturated ethane bridge between the two functional parts of the molecule was prepared by hydrogenation of iminonitroxyl **15a** with molecular hydrogen over Pd/C followed by oxidation with sodium periodate. The results of a successful experiment with this type of the terphenyl derivative are shown in Figure 6b. For comparison, the same figure shows MARY spectra from systems with the corresponding non-hydrogenated nitroxyl (Figure 6c) and with *p*-terphenyl without the radical fragment (Figure 6a). The other partner of the radical pair in this case is the solvent (*n*-hexane) radical cation. The lower traces in the figure show experimental MARY spectra after addition of 0.1 M isooctane in the same systems. The ionization potential of isooctane is lower than that of hexane; therefore, in hexane solution it readily forms radical cations isooctane $^{+\bullet}$ with considerable HFI, 27 thus providing better conditions for observation of the MARY spectrum in the pair “isooctane $^{+\bullet}$ /spin-labeled luminophore $^{\bullet-}$ ”. Thus, in these experiments the first reproducible signal from the pair “radical cation/biradical anion” in weak field was obtained.

The phenyl fragment conjugated with the 2-imidazolin-1-oxyl present in all the synthesized thus far spin-labeled luminophores leads to the fact that the radical moiety of the molecule has an optical absorption band overlapping the emission band of the luminophore moiety, which in turn leads to a decrease in the fluorescence efficiency of the compound. 11 This was improved by synthesizing a *p*-terphenyl derivative **9** with the aromatic part linked through ethane bridge directly to the nitroxyl fragment (Scheme 2).

Luminophore **9** made it possible to obtain a reproducible signal in weak field (Figure 7b). Moreover, it allowed for the first registration of the ESR signal from a triad (Figure 7a) using OD ESR technique, which was designed as an extremely sensitive radiospectroscopic method specially for studying short-lived radical ion pairs. 28 Despite the ultimate sensitivity of the OD ESR technique as compared to other ESR methods, it is still much more demanding on the relaxation time of the pair than the MARY technique. 29 Luminophore **9**, in which the

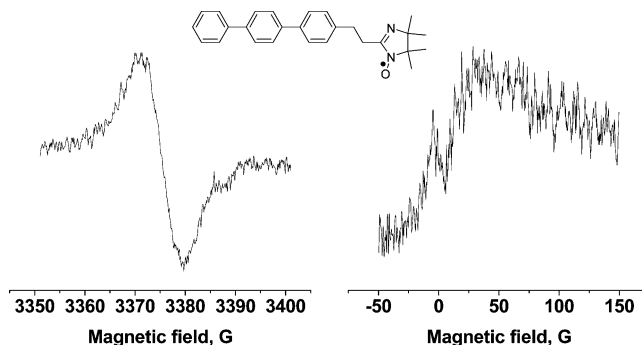


Figure 7. OD ESR (left-hand curve) and MARY (right-hand curve) spectra of solution of 2.5×10^{-4} M nitroxyl **11** in *n*-hexane taken at temperature $T = -20$ °C. The amplitude of the magnetic field modulation $M = 6$ G.

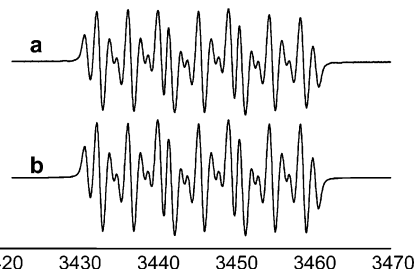


Figure 8. OD ESR spectrum of solution of 10^{-4} M nitroxyl **9** in *n*-hexane taken at room temperature (a) and its simulation with parameters $A_N(N_1) = 9.0$ G, $A_N(N_2) = 4.0$ G, $A_H(\text{CH}_3)(2\text{H}) = 0.24$ G (b).

impeding effect of the interaction between the two spins on the OD ESR signal formation has been minimized, was the first real system yielding an experimental OD ESR signal from a spin-labeled radical ion pair.

