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Spirocyclic 2,5-Dihydro-1*H*-imidazole 1-Oxyl Radicals with a Mesogenic Substituent on C^4. Synthesis and Crystal Structure

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Abstract—Stable spirocyclic 2,5-dihydro-1*H*-imidazole 1-oxyl radicals containing a mesogenic fragment were synthesized on the basis of 1-[4-hydroxy(alkoxy)phenyl]-2-hydroxyamino-2-methylpropan-1-ones. The crystalline structure of two aminoxyl radicals was determined by X-ray analysis.

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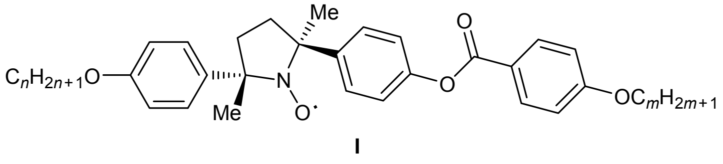
Paramagnetic properties of liquid crystals attract interest from the viewpoint of variation of magnetic, electrical, and optical characteristics of these compounds depending on their phase state [1]. Tamura et al. [2] reported on the synthesis of all-organic rod-shaped liquid crystals **I** containing a chiral five-membered cyclic aminoxyl unit. These liquid crystals were shown to possess such extraordinary properties as ferroelectricity [3], nonlinear paramagnetic susceptibility induced by a weak permanent magnet [4], and optical second harmonic generation [5] in different liquid crystalline phases.

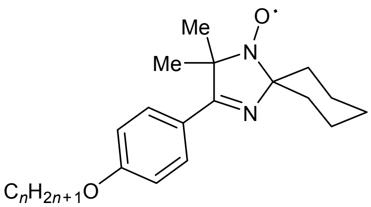
In view of the above stated, it seems promising to synthesize and explore new organic liquid crystalline paramagnetics having an aminoxyl fragment as a component of a different heterocycle, e.g., of the dihydroimidazole series. The presence of an additional imine-type nitrogen atom was expected to extend the scope of possible modification of their molecules due to appearance of an additional functionalization center, e.g., for controlling liquid crystalline state by varying pH or for obtaining an organic magnetic ionic liquid (cf. [6]).

Introduction of a spirocyclic fragment as building block into a thermotropic liquid crystal molecule was the subject of studies performed by several research teams. Vögtle and co-workers [7] synthesized rod-shaped liquid crystals on the basis of mono- and dispiro derivatives of the cyclobutane, cyclopentane, and cyclohexane series. Promising results have been achieved in the synthesis of ferroelectric liquid crystals from triangulane structures (3+3+3) [8] and *gem*-difluorodispirocyclopropanes (3+6+3) [9], which formed smectic SmA and SmC* phases under different conditions.

One more attractive feature provided by introduction of a spiro entity into a paramagnetic molecule is possible increase in the stability of the radical center toward biogenic reducing agents, which was recently demonstrated with cyclic aminoxyl radicals derived



I



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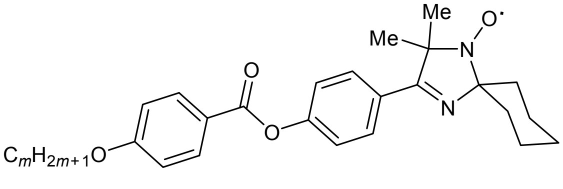


