

## Synthesis of nitroxyl radical by direct nucleophilic functionalization of a C—H bond in the azadiene systems<sup>\*,\*\*</sup>

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Cyclic dinitrones underwent nucleophilic substitution of the hydrogen atom in the reaction with a paramagnetic carbanion, the lithium derivative of 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, to give polyfunctional nitronyl nitroxyls.

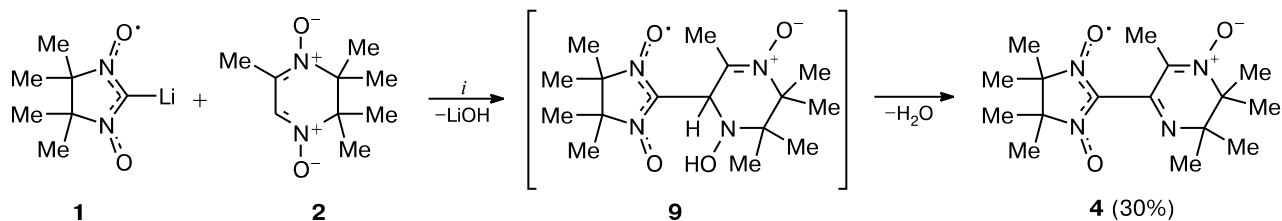
**Key words:** nitrones, nitronyl nitroxyls, reaction of nucleophilic substitution of hydrogen, ESR spectra.

Development<sup>1</sup> and further improvement<sup>2,3</sup> of efficient methods for the synthesis of lithium derivative of 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (**1**) stimulated interest of researchers to the reactions of **1** with electrophiles. As a result, a representative series of new polyfunctional mono- and polynitroxyls and their heterospin complexes were obtained.<sup>4–7</sup> The present work continued these investigations and was devoted to the studies of the products of the reaction of **1** with sterically hindered cyclic dinitrones **2** and **3**. Based on the known data on the ability of nitrones to be involved into the nucleophilic addition reaction at the double bond carbon atom,<sup>8–11</sup> we

suggested that the reaction of **1** with **2** or **3** would allow us to furnish an original group of spin-labeled derivatives. In fact, the reaction of **1** with nitrone **2** led to a mixture of products, from which a hetaryl substituted nitronyl nitroxyl **4**, the product of the S<sub>N</sub><sup>H</sup>-reaction, was isolated in 30% yield (Scheme 1).

The reaction of **1** with dinitrone **3** containing no methyl group at the double bond led to nitronyl nitroxyl **5**, the elimination product, in no more than 5% yield (Scheme 2). The main pathway of the reaction was oxidation of adduct **6** to yield product **7**. In this case, either atmospheric oxygen or nitroxyl present in the reaction

Scheme 1



i. 1) THF,  $-78$ – $+25$  °C; 2) H<sub>2</sub>O.

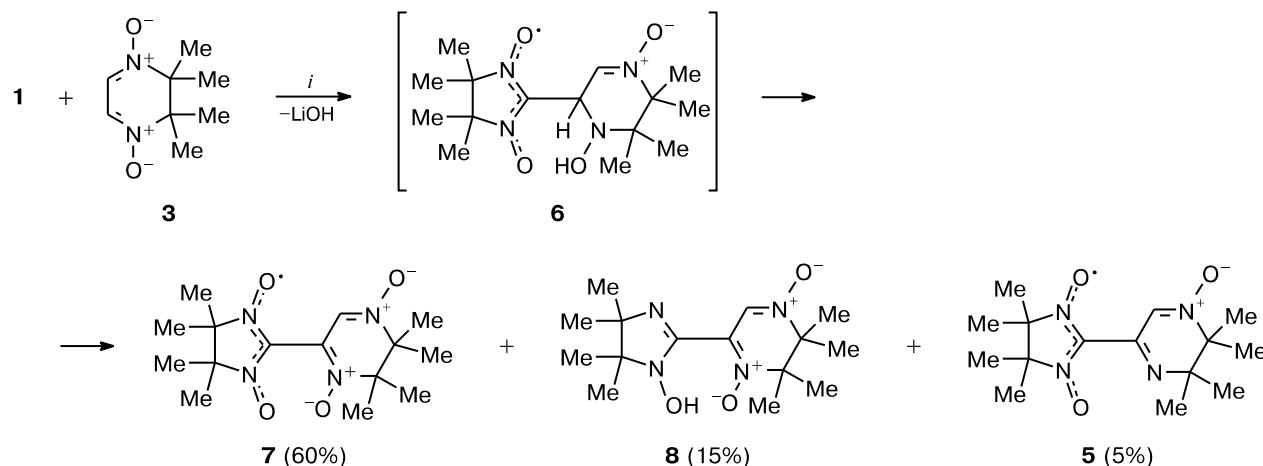
\* Dedicated to academician of the Russian Academy of Sciences A. I. Rusanov on the occasion of his 80th birthday.