The obtained MARY spectra and the OD ESR spectrum of the spin-labeled luminophores are single noncharacteristic structureless lines that cannot distinguish the species from nonradical luminophores (see, e.g., Figure 3). To check that the radical fragment of the luminophore is effective, the CW ESR spectrum of nitroxyl **9** was analyzed (Figure 8). Considerable HFI constants (1.5 G) are seen at the two methylene protons of the first CH_2 group of the ethane bridge. Of the same order of magnitude (2.14 G) are HFI constants of the methylene protons of the first CH_2 group of the ethane bridge in similar 3-oxide-1-oxyl **8** (Table 1). Because of the phenyl ring conjugated with the radical fragment, the ESR spectra of the other synthesized radicals turned out to be almost insensitive to the luminophore/bridge substitute.

Now it is possible to obtain a lower estimate for the exchange interaction between the two paramagnetic fragments of the biradical anion from the observed ESR and OD ESR spectra. The measured peak-to-peak line width of the experimental OD ESR signal (Figure 7a) is approximately 8.5 G, which is substantially larger than the expected spectrum width for the *p*-terphenyl- h_{14} radical anion ($A_H(4\text{H}) = 1.61$ G, $A_H(4\text{H}) = 0.46$ G, $A_H(2\text{H}) = 2.47$ G, $A_H(4\text{H}) = 1.2$ G, $\Delta H_{pp} = 2\sigma = 5.4$ G). 30 The effect of the saturated bridge on the ESR spectrum width can be accounted for as CH_2 -substitution of the *p*-terphenyl fragment in the fourth position. This leads to substitution of one α proton with $A_{H\alpha} = 2.47$ G by two β methylene protons with $A_{H\beta}(2\text{H}) \approx Q_\beta/Q_\alpha \times A_{H\alpha} \approx 28/22 \times 2.47$ G = 3.14 G.

(27) Anishchik, S. V.; Borovkov, V. I.; Ivannikov, V. I.; Shebolaev, I. V.; Chernousov, Yu. D.; Anisimov, O. A.; Molin, Yu. N. *Chem. Phys.* **1999**, *242*, 319.

(28) (a) Anisimov, O. A. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds., Kluwer Academic Publishers: Amsterdam, 1991; p 285. (b) Trifunac, A. D.; Werst, D. V. In *Radical Ionic Systems*; Lund, A., Shiotani, M., Eds., Kluwer Academic Publishers: Amsterdam, 1991; p 195.

(29) Tadjikov, B. M.; Stass, D. V.; Molin, Yu. N. *J. Phys. Chem. A* **1997**, *101*, 377.

(30) Gerson, F. *High Resolution ESR Spectroscopy*; Wiley: New York, 1970.

All other hyperfine couplings are assumed to remain unchanged, and the ESR spectrum width becomes $2\sigma_{\text{ptp}} = 6.5$ G, which is still notably smaller than the measured value. This, however, can be accounted for by fast exchange with the stable radical moiety. Indeed, the calculated ESR spectrum width of the stable radical fragment (see HFI parameters in Table 1) is $2\sigma_{\text{rad}} = 16.3$ G. In the approximation of fast exchange between the two electrons of the biradical ion the effective spectrum width of the anion partner of the radical ion pair can be estimated as $\Delta H_{\text{pp}} = 2\sigma_{\text{eff}} = 2(\sigma_{\text{ptp}}^2 + \sigma_{\text{rad}}^2)^{1/2}/2 \approx 8.8$ G, which is in good agreement with the observed line width. As it was concluded in the case of stable biradicals (Figure 5), this suggests an exchange interaction exceeding at least by an order of magnitude the HFI constants in the biradical anion, i.e., hundreds of gauss.

On the other hand, a complementary estimate can be obtained from the CW ESR spectrum of **9** (Figure 8). The coupling of 1.5 G at the two CH₂ protons at the radical end of the ethane bridge corresponds to a spin density at the C atom $\rho_{\text{rad}} \approx 1.5/507 \approx 3 \times 10^{-3}$ due to the effect of hyperconjugation. A similar value $\rho_{\text{ptp}} \approx 3/507 \approx 6 \times 10^{-3}$ can be derived from the estimated HFI of 3.14 G at the other pair of the bridge CH₂ protons (β methylene protons to *p*-terphenyl). Now, the exchange coupling through the bridge can be roughly estimated as an imaginary π -bond energy $J_{\pi} \approx 10^{15}$ Hz factored by the two estimated spin densities at the C atoms $J \approx J_{\pi} \times \rho_{\text{rad}} \times \rho_{\text{ptp}} \approx 10^{10}$ Hz ($\sim 10^3$ G). This estimate agrees well with the experimental spectrum width and far exceeds the HFI constants in the biradical anion. On the other hand, it is far below the thermal energy $kT \approx 10^{13}$ Hz. Qualitatively, this is an optimal system to demonstrate the effect of the third spin in this type of experiment, because the exchange is fast enough to mix the spectra of the two moieties but at the same time it is too weak to rearrange the energy levels of the system.