III

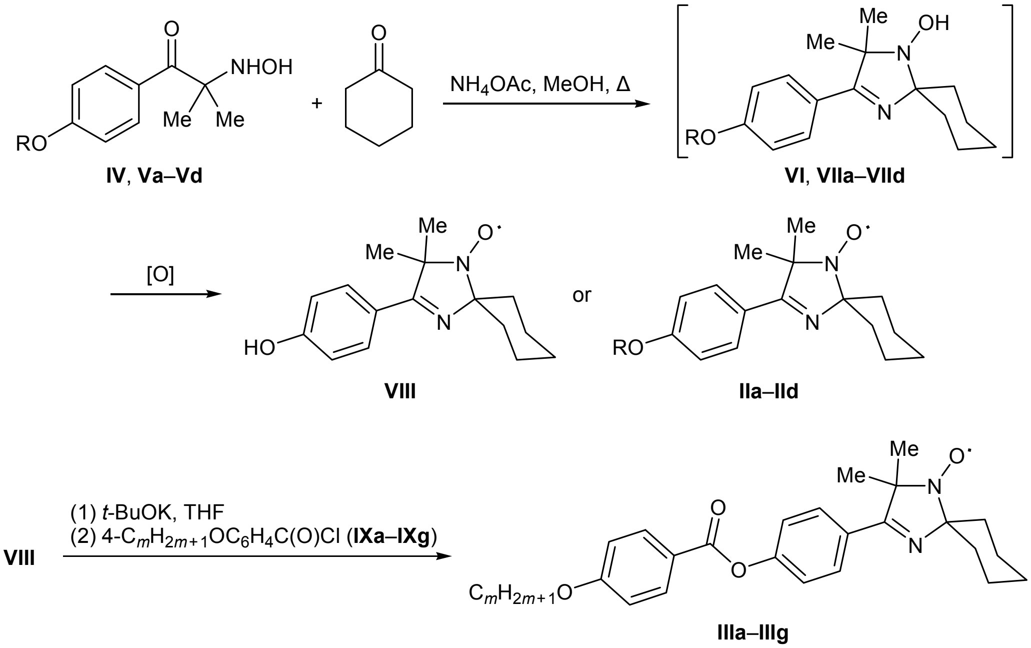
from piperidine (TEMPO) [10] and pyrrolidine (PROXYL) [11]. This may be important in the use of paramagnetic liquid crystals in magnetically controlled targeted drug delivery *in vivo* [1].

The present work continues our previous studies directed toward the synthesis of mesogenic spirocyclic mono- and diradicals of the azole series [12], which can also acts as spin probes for studying liquid crystals by ESR methods when dissolved in diamagnetic liquid crystals [13]. We now describe the synthesis and structural features of stable 2,5-dihydro-1*H*-imidazole 1-oxyl radicals **II** and **III** containing a spirocyclic moiety and a mesogenic substituent in position *4* of the heteroring.

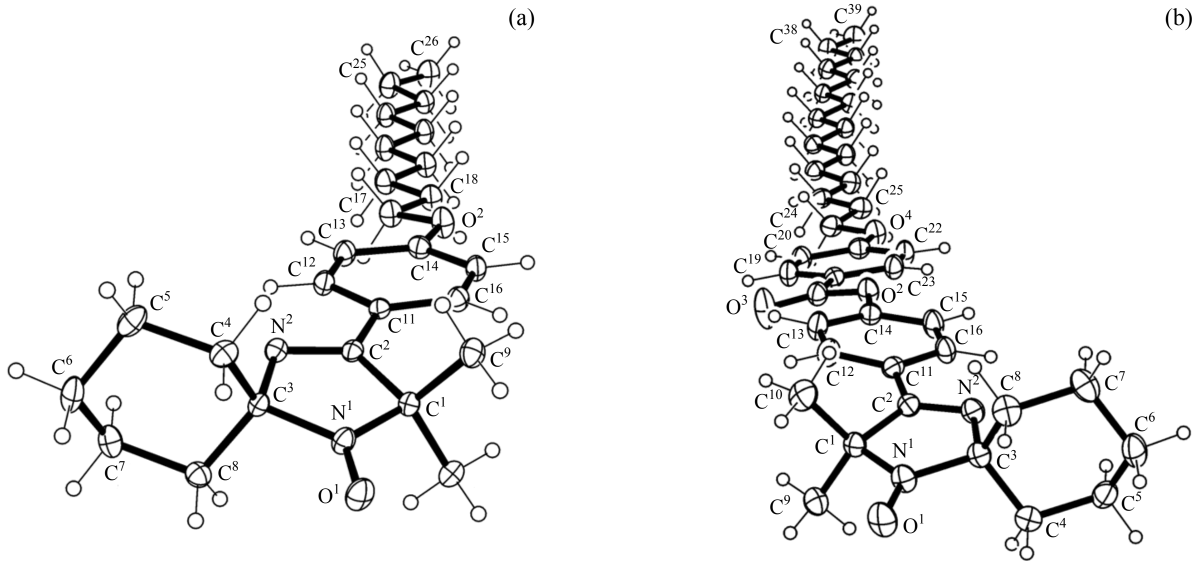
An effective synthetic approach to dihydroimidazole functional radicals is based on the condensation of substituted 1-hydroxyaminoalkyl aryl ketones with aliphatic ketones in the presence of ammonia or ammonium acetate, followed by oxidation of intermediate 1-hydroxy-2,5-dihydro-1*H*-imidazoles [14]. High thermodynamic stability of aminoxyl radicals derived from dihydroimidazoles [15] ensures their subsequent chemical modification at an available functional group in the benzene ring with retention of the radical center.