\*\* Based on the Materials of the International Congress on Organic Chemistry dedicated to the 150th anniversary of the Butlerov's Theory of Chemical Structure of Organic Compounds (September 19–23, 2011, Kazan, Russia).

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Scheme 2



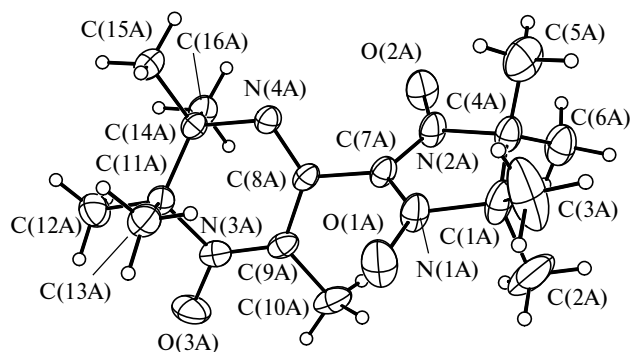
*i.* 1) THF,  $-78$ – $+25$  °C; 2) H<sub>2</sub>O.

mixture played the role of the oxidant. The oxidative function of the nitroxyl was confirmed by the isolation from the reaction mixture of hydroxylamine **8**, the product of three-electron reduction of **7**, in 15% yield. The lower steric hindrance of adduct **6** as compared to the intermediate **9** (see Scheme 1), apparently, favored the oxidative transformation of the adduct. It should be noted that such a process, formally leading to the replacement of the hydride ion by a nucleophilic group, is also characteristic of the S<sub>N</sub><sup>H</sup>-reactions of aromatic substrates.<sup>12</sup>

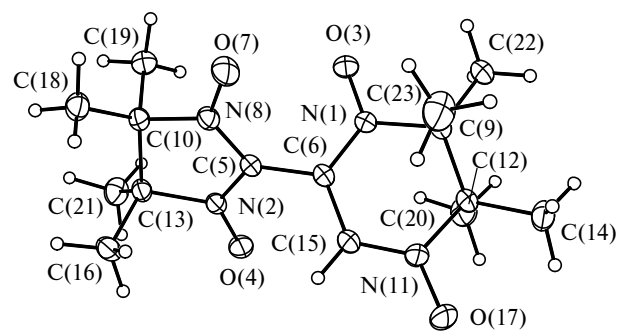
The structures of all the compounds obtained were confirmed by X-ray crystallographic data, magnetochemical measurements, and spectroscopic methods. According to the data of X-ray diffraction studies, nitroxyls **4**, **5**, and **7** (Figs 1–3) have molecular structure. In hydroxylamine **8**, the presence of the OH group promotes formation of the H-bonds combining the molecules in the chains (Fig. 4). The bond distances of all the N<sub>Im</sub>–O bonds (Table 1) are in range of 1.263(4)–1.281(3) Å, which is typical of a nitronyl nitroxyl fragment incorporated into

a 2-imidazoline ring. The shortest bond between the heterocycles C<sub>Im</sub>–C<sub>Pyr</sub> is in compound **7**, it is equal to 1.453(2) Å; in other compounds, the bond distances C<sub>Im</sub>–C<sub>Pyr</sub> lie in the range 1.479(4)–1.483(5) Å within the error limit. The angles between the planes of the CN<sub>2</sub> fragment of imidazoline ring and the (CCN)<sub>Pyr</sub> fragment of 2,3-dihydropyrazine ring vary within wide limits: from 26.9(4) to 62.3(3)°. The imidazoline rings have a typical *twist*-conformation, the pyrazine rings are in the envelope form, in which the C atom in *trans*-position to the imidazoline ring and the adjacent to it N atom of the NO group deviate the most from the plane (CCN)<sub>Pyr</sub> (0.577(6)–0.82(1) Å and 0.198(4)–0.32(1) Å, respectively).

