Synthesis and properties of paramagnetic derivatives of linear and fused polyaromatic compounds

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Paramagnetic derivatives of tolan, anthracene, and terphenyl of the A-Sp-R^{*} type, where A is an aromatic group, R^{*} is a stable radical center, and Sp is a spacer, were synthesized. The electronic absorption and luminescence spectra of these compounds were examined. The introduction of the paramagnetic dihydroimidazole fragment causes a decrease (10-500-fold) in the quantum yield of luminescence compared to emission of the individual aromatic luminophore. The presence of a radical center (R^{*}) in the (alkane)^{*+/-*}A-Sp-R^{*} radical-ionic pair leads to the disappearance or fast (nanoseconds) damping of the magnetic effect of luminescence arising upon recombination of these pairs.

Key words: tolan, anthracene, terphenyl, alkynes, nitroxyl radicals, radical ions, magnetic effects, luminescence.

Previously,^{1,2} we have developed procedures for the synthesis of spin-labeled acetylenes which contain heterocyclic (π -electron-excessive pyrazole and π -electrondeficient pyridine) or π -carbocyclic residues (including benzo-crown ether) and derivatives of 4,4,5,5-tetramethyldihydroimidazole 1-oxyl 3-oxide (nitronylnitroxyl radicals (NNR)) or 4,4,5,5-tetramethyldihydroimidazole 1-oxyl (iminonitroxyl radicals (INR)) as a radical component. These compounds serve as a basis for the construction of multispin structures containing paramagnetic metals along with a radical center. In this work, we consider the problems of the preparation of linear and fused polyaromatic compounds containing fragments of nitroxyl radicals of the dihydroimidazole series. Compounds of this type may be convenient model systems for the observation of the phenomenon of spin catalysis^{3,4} in recombination of radical-ionic pairs generated in solutions of alkanes upon radiolysis. The structure of the $A-Sp-R^*$ type consists of an aromatic group (A), which can accept a positive or a negative charge and serve as a luminophore, a stable radical center (R^{*}) acting as a spin catalyst, and a spacer (Sp) between the group A and the radical center R*. In dilute solutions of A-Sp-R', ionization of alkane (C_nH_{2n+2}) is accompanied by rapid electron capture to form a singlet-corre-lated radical-ionic pair $(C_nH_{2n+2})^{+\uparrow}...\downarrow^{-*}A-Sp-R^*$.

The interaction between the spin of the fragment \downarrow ⁻A and the radical center R⁺ leads to destruction of singlet correlation of the pair, resulting in a decrease in the magnetic effect in recombination fluorescence of this pair.

To observe these effects, it is necessary that the singlet-excited molecule *A--Sp--R^{*}, which is generated upon charge recombination, retained its ability to exhibit luminescence in spite of the quenching effect of the radical R^{*} in these systems.^{5,6} Therefore, we performed preliminary studies of spectral-luminescent properties of the synthesized compounds and carried out experiments aimed at recording the magnetic effects.

Results and Discussion

Synthesis of paramagnetic derivatives of tolan, anthracene, and terphenyl. Although many studies were devoted to the chemistry of radicals of the dihydroimidazole series, data on paramagnetic polyaromatic derivatives are scarce. In our opinion, this situation stems primarily from the fact that convenient and versatile procedures for their synthesis are lacking rather than from the fact that these compounds are of little interest. Hence, the major aim of this work was to synthesize polyarenes linked to stable nitroxyl radicals through spacers.

One of the approaches to the synthesis of compounds of the A-Sp-R type, where R is dihydroimidazole 1-oxyl 3-oxide, is based on the fact that the methyl group at position 4 of 1-hydroxy-2,2,4,5,5-pentamethyl-2,5-dihydro-1*H*-imidazole 3-oxide (1) is activated by the nitrone group. Thus the reactions of compound 1 with aromatic aldehydes in the presence of bases afford 4-arylvinyl-1-hydroxy-2,5-dihydro-1*H*-imidazole 3-oxides, whose oxidation gives rise to nitroxyl radicals. This

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approach was used for the synthesis of 2,2,5,5tetramethyl-4-[2-(4-phenylethynylphenyl)vinyl]-2,5dihydro-1*H*-imidazole 1-oxyl 3-oxide (2) (Scheme 1).