By heating α-hydroxyamino ketones **IV** and **Va**–**Vd** with cyclohexanone in boiling methanol in the presence of ammonium acetate we obtained 1-hydroxy-2,5-dihydro-1*H*-imidazoles **VI** and **VIIa**–**VIId** which were oxidized (without additional purification) with manganese dioxide in methanol (**VI**) or with sodium periodate in chloroform–water (**VIIa**–**VIId**) to the corresponding stable aminoxyl radicals **VIII** and **IIa**–**IId** (Scheme 1). Acyl derivatives **IIIa**–**IIIg** containing a 4-[4-(alkoxy)benzoyloxy]phenyl group were synthesized by treatment of **VIII** with potassium *tert*-butoxide to generate phenoxide ion which was involved in reaction with 4-alkoxybenzoyl chlorides **IXa**–**IXg**. The desired stable aminoxyl radicals **IIIa**–**IIIg** were isolated in 25–73% yield (Scheme 1). The IR and ESR

Scheme 1.



IV, **VI**, **VIII**, R = H; **II**, **V**, **VII**, R = C_nH_{2n+1}; n = 8 (**a**), 10 (**b**), 12 (**c**), 16 (**d**);
III, **IX**, m = 8 (**a**), 9 (**b**), 10 (**c**), 11 (**d**), 12 (**e**), 14 (**f**), 16 (**g**).



Molecular structures of aminoxyl radicals (a) **IIb** and (b) **IIIg** in crystal according to the X-ray diffraction data.

spectra and elemental analyses of the isolated radicals were consistent with the assumed structures.

The structure of **IIb** and **IIIg** was proved by X-ray analysis (see figure). The dihydroimidazole rings in molecules **IIb** and **IIIg** are planar within ±0.023(2) and ±0.025(3) Å, respectively, and the bond lengths therein are very similar and close to the corresponding bond lengths in 2,2,5,5-tetramethyl-4-phenyl-2,5-dihydro-1*H*-imidazole 1-oxyl [16]. The cyclohexane fragments adopt a *chair* conformation. The decyl and hexadecyl groups have linear structure typical of long-chain alkyl groups such as those in *N*-[amino(phenyl)-methylidene]-3,4-bis(decyloxy)benzamide [17] and 4-(benzyloxy)phenyl 4-(hexadecyloxy)-3-methoxybenzoate [18]. The crystal packing of **IIb** and **IIIg** is characterized by association of alkyl groups with formation of “alkyl layers.” In the crystalline structure of **IIIg** such layers consist of parallel alkyl groups [18], whereas the alkyl groups of **IIb** are oriented crosswise [17].

According to the differential scanning calorimetry (DSC) data, aminoxyl radicals **IIa**–**IId** and **IIIa**–**IIIg** are stable in the temperature range from 25 to 120°C. Radicals **IIa**–**IId**, **IIIb**–**IIIe**, and **IIIg** displayed on the DSC curves only peaks corresponding to transition from the crystalline state to isotropic. Radicals **IIIa** and **IIIf** (m = 8, 14) showed peaks in a narrow range (2–6°C) preceding the melting point transition. Presumably, compounds **IIIa** and **IIIf** undergo phase transition to mesophase, but further physical studies are necessary to confirm this assumption and identify the transition character.