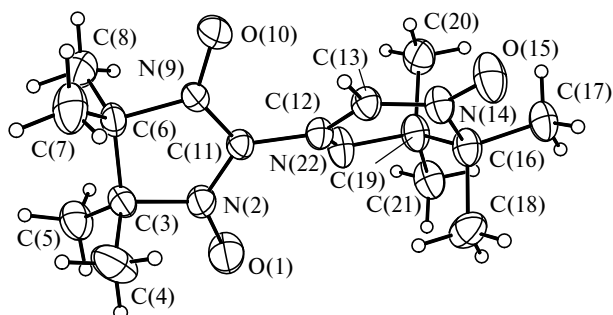
The ESR spectrum of nitroxyl **4** and its simulated counterpart are shown in Fig. 5. The spectrum has a characteristic of 2-imidazoline nitroxyls pattern of a dominating quintet from two equivalent N nuclei with the additionally resolved substructure from one of the N nuclei of the dihydropyrazine ring and the broadening from 12 equivalent protons of the methyl groups. The multiplet patterns in



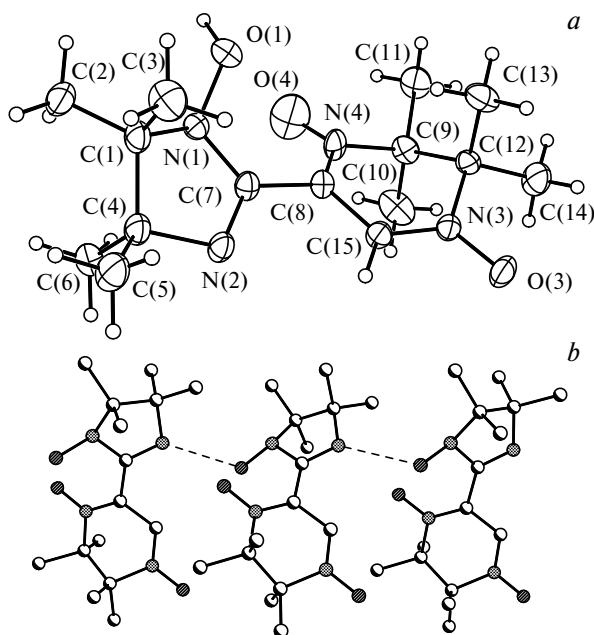
**Fig. 1.** Molecular structure of **4**. Ellipsoids are given with 25% probability.



**Fig. 2.** Molecular structure of **7**. Ellipsoids are given with 35% probability.



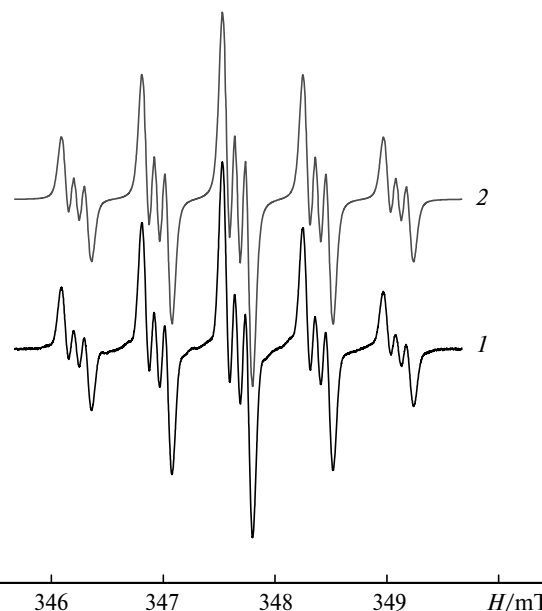
**Fig. 3.** Molecular structure of **5**. Ellipsoids are given with 35% probability.