4-Phenylethynylbenzaldehyde (3) was condensed with compound 1 under the action of NaOH in MeOH. 1-Hydroxy-2.2,5,5-tetramethyl-4-[2-(4-phenylethynylphenyl)vinyl]-2,5-dihydro-1H-imidazole 3-oxide (4) wasobtained in 48% yield and was oxidized with PbO₂ to thetarget nitroxyl radical 2.

4-[2-(9-Anthryl)vinyl]-1-hydroxy-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazole 3-oxide (5) and<math>4-[2-(9-anthryl)vinyl]-2,2,5,5-tetramethyl-2,5-dihydro-1*H*-imidazole 1-oxyl 3-oxide (6) were synthesized analogously (Scheme 2). However, we could prepare theprecursor of the nitroxyl radical,*viz.*, compound 5, onlyby using a slightly modified procedure, in 6% yield. Inthis case, <math>4-[2-(9-anthryl)vinyl]-2,2,5,5-tetramethyl-2,5dihydro-1*H*-imidazole 3-oxide was obtained as the major product (8).

Presently, a classical procedure for the synthesis⁷ of derivatives of 4,5-dihydro-1*H*-imidazole nitroxides involves condensation of aldehydes with 2,3-dimethyl-2,3bis(hydroxyamino)butane followed by oxidation of cyclic adducts with sodium periodate or lead dioxide. However, we failed to use this procedure for the preparation of polyaromatic dihydroimidazole nitroxides. We used benzene, tetrahydrofuran, dioxane, or methanol as the solvent: the temperature and the reaction time were varied. However, all attempts to prepare the target derivatives by condensation of aldehydes, such as 4-phenylethynylbenzaldehyde, biphenyl-4-ylbenzaldehyde,



and [1,1';4',1"]terphenyl-4-ylethynylbenzaldehyde, with 2,3-dimethyl-2,3-bis(hydroxyamino)butane were unsuccessful.

Cross-coupling of aryl halides with terminal acetylenes^{8,9} catalyzed by complex palladium or copper salts made it possible to perform an alternative synthesis of 2-(arylethynylphenyl)-4,5-dihydro-1H-imidazole 1-oxyl 3-oxides, viz., to construct a paramagnetic molecule by condensation of aryl halide with paramagnetic 2-(4-ethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole 1-oxyl 3-oxide (9). However, an attempt to introduce spin-labeled acetylene 9 into the reaction with 4-iodotoluene under standard conditions (PdCl₂(PPh₃)₂, Cul, NEt₃, C₆H₆, 55-80 °C) failed and the reaction gave rise to homo-coupling products. The use of piperidine, which is a stronger base than triethylamine, made it possible to perform the reaction at room temperature, thus suppressing to some extent side processes. Cross-coupling of an iodo derivative of terphenyl 10 with alkyne 9 under the above-mentioned conditions (Scheme 3) afforded a mixture of 4,4,5,5-tetramethyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)-4,5-dihydro-1H-imidazole 1-oxyl 3-oxide (12) (the yield was 20%), 4.4.5.5-tetramethyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)-4,5-dihydro-1H-imidazole, 4,4,5,5-tetra-



methyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)-4,5-dihydro-1*H*-imidazole 1-oxyl, terphenyl, and homocoupling products of alkyne 9.

Hydrogenation of nitronylnitroxyl radical 12 over Pd/C followed by oxidation with NaIO₄ yielded 4,4,5,5-tetramethyl-2-[4-(2-[1,1';4',1"]terphenyl-4-ylethyl)-phenyl]-4,5-dihydro-1*H*-imidazole 1-oxyl 3-oxide (13) and 4,4,5,5-tetramethyl-2-[4-(2-[1,1';4',1"]terphenyl-4-ylethyl)phenyl]-4,5-dihydro-1*H*-imidazole 1-oxyl (14).