To conclude, we have developed a procedure for the synthesis of stable spirocyclic aminoxyl radicals of the 2,5-dihydroimidazole series containing mesogenic substituents of two types.

EXPERIMENTAL

The spectral studies were performed at the Joint Chemical Service Center, Siberian Branch, Russian Academy of Sciences. Elemental analyses and DSC measurements were carried out at the Microanalysis Laboratory, Novosibirsk Institute of Organic Chemistry (Siberian Branch, Russian Academy of Sciences). The IR spectra were recorded in KBr on a Bruker Vector-22 spectrometer. The ESR spectra were measured on a Bruker ESP 300 instrument from solutions in chloroform with a concentration of 10^{-4} M. The melting points were determined using a Mettler Toledo FP81NT automatic hot stage. The DSC curves were obtained on a Netzsch STA 409 PC/PG instrument in a helium atmosphere at a heating rate of 5 deg/min. The progress of reactions was monitored by TLC on Sorbfil UV-254 and Polygram Alox N/UV$_{254}$ plates using chloroform, chloroform–methanol, and hexane–ethyl acetate as eluents. Aminoxyl radicals **II**, **III**, and **VIII** were isolated by column chromatography on silica gel (0.060–0.200 mm, Acros Organics). The solvents used were not additionally purified unless otherwise stated.

α-Hydroxyamino ketones **IV** and **Va**–**Vd** were synthesized by analogy with [19], and 4-alkoxybenzoic acids were prepared according to [20].

The X-ray diffraction data for compounds **IIb** and **IIIg** were obtained on a Bruker Kappa Apex diffractometer (MoK_α radiation, graphite monochromator). Corrections for absorptions were applied empirically using SADABS program. The structures were solved by the direct method and were refined by the least-squares procedure for all independent reflections using SHELXTL-97 software package. The positions of non-hydrogen atoms were refined in anisotropic approximation, and hydrogen atoms were refined according to the riding model. The sets of crystallographic data for **IIb** and **IIIg** were deposited to the Cambridge Crystallographic Data Centre (entry nos. CCDC 938838 and 938839, respectively).

[2,2-Dimethyl-3-(4-alkoxyphenyl)-1,4-diazaspiro[4.5]dec-3-en-1-yl]oxidanyls IIa–IId (*general procedure***).** A mixture of 2 mmol of 1-(4-alkoxyphenyl)-2-hydroxyamino-2-methylpropan-1-one **Va**–**Vd**, 2 mmol (0.196 g) of cyclohexanone, and 8 mmol (0.624 g) of ammonium acetate in 10 mL of methanol was heated for 5 h under reflux. The mixture was cooled in an ice bath, and the precipitate was filtered off, washed with methanol, and dried. Intermediate 1-hydroxy-2,5-dihydro-1*H*-imidazole **VIIa**–**VIId** thus isolated was oxidized without purification. A two-phase mixture consisting of a solution of **VIIa**–**VIId** in 10 mL of chloroform and a solution of 6.92 mmol (1.48 g) of sodium periodate in 10 mL of water was stirred for 1 h at room temperature. The organic phase was separated, washed with 10 mL of water, dried over $MgSO_4$, and concentrated, and the residue was purified by column chromatography on silica gel using chloroform as eluent. Samples of **IIa**–**IId** for elemental analysis and single crystals for X-ray analysis were obtained by crystallization from ethanol.

{2,2-Dimethyl-3-[4-(octyloxy)phenyl]-1,4-diazaspiro[4.5]dec-3-en-1-yl}oxidanyl (IIa). Yield 61%, mp 61°C (from EtOH). IR spectrum, ν, cm^{-1}: 1599, 1568 (C=N). ESR spectrum: triplet, A_N = 14.56 G, g_{iso} = 2.0058. Found, %: C 75.17; H 10.04; N 7.35. $C_{24}H_{37}N_2O_2$. Calculated, %: C 74.76; H 9.67; N 7.27.

{3-[4-(Decyloxy)phenyl]-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl}oxidanyl (IIb). Yield 43%, mp 88°C (from EtOH). IR spectrum, ν, cm^{-1}: 1599, 1568 (C=N). ESR spectrum: triplet, A_N = 14.56 G, g_{iso} = 2.0058. Found, %: C 75.69; H 9.93; N 6.80. $C_{26}H_{41}N_2O_2$. Calculated, %: C 75.50; H 9.99; N 6.77.