**Fig. 4.** The structure (ellipsoids are given with 35% probability) (*a*) and the chain (*b*) of molecules **8**. Parameters of the H-bond O(1)–H(1A)···N(2') (symmetry operation code:  $x, 1-y, z-1/2$ ) in the chain: O–H 0.83, H···N 2.01, O···N 2.829(4) Å, the angle OHO 172°.

the ESR spectrum of nitroxyl **4** is well enough simulated when the following parameters are used:  $a_{N(1)} = a_{N(3)} = 0.720$  mT,  $a_{N(4')} = 0.096$  mT,  $a_{12H} = 0.018$  mT;  $g_{iso} = 2.0065$  mT.

As compared to the spectrum of nitroxyl **4**, the ESR spectrum of compound **5** (Fig. 6, *a*) has more complicated structure of multiplets. Its satisfactory simulation was achieved with the assumption of a hyperfine coupling (HFC) on two N nuclei of the dihydropyrazine ring:  $a_{N(1)} = a_{N(3)} = 0.718$  mT,  $a_{N(4')} = 0.080$  mT,  $a_{N(1')} = 0.018$  mT,  $a_{12H} = 0.017$  mT,  $a_H = 0.008$  mT;  $g_{iso} = 2.0068$ . Unlike the spectra of the preceding compounds, the simulation of the ESR spectrum of nitroxyl **7** (Fig. 6, *b*) consistently gives different HFC constants on two N nuclei of the imidazole fragment:  $a_{N(1)} = 0.728$  and  $0.708$  mT,



**Fig. 5.** The ESR spectrum of nitroxyl **4** as the first derivative (*1*) and its simulated counterpart (*2*).

$a_{N(4')} = 0.086$  mT,  $a_{12H} = 0.018$  mT;  $g_{iso} = 2.0067$  mT. Similarly to the spectrum of **4**, the spectrum of **7** exhibits only one N atom of the dihydropyrazine ring with slightly lower HFC constant.

In conclusion, the studies undertaken in this work showed that the spin-labeled **1** was involved into the  $S_N^H$ -reaction with nonaromatic 2,3-dihydropyrazine 1,4-dioxides, leading to new polyfunctional nitronyl nitroxyls, whose structures were confirmed by X-ray crystallography. This result deserves attention as a methodical approach to the synthesis of spin-labeled nitrones and, in the prospect, as a new possibility of introduction of spin labels at the  $sp^2$ -hybridized carbon atom of carbonyl compounds.

**Table 1.** Selected bond distances and bond angles in the molecules of compounds **4**, **5**, **7**, and **8**

Parameter	<b>4*</b>	<b>5</b>	<b>7</b>	<b>8</b>
Bond	<i>d</i> /Å			
N <sub>Im</sub> –O	1.270(3), 1.274(3)	1.268(3), 1.281(3)	1.270(1), 1.276(1)	1.413(3)
N <sub>Pyr</sub> –O	1.292(3)	1.278(3)	1.274(1), 1.283(1)	1.246(5), 1.279(3)
C <sub>Im</sub> –C <sub>Pyr</sub>	1.483(4)	1.478(4)	1.453(2)	1.480(4)
Angle	$\omega$ /deg			
CN <sub>2</sub> –(CCN) <sub>Pyr</sub>	62.3(2)	42.7(3)	57.0(1)	26.9(4)

\* In the structure of **4**, one of two crystallographically independent molecules is disordered over two positions with the population of 0.5. The Table and the Figure 1 show the data for the ordered molecule.