Spectral-luminescent properties. The attachment of the tolan, p-terphenyl, or anthracene nucleus to the dihydroimidazole ring affects only slightly the characteristics of optical absorption associated with $n-\pi^*$ transitions in the original heterocyclic fragment. This result agrees with the published data.^{2,5} In the case of compounds with additional π -conjugation (2, 4, 5, 6, 8, and 12), the optical absorption spectra of tolan, *p*-terphenyl, and anthracene change substantially. As expected, $\pi - \pi^*$ absorption bands of the original luminophores are shifted by 3000-5000 cm⁻¹ to the red region and lose their characteristic vibrational structure. The observed absorption spectrum of the adduct does not obviously represent the sum of spectral absorption of the individual luminophore and the heterocycle. When conjugation is absent (13 and 14), the absorption spectra retain the major absorption characteristics of the individual fragments according to the additive concepts of supramolecular photochemistry.6,10

The introduction of the paramagnetic dihydroimidazole fragment led to a substantial decrease (by a factor of 10-500) in the quantum yield of luminescence compared to emission of the individual aromatic luminophore. For example, the quantum yield of compound **6** was no higher than 0.005. In the case of very low quantum yields, the luminescence spectra were difficult to record due to emission of diamagnetic microimpurities in samples.

In our case, the low quantum yields of luminescence may be a consequence of overlapping of emission bands of the luminophore with rather intense $\pi - \pi^*$ absorption of the heterocycle ($\lambda = (25-35) \cdot 10^3$ cm⁻¹, $\varepsilon \approx$ (6-12) $\cdot 10^3$ L mol⁻¹ cm⁻¹),⁵ due to which an efficient intramolecular energy transfer can occur according to the dipole-dipole mechanism.¹⁰ This process should lead to quenching of emission of the adduct because dihydroimidazole radicals do not exhibit luminescence.⁵

Yet another mechanism of quenching associated with paramagnetism of the dihydroimidazole ring may involve long-range quenching by electron exchange.⁶ This mechanism results only in the local relaxation of the excited singlet state of the luminophore to the ground state virtually without electronic-excitation energy transfer to other fragments of the molecule.

To estimate the contribution of electron-exchange quenching, we compared the quantum yields for compounds 2 and 4. The quantum yield for paramagnetic adduct 4 decreases by a factor of 50 compared to that for diamagnetic compound 2, whereas the intensity of luminescence of diamagnetic analog 2 is quenched less than tenfold compared to that of tolan. The efficiency of luminescence quenching according to the mechanism of intramolecular dipole-dipole energy transfer of singlet excitation of the luminophore to the dihydroimidazole fragment would be expected to be equal for compounds 2 and 4. Actually, the optical absorption spectra and the emission spectra of adducts 2 and 4 are similar, the latter spectra overlapping substantially with absorption. Therefore, it can be suggested that the major mechanism of quenching is associated with the paramagnetic properties of the dihydroimidazole fragment.

Magnetic effects. Initially, we attempted to detect spin catalysis using compound **6**, in which the luminophore is conjugated with the heterocycle, and compounds **13** and **14**, in which this conjugation is blocked. Solutions of these compounds in dodecane $(10^{-4} \text{ mol } \text{L}^{-1})$ were irradiated with fast electrons using a ⁹⁰Sr radioactive source on an instrument described previously.¹¹ Under these conditions, magnetically sensitive fluorescence can occur due to recombination of singlet-correlated radicalionic pairs $(C_{12}H_{26})^{++/-}A-Sp-R^{+}$.

The time-resolved magnetic effect was recorded as the ratio between the curves of fluorescence decay in a magnetic field of 9600 G and in the absence of the external field. Due to the weak intensity of fluorescence, the curves were accumulated for many hours, this time being substantially larger than the typical time of accumulation for systems with a diamagnetic luminophore.