To get more informative MARY spectra a radical ion pair may be considered where the radical anion is formed from a nonluminescing spin-labeled electron acceptor, and the function of the luminophore is performed by the counterion. This pattern will provide more freedom in choosing a luminophore with special properties and will also help avoid the quenching of the recombination fluorescence by the radical. To this end, crown ether derivatives (**3d–f,j,k**) were tried as spin-labeled electron acceptors. Crown ethers in nonpolar solution were expected to behave similarly to clusters of polar molecules (e.g., alcohol) that can solvate electrons to form effective radical anions with molecular diffusion mobility.³¹ The expectation is also supported by the observation that in pure 1,4-dioxane as solvent, as opposed to alkanes, MARY signal is rather prominent even without using electron acceptors (see below), which points to a lowered diffusional mobility of the negative charge. Although test experiments with bare crown ethers (18-crown-6 and 15-crown-5) in alkanes did not unambiguously indicate negative charge capture, the studies with the spin-labeled crown ether derivatives were nevertheless attempted.

Since the synthesized derivatives poorly dissolve in alkanes (less than 10^{-5} M), 1,4-dioxane was taken as solvent. For a start-up experiment, radical ion pair “durene^{•+}/electron^{•-}” was chosen where durene was the luminophore and the driver of

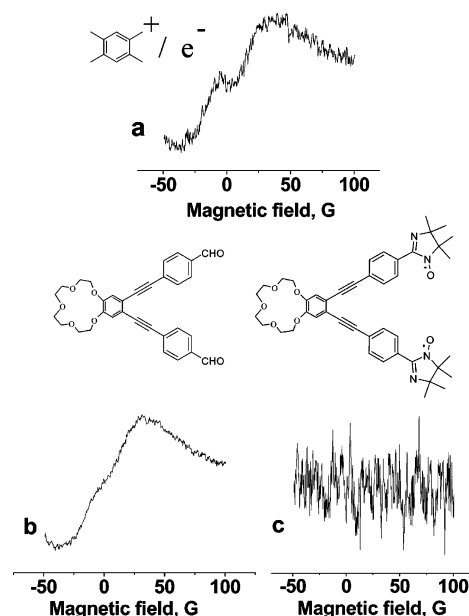


Figure 9. Experimental MARY spectrum of solution of 3×10^{-2} M durene in 1,4-dioxane at room temperature (a) and its transformation after addition of 10^{-4} M diamagnetic (b) and paramagnetic (c) crown ether derivatives.

the spin evolution in the pair ($A_{\text{H}}(12\text{H}_{\text{CH}_3}) = 10.7$ G, $A_{\text{H}}(2\text{H}_{\text{ar}}) = 0.8$ G³²). Due to the solvation effect of the oxygen-containing solvent the mobility of the electron was not very high as compared to similar systems in nonviscous alkanes, so the lifetime of the radical ion pair before recombination was long enough for MARY signal to be observed. A typical MARY spectrum obtained in this sort of solution (Figure 9a) is a noisy MFE curve with the MARY line “inversion” in the vicinity of zero field. When a diamagnetic crown ether derivative **18** was added in the solution, the signal improved markedly (Figure 9b), presumably due to a longer lifetime of the radical ion pair after the electron had been accepted by the molecule, thus forming a radical ion with even lower diffusional mobility.

When a similar spin-labeled crown ether derivative **15k** with continuous conjugation through the bridge was introduced into the solution, the magnetosensitive signal completely disappeared (Figure 9c), although the overall level of fluorescence intensity from the sample did not change noticeably. Since rather low concentration of the acceptor (10^{-4} M) was used, and the role of luminophore in the pair was played by the positive charge acceptor, the observed effect unequivocally came from electron capture by the spin-labeled crown ether derivative and not from bulk processes or channels involving the radical cation of the pair. However, from this experiment we cannot determine which fragment of the crown ether derivative accepts the electron: phenylacetylene, the ether ring, or the radical moiety, and this problem is now under investigation. To the best of our knowledge, this is the first application of crown ether derivatives in the context of spin chemistry under ionizing irradiation. The observation that they can capture electrons in solution makes them worth further investigation. For example, the crown could be used to introduce a paramagnetic ion in the radical ion pair and thus explore a new class of experimental systems.