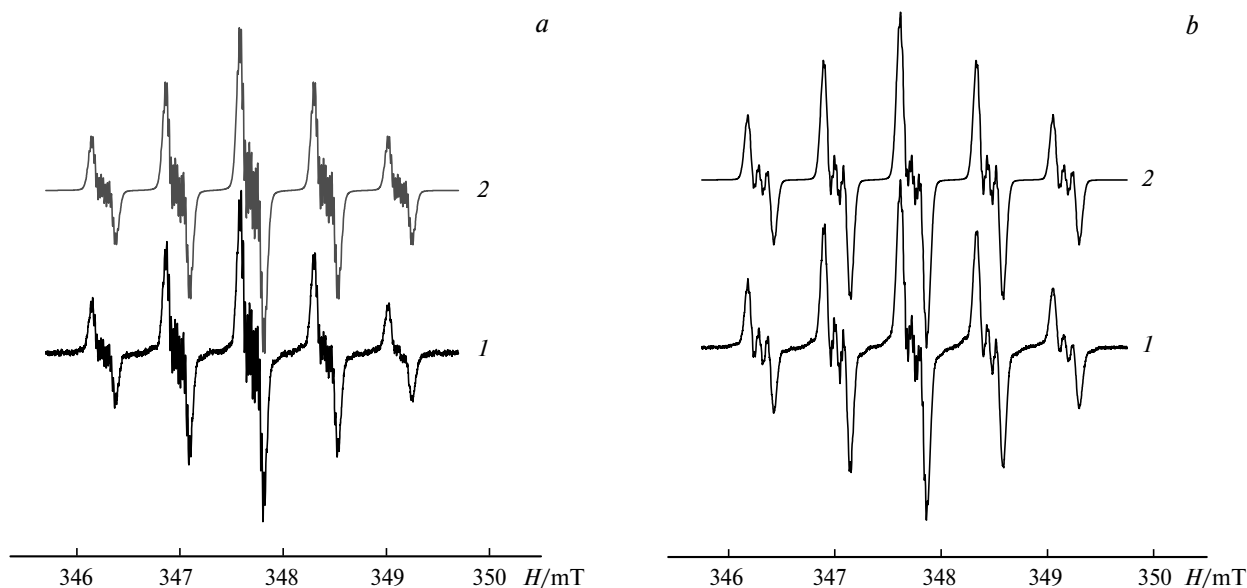


Fig. 6. The ESR spectra of nitroxyls 5 (a) and 7 (b) as the first derivatives (1) and their simulated counterparts (2).

### Experimental

$^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE II spectrometer (400 MHz) in  $\text{CDCl}_3$ , chemical shifts are given in the  $\delta$  scale relative to the internal standard  $\text{Me}_4\text{Si}$ . IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded on a Perkin Elmer Spectrum One B FTIR spectrometer for neat samples (DRA). Mass spectra (ESI) were recorded on a Bruker Daltonics micrOTOF-Q II instrument. Elemental analysis (C, H, N) was performed on a Perkin Elmer 2400-II CHNS/O analyzer. Spectra of the stationary ESR X-range were recorded on a Bruker EMX spectrometer in dilute toluene solution (the concentration was  $\sim 10^{-5}\text{ mol L}^{-1}$ ) at room temperature and were simulated using the Winsim version 0.96 program package,<sup>13</sup> the isotropic values of  $g$ -factor were determined using solid DPPH as a standard. The accuracy of measurements of the hyperfine coupling constants and the  $g$ -factor values was 0.005 mT and 0.0001, respectively. Magnetochemical experiments were carried out on a MPMSXL Quantum Design SQUID magnetometer in the temperature range of 2–300 K. Melting points were measured on a Boetius heating stage. The  $R_f$  values were measured on precoated plates Alugram Sil G/UV-254 (Macheray–Nagel). Merck 60 silica gel (0.063–0.200 mm) was used for column chromatography. Solvents were purified and dried according to the standard procedures. The reactant  $(\text{Me}_3\text{Si})_2\text{NLi}$  (1.06 M in THF) used in the work was purchased from Alfa Aesar. 4,4,5,5-Tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide,<sup>14</sup> 2,2,3,3,5-pentamethyl-2,3-dihydropyrazine-1,4-dioxide 2, 2,2,3,3-tetramethyl-2,3-dihydropyrazine-1,4-dioxide 5 (see Ref. 15) were synthesized according to the procedures described in the literature.