Unlike diamagnetic compound 5, whose magnetic effect was ~15% and reached the plateau in 15-20 ns, paramagnetic analog 6 does not exhibit the magnetic effect. Apparently, the spin interaction between R⁺ and - A in molecule 6 is so much larger that spin correlation in the radical-ionic pair disappears over a time much shorter than can be detected by the available instrument. In the cases of compounds 13 and 14, in which the systems of the luminophore and the radical fragment are separated by three C--C bonds, we detected a substantial (20-30%) magnetic effect, which, however, disappeared in several nanoseconds. In these cases, the radical R⁺ destroyed the spin correlation in the pair in a time comparable with the resolving power of the instrument (1 ns).

Thus, the structures synthesized, generally speaking, are suitable for investigation of spin catalysis in recombination of radical-ionic pairs. However, to perform quantitative studies, it is necessary to weaken interactions between the R⁺ and ⁻⁺A fragments by introducing, for example, additional saturated units into the bridging spacer Sp. This will allow one to improve conditions of observations both due to an increase in the fluorescence yield and owing to the shift of the time-resolved magnetic effect to the range of 10-100 ns, corresponding to the time window of the recording instrument.

Experimental

The ¹H NMR spectra were recorded on a Bruker Avance-300 spectrometer. The 1R spectra were measured on a Bruker

IFS-66 spectrometer in KBr pellets. The ESR spectra were obtained on a Bruker EMX radiospectrometer at room temperature; the concentrations of the solutions were in the range of $5 \cdot 10^{-5} - 5 \cdot 10^{-4}$ mol L⁻¹. The mass spectra (electron impact) were measured on a Finnigan SSQ-710 instrument with direct inlet of the sample (the temperature of the ionization chamber was 220-270 °C; ionizing voltage was 70 eV). The column chromatography was carried out using KSK silica gel (SiO_2) (60/200 µm). The electronic absorption spectra were recorded on a Specord UV-Vis spectrophotometer in methanol, methylcyclohexane, and acetonitrile at room temperature. Luminescence was studied on an instrument for stationary luminescence measurements both at room and low (77 K) temperatures. Luminescence was excited with the line λ = 314 nm of a DRSh mercury lamp using frontal illumination of the sample. The luminescence spectra were recorded in the region of 320-700 nm using an FEU-119 instrument and an H-307/1 XY recorder (without correction for the spectral sensitivity of the instrument).

1-Hydroxy-2,2,5,5-tetramethyl-4-{2-(4-phenylethynylphenyl)vinyl]-2,5-dihydro-1H-imidazole 3-oxide (4). The synthesis was carried out according to a known procedure.12 A mixture of 4-phenylethynylbenzaldehyde $(3)^{13}$ (1.63 g, 7.9 mmol), 1-hydroxy-2,2,4,5.5-pentamethyl-2,5-dihydro-1Himidazole 3-oxide (1) (1.63 g, 7.9 mmol), NaOH (0.34 g), and MeOH (10 mL) was refluxed for 1.5 h and then poured into water (100 mL). The precipitate that formed was filtered off and dissolved in trichloroethylene. The resulting solution was filtered through a layer of silica gel. The solvent was evaporated and the residue was recrystallized from a C₆H₆-hexane mixture. Compound 4 was obtained in a yield of 1.36 g (48%), m.p. 198-200 °C. 1R, v/cm⁻¹: 2230 (C≡C); 2935, 2979 (CH₃); 3244 (OH). ¹H NMR, δ: 1.52 (s, 6 H, CH₃); 1.62 (s, 6 H, CH₃); 4.85 (br.s, 1 H, OH); 6.86 (d, 1 H, =CH-Im, J = 16.2 Hz); 7.26-7.57 (m, 9 H, H arom.); 8.42 (d, 1 H, -CH=, J = 16.2 Hz). MS, m/z (I_{rej} (%)): 360.1 [M]⁺ (21.6), 344.1 (10.0), 329.1 (10.1), 314.1 (15.2), 312.1 (22.4), 287.0 (21.5), 271.0 (14.7), 270.0 (19.6), 258.0 (42.1), 257.0 (100), 243.0 (19.5), 242.0 (83.0), 241.0 (36.0), 215.0 (29.4), 203.0 (7.5), 202.0 (16.7), 177.0 (3.1), 129.0 (3.0), 101.0 (5.3), 91.0 (41.6), 77.0 (3.7), 73.0 (2.2), 42.0 (17.6), 31.0 (5.4), 28.0 (5.7). Found: m/z 360.1850 [M]⁺. C₂₃H₂₄N₂O₂. Calculated: M = 360.1838.