{3-[4-(Dodecyloxy)phenyl]-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl}oxidanyl (IIc). Yield 44%, mp 70°C (from EtOH). IR spectrum, ν, cm^{-1}: 1597, 1568 (C=N). ESR spectrum: triplet, A_N = 14.56 G, g_{iso} = 2.0058. Found, %: C 76.43; H 10.23; N 6.20. $C_{28}H_{45}N_2O_2$. Calculated, %: C 76.14; H 10.27; N 6.34.

{3-[4-(Hexadecyloxy)phenyl]-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl}oxidanyl (IId). Yield 45%, mp 91°C (from EtOH). IR spectrum, ν, cm^{-1}: 1597, 1568 (C=N). ESR spectrum: triplet, A_N = 14.56 G, g_{iso} = 2.0058. Found, %: C 77.07; H 10.70; N 5.62. $C_{32}H_{53}N_2O_2$. Calculated, %: C 77.21; H 10.73; N 5.63.

X-Ray diffraction data for IIb. $C_{26}H_{41}N_2O_2$, *M* 413.61, monoclinic crystal system, space group *C*2/*c*; unit cell parameters (150 K): $a = 44.254(3)$, $b = 6.0278(4)$, $c = 18.314(1)$ Å; $\beta = 95.656(3)°$; $V = 4861.7(5)$ Å^3; $Z = 8$; $d_{calc} = 1.130$ g/cm^3; μ 0.071 mm^{-1}. Total of 23882 reflection intensities were measured, 4265 of which were independent ($R_{int} = 0.0578$); $wR_2 = 0.1431$, $S = 1.073$ (all reflections); $R = 0.0471$ [2895 reflections with $I > 2\sigma(I)$].

[3-(4-Hydroxyphenyl)-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl]oxidanyl (VIII). A mixture of 3 mmol (0.591 g) of 2-(hydroxyamino)-1-(4-hydroxyphenyl)-2-methylpropan-1-one (**IV**), 3.6 mmol (0.353 g) of cyclohexanone, and 12 mmol (0.936 g) of ammonium acetate in 15 mL of methanol was heated for 4 h under reflux. The mixture was concentrated, the residue was treated with 10 mL of acetone, the precipitate was filtered off, and the filtrate was evaporated. The oily residue was dissolved in 25 mL of methanol, 15 mmol (1.305 g) of manganese(IV) oxide was added, the mixture was stirred for 2 h at 20°C and filtered, the filtrate was concentrated, and the residue was subjected to column chromatography on silica gel using chloroform as eluent. Yield 0.424 g (52%), mp 190°C (decomp., from hexane–EtOAc). IR spectrum, ν, cm^{-1}: 3258 (OH), 1599, 1582 (C=N). ESR spectrum: triplet, A_N = 14.56 G, g = 2.0058. Found, %: C 70.44; H 7.53; N 10.22. $C_{16}H_{21}N_2O_2$. Calculated, %: C 70.30; H 7.74; N 10.25.

{3-[4-(4-Alkoxybenzoyloxy)phenyl]-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl}oxidanyls IIIa–IIIg (*general procedure***).** A solution of 0.9 mmol of 4-alkoxybenzoic acid in 2 mL of thionyl chloride was heated for 90 min under reflux. Excess thionyl chloride was distilled off under reduced pressure (water-jet pump), the residue was dissolved in 10 mL of anhydrous THF, and the solution was added to a suspension of 0.082 g (0.3 mmol) of compound **VIII** and 0.101 g (0.9 mmol) of potassium *tert*-butoxide in 10 mL of anhydrous THF. The mixture was stirred for 1 h and concentrated under reduced pressure, the residue was treated with 15 mL of diethyl ether, and the organic extract was washed with a saturated aqueous solution of $NaHCO_3$ (2×10 mL) and with water (2×10 mL), dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent. Samples of **IIIa–IIIg** for elemental analysis and single crystals of **IIIg** for X-ray analysis were obtained by crystallization from ethanol.