**4,4,5,5-Tetramethyl-2-(2,2,3,3,6-pentamethyl-1-oxido-2,3-dihydropyrazin-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (4).** A 1.06 M solution of  $(\text{Me}_3\text{Si})_2\text{NLi}$  in THF (1.04 mL, 1.1 mmol) was added to a stirred solution of 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (0.157 g, 1.0 mmol) in THF (4 mL) at  $-78^\circ\text{C}$  under argon. The reaction mixture was

stirred for 30 min at  $-78^\circ\text{C}$ , followed by addition of a solution of nitron 2 (0.184 g, 1.0 mmol) in THF ( $\sim 3\text{ mL}$ ). The cooling was removed, the reaction mixture was allowed to warm up to room temperature, stirred for 2 h, and concentrated. The residue was subjected to chromatography on  $\text{SiO}_2$ , using diethyl ether as an eluent. The fraction containing 4 was concentrated, the residue was recrystallized from a mixture of  $\text{CH}_2\text{Cl}_2$ –*n*-heptane. The yield was 0.10 g (30%), m.p. 186–187  $^\circ\text{C}$ , claret-colored crystals.  $R_f$  0.18 (EtOAc). IR (KBr),  $\nu/\text{cm}^{-1}$ : 540, 574, 611, 712, 759, 790, 849, 868, 900, 965, 1071, 1135, 1174, 1217, 1314, 1373, 1417, 1453, 1509, 1612, 2945, 2986. ESR:  $A_{2\text{N}} = 0.720\text{ mT}$ ,  $A_{\text{N}} = 0.096\text{ mT}$ ,  $A_{12\text{H}} = 0.018\text{ mT}$ ,  $g_{\text{iso}} = 2.0065\text{ mT}$ .  $\mu_{\text{eff}} \approx 1.73\ \mu_{\text{B}}$  (50–300 K). MS (ESI),  $m/z$ : 324 [M + H]<sup>+</sup>. Found (%): C, 59.9; H, 8.9; N, 17.2.  $\text{C}_{16}\text{H}_{27}\text{N}_4\text{O}_3$ . Calculated (%): C, 59.4; H, 8.4; N, 17.3.

**4,4,5,5-Tetramethyl-2-(2,2,3,3-tetramethyl-1,4-dioxido-2,3-dihydropyrazin-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (7)** was obtained similarly to 4. In this case, the chromatographic purification of 7 also gave **4,4,5,5-tetramethyl-2-(2,2,3,3-tetramethyl-1-oxido-2,3-dihydropyrazin-5-yl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (5)** and **5-(1-hydroxy-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl)-2,2,3,3-tetramethyl-2,3-dihydropyrazine 1,4-dioxide (8)**.

**Compound 7.** The yield was 0.2 g (60%), m.p. 195–197  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ –*n*-heptane), dark green crystals,  $R_f$  0.20 (EtOAc). IR (KBr),  $\nu/\text{cm}^{-1}$ : 539, 720, 736, 799, 864, 888, 1022, 1095, 1135, 1175, 1207, 1260, 1318, 1369, 1417, 1450, 1529, 1602, 2853, 2923, 2958, 2984.  $\mu_{\text{eff}} \approx 1.73\ \mu_{\text{B}}$  (50–300 K). MS (ESI),  $m/z$ : 326 [M + H]<sup>+</sup>. Found (%): C, 55.4; H, 7.8; N, 17.2.  $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_4$ . Calculated (%): C, 55.4; H, 7.7; N, 17.2.

**Compound 5.** The yield was 0.01 g (5%), m.p. 170–171  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ –*n*-heptane), greenish brown crystals,  $R_f$  0.25 (EtOAc). IR (KBr),  $\nu/\text{cm}^{-1}$ : 540, 564, 628, 668, 736, 791, 816, 865, 890, 963, 1000, 1097, 1138, 1178, 1207, 1299, 1370, 1420, 1452, 1531, 1604, 2943, 2988. Found (%): C, 58.1; H, 8.4; N, 18.1.  $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_3$ . Calculated (%): C, 58.2; H, 8.1; N, 18.1.