2,2,5,5-Tetramethyl-4-[2-(4-phenylethynylphenyl)vinyl]-2,5-dihydro-1H-imidazole 1-oxyl 3-oxide (2). The synthesis was carried out according to a procedure reported previously.¹² A mixture of compound 4 (0.30 g, 8 mmol) and PbO_2 (0.93 g) in benzene (10 mL) was stirred at ~20 °C for 20 h. The oxidant was filtered off, the solution was filtered through a layer of silica gel, the solvent was distilled off, and the residue was recrystallized from a C₆H₆-hexane mixture. Compound 2 was obtained in a yield of 0.21 g (70%), m.p. 205-207 °C. IR, v/cm⁻¹: 2230 (C≡C); 2936, 2985 (CH₃). MS, m/z (I_{rel} (%)): 359.2 [M]⁺ (21.3), 330.0 (12.8), 329.0 (50.4), 314.0 (59.7), 312.0 (100), 271.0 (48.3), 270.0 (43.6), 241.9 (26.4), 241.0 (21.5), 215.0 (60.2), 203.0 (9.3), 202.0 (19.7), 177.0 (94.1), 156.0 (2.6), 101.0 (94.6), 77.0 (4.3), 56.0 (25.3), 41.0 (11.1), 28.0 (3.7). Found: m/z 359.1758 [M]⁺. C₂₃H₂₃N₂O₂. Calculated: M = 359.1759. ESR: $a_N (1 \text{ N}) = 0.74 \text{ mT}$, $a_{H(Me)} (12 \text{ H}) = 0.021 \text{ mT}$.

4-[2-(9-Anthryl)vinyl]-1-hydroxy-2,2,5,5-tetramethyl-2,5dihydro-1*H*-imidazole 3-oxide (5). A mixture of 9-anthraldehyde (7) (2.6 g, 13 mmol), compound 1 (2.15 g, 13 mmol), NaOH (2 g), and MeOH (20 mL) was refluxed for 6 h and poured into water. The precipitate that formed was filtered off, dissolved in a minimum amount of chloroform, and chromatographed. Aldehyde 7 and compound 5 were eluted with benzene in yields of 0.36 g and 0.26 g (6%), respectively, and compound 8 was