The introduction of 1,4-dioxane as solvent in MARY-type experiments is also worth stressing. Like *n*-alkanes, it is a

(31) (a) Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572. (b) Smirnov, S. N.; Anisimov, O. A.; Molin, Yu. N. *Chem. Phys.* **1986**, *109*, 321.

(32) Dessau, R. M.; Shih, S.; Heiba, E. I. *J. Am. Chem. Soc.* **1970**, *92*, 412.

Table 2. Summary of the Key Results of the MARY and OD ESR Experiments with the Synthesized Spin-Labeled Charge Acceptors^a

SYSTEM (spin-labeled radical ion pair)			RESULTS	
Cation partner	Anion partner	Solvent	MARY signal	OD ESR signal
		<i>n</i> -octane	No	-
		<i>n</i> -octane	Yes	-
$n\text{-C}_{12}\text{H}_{14}^{\bullet+}$		<i>n</i> -hexane	No	No
$n\text{-C}_{12}\text{H}_{14}^{\bullet+}$		<i>n</i> -hexane	No	No
$n\text{-C}_{12}\text{H}_{14}^{\bullet+}$		<i>n</i> -hexane	Yes	No
$n\text{-C}_{12}\text{H}_{14}^{\bullet+}$		<i>n</i> -hexane	Yes	Yes
	solvated electron	1,4-dioxane	Yes	-
		1,4-dioxane	Yes	-
		1,4-dioxane	No	-

^a The lamp sign indicates the luminescing partner/moiety in the triad. The dash sign means that this type of experiment was not performed.

nonpolar solvent and reasonably stable under ionizing irradiation, but its capability for electron solvation and dissolving certain compounds is remarkable. This can make 1,4-dioxane the best solution for experimental situations when alkanes are, for some reason, inapplicable. However, since it has not yet been systematically employed in radiation chemistry experiments, it should be studied in detail before it can be routinely used.

Conclusions

A series of **A-Sp-R** paramagnetic derivatives of charge acceptors suitable for studies of three-spin systems in X-irradiated liquid alkane solutions have been developed and analyzed by CW ESR. The synthesized spin-labeled compounds have proved to be a convenient set of charge acceptors to introduce the "third" spin and/or the luminescing moiety into either of the partners of the spin-correlated radical ion pair. The pair thus becomes a three-spin system "radical cation/radical anion/stable radical" with variable spin exchange between the paramagnetic fragments in the biradical ion partner. The degree of the exchange coupling can be controlled by conjugation in the bridge that links the two functional fragments (charge acceptor and radical) of the compound, and by the structure of the radical moiety.

It has been shown that, despite the seemingly poor signal-to-noise ratio inherent for such short-lived systems, radiation-generated spin triads can be conveniently studied using MARY spectroscopy in a "yes/no" type experiment. Optimal experi-

mental conditions and acceptor structures within the studied class of compounds have been found. With the most optimal structure of the radical and the bridge, an experimental OD ESR signal from the spin triad has been registered, and the value of the exchange integral between the two paramagnetic moieties of the biradical ion living as short as about 100 ns has been estimated to be ca. 10^3 G. This value is, however, too large for more informative experimental techniques (e.g. quantum beats in recombination fluorescence) to be applied, and further reduction of the exchange by lengthening the alkane chain would make the bridge too floppy. It is possible to introduce a rigid saturated bridge, e.g., a six-membered cycle, but that would be a synthetic task beyond the scope of this work. A simpler way to improve the system is synthesizing similar luminophores with 3-imidazoline radicals to reduce conjugation within the radical fragment and thus provide more freedom in choosing the structure of the bridge. This work is currently on the way.

For convenience the main results of the work are collected in Table 2.

Acknowledgment. We are indebted to Dr. A. I. Kruppa for valuable discussion during the preparation of the manuscript, especially for his input on the estimation of the value of the exchange integral in the biradical ion. The work was supported by RFBR, projects 01-03-33292 and 02-03-32265, and INTAS, project 99-01766. D.V.S. is grateful to the Russian Science Support Foundation for awarding a personal scholarship.

JA037157M