(2,2-Dimethyl-3-{4-[4-(octyloxy)benzoyloxy]-phenyl}-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIIa). Yield 43%. The DSC curve (heating) showed two peaks at 82.2 and 84.9°C (EtOH). IR spectrum, ν, cm^{-1}: 1734 (C=O); 1603, 1578 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 73.85; H 8.01; N 5.46. $C_{31}H_{41}N_2O_4$. Calculated, %: C 73.63; H 8.17; N 5.54.

(2,2-Dimethyl-3-{4-[4-(nonyloxy)benzoyloxy]-phenyl}-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIIb). Yield 48%, mp 57°C (from EtOH). IR spectrum, ν, cm^{-1}: 1734 (C=O); 1603, 1576 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 73.93; H 8.21; N 5.34. $C_{32}H_{43}N_2O_4$. Calculated, %: C 73.96; H 8.34; N 5.39.

(3-{4-[4-(Decyloxy)benzoyloxy]phenyl}-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIIc). Yield 25%, mp 71°C (from EtOH). IR spectrum, ν, cm^{-1}: 1730 (C=O); 1603, 1578 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 74.10; H 8.26; N 5.23. $C_{33}H_{45}N_2O_4$. Calculated, %: C 74.26; H 8.50; N 5.25.

(2,2-Dimethyl-3-{4-[4-(undecyloxy)benzoyloxy]-phenyl}-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIId). Yield 73%, mp 76°C (from EtOH). IR spectrum, ν, cm^{-1}: 1734 (C=O); 1603, 1576 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 74.37; H 8.69; N 4.99. $C_{34}H_{47}N_2O_4$. Calculated, %: C 74.55; H 8.65; N 5.11.

(3-{4-[4-(Dodecyloxy)benzoyloxy]phenyl}-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIIe). Yield 41%, mp 72°C (from EtOH). IR spectrum, ν, cm^{-1}: 1736 (C=O); 1603, 1576 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 75.41; H 8.80; N 5.11. $C_{35}H_{49}N_2O_4$. Calculated, %: C 74.83; H 8.79; N 4.99.

(2,2-Dimethyl-3-{4-[4-(tetradecyloxy)benzoyloxy]phenyl}-1,4-diazaspiro[4.5]dec-3-en-1-yl)-oxidanyl (IIIf). Yield 53%. The DSC curve (heating) contained two peaks at 58.2 and 64.4°C (EtOH). IR spectrum, ν, cm^{-1}: 1728 (C=O); 1605, 1572 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 75.49; H 9.05; N 4.67. $C_{37}H_{53}N_2O_4$. Calculated, %: C 75.34; H 9.06; N 4.75.

3-{4-[4-(Hexadecyloxy)benzoyloxy]phenyl}-2,2-dimethyl-1,4-diazaspiro[4.5]dec-3-en-1-yl)oxidanyl (IIIg). Yield 55%, mp 64°C (from EtOH). IR spectrum, ν, cm^{-1}: 1728 (C=O); 1604, 1571 (C=N). ESR spectrum: triplet, $A_N = 14.51$ G, $g_{iso} = 2.0058$. Found, %: C 76.01; H 9.30; N 4.49. $C_{39}H_{57}N_2O_4$. Calculated, %: C 75.81; H 9.30; N 4.53.

X-Ray diffraction data for IIIg. $C_{39}H_{57}N_2O_4$, M 617.87; triclinic crystal system, space group P-1; unit cell parameters (200 K): $a = 5.7726(15)$, $b = 11.567(4)$, $c = 27.462(9)$ Å; $\alpha = 92.98(1)$, $\beta = 94.34(1)$, $\gamma = 102.69(1)°$; $V = 1779.4(9)$ Å^3; $Z = 2$; $d_{calc} = 1.153$ g/cm^3; $\mu = 0.073$ mm^{-1}. Total of 22016 reflection intensities were measured, 5999 of which were independent ($R_{int} = 0.0513$); $wR_2 = 0.2056$, $S = 1.041$ (all reflections); $R = 0.0615$ [3351 reflections with $I > 2\sigma(I)$].

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