eluted with chloroform in a yield of 1.4 g (32%). 1-Hydroxy-2,5-dihydro-1H-imidazole 3-oxide (5), m.p. 217-218 °C (from benzene). IR, v/cm⁻¹: 3425 (OH), ¹H NMR (CD₂Cl₂), δ: 1.52, 1.62 (both s, 6 H each, CH₃); 5.12 (br.s, 1 H, OH); 6.57 (d, 1 H. = CH-Im, J = 17.2 Hz); 7.48-8.48 (m, 9 H, H arom.); 9.41 (d, 1 H, -CH=, J = 17.2 Hz). Found: m/z 360.1858 [M]⁺ $C_{23}H_{24}N_{2}O_{2}$. Calculated: M = 360.1838. 4-[2-(9-Anthryl)vinyl]-2,2,5,5-tetramethyl-2,5-dihydro-1H-imidazole 3-oxide (8), m.p. 175-176 °C (from benzene). IR, v/cm⁻¹: 3049 (C-H arom.); 2931, 2979 (CH₃); 3288 (N-H). ¹H NMR (CD₂Cl₂), δ: 1.58 $(s, 6 H, CH_3)$; 1.65 $(s, 6 H, CH_3)$; 6.63 (d, 1 H, =CH-Im, J =17.0 Hz); 7.43-7.54 (m, 4 H, H arom.); 8.01-8.10 (m, 2 H, H arom.): 8.31-8.40 (m, 2 H, H arom.); 8.48 (s, 1 H, H arom.); 9.28 (d, 1 H, $-CH_{=}$, J = 17.0 Hz). MS, m/z (I_{rel} (%)): 344.2 [M]⁺ (50.0), 288.2 (7.4), 287.1 (31.5), 270.2 (8.9), 258.1 (27.1), 257.1 (100), 243.0 (10.0), 241.9 (37.0), 241.2 (35.0), 215.1 (17.5), 203.1 (10.2), 202.1 (19.0), 114.1 (2.7), 99.1 (5.5), 98.1 (11.6), 84.1 (3.4), 69.1 (0.8), 68.1 (1.4), 43.1 (1.4), 42.1 (9.9), 28.0 (1.0).

4-[2-(9-Anthryl)vinyl]-2,2,5,5-tetramethyl-2,5-dihydro-1*H*imidazole 1-oxyl 3-oxide (6). A mixture of compound 5 (0.21 g, 0.5 mmol) and PbO₂ (0.72 g) in benzene (10 mL) was stirred at -20 °C for 15 min. The oxidant was filtered off, the solution was filtered through a layer of silica gel, the solvent was distilled off, and the residue was recrystallized from a C₆H₆--hexane mixture. Radical 6 was obtained as yellow crystals in a yield of 0.15 g (71%), m.p. 185-186 °C. IR, v/cm⁻¹: 1255 (N→O); 1518 (C=N). MS, *m/z* (*I*_{rel} (%)): 359.1 [M]⁺ (100), 329.2 (26.9), 315.2 (24.7), 314.2 (95.7), 297.2 (33.7), 257.2 (25.8), 256.2 (31.2), 241.2 (30.8), 239.2 (20.8), 229.2 (18.5), 215.2 (56.3), 202.1 (32.1), 127.7 (15.9), 98.1 (36.1), 41.1 (12.2). Found: *m/z* 359.1784 [M]⁺. C₂₃H₂₃N₂O₂. Calculated: M = 359.1760. ESR: *a*_N (1 N) = 1.39 mT. *a*_{H(Me)} (12 H) = 0.023 mT.

4-Iodo[1,1';4',1"]terphenyl (10). A mixture of p-terphenyl (11) (2.3 g, 10 mmol), HIO₃ (0.34 g, 20 mmol), I₂ (1.03 g, 40 mmol), 30% H₂SO₄ (2.5 mL), CCl₄ (3 mL), and glacial AcOH (150 mL) was stirred at 90 °C for 4 h and poured into water. The precipitate that formed was filtered off and washed with water until the reaction became neutral. Then the precipitate was washed with a saturated aqueous solution of Na₂SO₃ and dried in air. The product was dissolved in benzene (100 mL) with heating, the solution was filtered through a layer of silica gel, and the sorbent was washed with several portions of hot benzene. The solvent was evaporated, the residue was recrystallized from benzene, and iodide 10 was obtained in a yield of 1 g (28%), m.p. 246-247 °C (cf. lit. data¹⁴: m.p. 245-246 °C).

4,4,5,5-Tetramethyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)-4,5-dihydro-1H-imidazole 1-oxyl 3-oxide (12). 2-(4-Ethynylphenyl)-4.4,5,5-tetramethyl-4,5-dihydro-1H-imidazole 1-oxyl 3-oxide15 (9) (0.45 g, 1.8 mmol) was added portionwise to a mixture of iodoterphenyl 10 (0.42 g, 1 mmol), Pd[PPh₃]₂Cl₂ (40 mg). CuI (20 mg), and piperidine (10 mL) under a constant flow of argon for 1 h. The solvent was removed in vacuo (~0.1 Torr) at ~20 °C, the residue was dissolved in benzene, the solution was filtered through a layer of Al_2O_3 , and the solvent was distilled off. The residue was dissolved in benzene and twice chromatographed on silica gel. 4,4,5,5-Tetramethyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)-4,5dihydro-1H-imidazole was eluted with benzene in a yield of 0.1 g (19%). Dihydroimidazole 1-oxyl 3-oxide 12 containing a small admixture of 4,4,5,5-tetramethyI-2-(4-[1,1';4',1"]terphenyl-4ylethynylphenyl)dihydroimidazole 1-oxyl was also eluted with benzene. Compound 12 was recrystallized three times from benzene and was obtained in a yield of 0.11 g (20%). A mixture containing a dimer of alkyne 9 and its iminonitroxyl analogs,

which were identified by TLC, were eluted with chloroform in a yield of 0.16 g. **Dihydroimidazole 1-oxyl 3-oxide 12** (blue-green crystals) was converted into orange 4,4,5,5-tetramethyl-2-(4-[1,1';4',1"]terphenyl-4-ylethynylphenyl)dihydroimidazole 1-oxyl at 238 °C. IR, v/cm⁻¹: 2213 (C=C); 2988 (CH₃); 3030 (C-H arom.). MS, m/z (I_{rel} (%)): 485.0 [M]⁺ (14.4), 454.0 (9.0), 439.0 (3.7), 398.0 (17.4), 396.9 (52.7), 356.9 (15.7), 355.9 (44.5), 354.9 (100), 329.0 (2.1), 327.90 (3.4), 253.0 (1.3), 251.9 (4.0), 151.9 (1.4), 114.0 (28.7), 84.1 (88.3), 69.1 (27.5), 56.0 (11.3), 41.0 (14.6), 28.0 (4.8). Found: m/z 485.2166 [M]⁺. C₃₃H₂₉N₂O₂. Calculated: M = 485.2189. ESR: a_N (2 N) = 0.73 mT, a_{n-H} (2 H) = 0.075 mT, $a_{H(Me)}$ (12 H) = 0.021 mT.

4,4,5,5-Tetramethyl-2-[4-(2-[1,1';4',1"]terphenyl-4ylethyl)phenyl]-4,5-dihydroimidazole 1-oxyl 3-oxide (13) and 4,4,5,5-tetramethyl-2-[4-(2-[1,1';4',1"]terphenyl-4-ylethyl)phenyl]-4,5-dihydro-1H-imidazole 1-oxyl (14). A solution of radical 12 (0.3 g, 0.62 mmol) was hydrogenated over 4% Pd/C until 49 mL of hydrogen was consumed. The catalyst was filtered off and the solvent was distilled off. Water (10 mL), CHCl₃ (10 mL), and NaHCO₃ (0.1 g) were added to the residue. Then NaIO₄ (0.3 g) was added with stirring and the reaction mixture was stirred for 30 min. The organic layer was separated and filtered through a layer of Al₂O₃, the solvent was distilled off, and the reaction product was chromatographed on a column with SiO₂. Compound 14 was eluted with benzene in a vield of 0.1 g (34%) and compound 13 was eluted with chloroform in a yield of 0.18 g (60%). Dihydroimidazole 1-oxyl 3-oxide 13, blue crystals, decomposition temperature 258 °C $(C_6H_6$ -hexane). MS, m/z (I_{rel} (%)): 489.1 [M]⁺ (6.8), 458.1 (5.6), 443.1 (2.0), 402.0 (10.7), 401.0 (32.6), 359.9 (12.4), 358.9 (42.3), 258.0 (19.5), 257.0 (7.8), 244.0 (17.6), 243.0 (83.5), 229.1 (3.6), 158.1 (12.4), 153.1 (0.7), 114.1 (23.0), 84.1 (100), 69.0 (32.4), 42.0 (3.9), 41.0 (11.0), 28.0 (2.1). Found: m/z 489.2557 [M]⁺. C₃₃H₃₃N₂O₂. Calculated: M = 489.2542. ESR: a_N (2 N) = 0.73 mT, a_{o-H} (2 H) = 0.054 mT, $a_{H(Me)}$ (12 H) = 0.021 mT, a_{H} (2 H) = 0.009 mT. Dihydroimidazole 1-oxyl 14, orange needle-like crystals. m.p. 180-182 °C (C_6H_6 -hexane). MS, m/z (I_{rel} (%)): 473.2 [M]⁺ (0.3), 458.1 (4.1), 402.1 (6.3), 401.0 (18.9), 360.0 (12.1), 358.9 (38.5), 257.0 (0.3), 244.0 (16.9), 243.0 (79.8), 230.0 (0.2), 229.0 (0.7), 216.0 (90.3), 114.0 (20.8), 84.0 (100), 77.0 (0.4), 69.0 (32.4), 41.0 (9.1), 30.0 (0.7), 28.0 (1.2). Found: m/z 473.2584 [M]⁻ $C_{33}H_{33}N_2O$. Calculated: M = 473.2593. ESR: a_{N1} (1 N) = 0.91 mT, a_{N3} (1 N) = 0.45 mT.

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References

- S. F. Vasilevsky, E. V. Tretyakov, O. M. Usov, Yu. N. Molin, S. V. Fokin, Yu. G. Shwedenkov, V. N. Ikorskii, G. V. Romanenko, R. Z. Sagdeev, and V. I. Ovcharenko. *Mendeleev Commun.*, 1998, 6, 216.
- E. V. Tretyakov, R. I. Samoilova, Yu. V. Ivanov, V. F. Plyusnin, S. V. Pashchenko, and S. F. Vasilevsky, *Mendeleev Commun.*, 1999, 3, 92.
- A. L. Buchachenko and V. L. Berdinsky, Chem. Phys. Lett., 1995, 242, 43.

- A. L. Buchachenko and V. L. Berdinsky, J. Phys. Chem., 1996, 100, 18292.
- 5. M. Ya. Mel'nikov and V. A. Smirnov, in Fotokhimiya organicheskikh radikalov [Photochemistry of Organic Radicals], Izd-vo MGU, Moscow, 1994, 87 (in Russian).
- S. A. Green, D. J. Simpson, G. Zhou, P. S. Ho, and N. V. Blough, J. Am. Chem. Soc., 1990, 112, 7337.
- 7. E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, and R. Darcy, J. Am. Chem. Soc., 1972, 94, 7049.
- 8. H. A. Dieck and F. P. Heck, J. Organomet. Chem., 1975, 93, 259.
- 9. K. Sonogashira, Y. Tohda, and N. A. Hagihara, Tetrahedron Lett., 1975, 50, 4467.
- J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London-New York-Sydney-Toronto, 1970, 704 pp.
- 11. O. A. Anisimov, V. L. Bizyaev, N. N. Lukzen, V. M. Grigoryants, and Yu. N. Molin, *Chem. Phys. Lett.*, 1983, 101, 131.

- 12. L. B. Volodarskii, I. A. Grigor'ev, S. A. Dikanov, V. A. Reznikov, and G. I. Shchukin, *Imidazolinovye nitroksil'nye* radikaly [Imidazoline Nitroxyl Radicals], Nauka, Novosibirsk, 1988, 216 pp. (in Russian).
- H. A. Dieck and F. R. Heck, J. Organomet. Chem., 1975, 93, 259.
- 14. H. France, I. M. Heilbron, and D. H. Hey, J. Am. Chem. Soc., 1938, 1374.
- 15. L. Dilog and J. S. Kim, Makromol. Chem., 1989, 190, 2609.

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