**Compound 8.** The yield was 0.05 g (15%), m.p. 160–162  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2$ –*n*-heptane),  $R_f$  0.15 (EtOAc–methanol, 9 : 1). IR

(KBr),  $\nu/\text{cm}^{-1}$ : 521, 688, 792, 806, 950, 980, 1070, 1105, 1143, 1160, 1205, 1269, 1289, 1339, 1383, 1454, 1495, 1627, 1567, 2904, 2923, 2976, 3114 (O—H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$ : 1.31–1.52 (m, 24 H, Me); 6.47 (s, 1 H,  $\text{HC}_{\text{sp}^2}$ ); 8.97 (s, 1 H, OH). MS (ESI),  $m/z$ : 311 [ $\text{M} + \text{H}$ ] $^+$ . Found (%): C, 57.6; H, 8.5; N, 17.9.  $\text{C}_{15}\text{H}_{26}\text{N}_4\text{O}_3$ . Calculated (%): C, 58.0; H, 8.4; N, 18.1.

**X-ray diffraction studies.** The masses of reflections were obtained on a SMART APEX II CCD diffractometer (Bruker AXS) ( $\text{MoK}\alpha$  irradiation,  $\lambda = 0.71073 \text{ \AA}$  (**4** and **7**) and  $\text{CuK}\alpha$  irradiation,  $\lambda = 1.54178 \text{ \AA}$  (**5** and **8**),  $T = 240 \text{ K}$ , allowance for absorption was made using the Bruker SADABS version 2.10 program). The structures were solved by direct methods and refined by the full-matrix least squares method in anisotropic approximation for all the nonhydrogen atoms. Positions of some H atoms were localized in the differential syntheses of electron density; for them, as well as for the rest of H atoms, whose positions were calculated geometrically, the refinement was performed using the riding model according to the standard procedure. All the calculations in the solving and refinement of the structures were performed using the Bruker Shelxtl Version 6.14 program package. In the structure of **4**, one of two crystallographically independent molecules was disordered over two positions with the population of 0.5 (in Fig. 1, the structure of the ordered molecule is shown).

**Compound 4**,  $\text{C}_{16}\text{H}_{27}\text{N}_4\text{O}_3$ ,  $M = 323.42$ , monoclinic crystals, the space group  $P2_1/n$ ,  $a = 10.2963(11) \text{ \AA}$ ,  $b = 18.681(2) \text{ \AA}$ ,  $c = 18.452(2) \text{ \AA}$ ,  $\beta = 94.552(9)^\circ$ ,  $V = 3537.9(7) \text{ \AA}^3$ ;  $Z = 8$ ,  $d_{\text{calc}} = 1.214 \text{ g cm}^{-3}$ ,  $\mu = 0.085 \text{ mm}^{-1}$ , 28547 measured reflections ( $2.35 < \theta < 27.00^\circ$ ), from them 7685 were independent, 2250 with  $I > 2\sigma(I)$ , 542 refined parameters, the final divergence factors  $R_1 = 0.0652$  and  $wR_2 = 0.1624$  on the reflections with  $I > 2\sigma(I)$ . The maximum and minimum values of electron density ( $\Delta\rho$ ) were equal to  $0.301/-0.198 \text{ e/\AA}^3$ , respectively.

**Compound 7**,  $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_4$ ,  $M = 325.39$ , monoclinic crystals, the space group  $P2_1/c$ ,  $a = 10.0384(9) \text{ \AA}$ ,  $b = 13.7959(12) \text{ \AA}$ ,  $c = 12.1488(10) \text{ \AA}$ ,  $\beta = 90.408(5)^\circ$ ,  $V = 1682.4(3) \text{ \AA}^3$ ;  $Z = 4$ ,  $d_{\text{calc}} = 1.285 \text{ g cm}^{-3}$ ,  $\mu = 0.094 \text{ mm}^{-1}$ , 8437 measured reflections ( $2.03 < \theta < 25.99^\circ$ ), from them 3216 were independent, 2465 with  $I > 2\sigma(I)$ , 309 refined parameters, the final divergence factors  $R_1 = 0.0369$ ,  $wR_2 = 0.1042$  on the reflections with  $I > 2\sigma(I)$ . The maximum and minimum values of electron density ( $\Delta\rho$ ) were equal to  $0.214/-0.160 \text{ e/\AA}^3$ .

**Compound 5**,  $\text{C}_{15}\text{H}_{25}\text{N}_4\text{O}_3$ ,  $M = 309.40$ , monoclinic crystals, the space group  $P2_1/n$ ,  $a = 11.3433(9) \text{ \AA}$ ,  $b = 11.1876(8) \text{ \AA}$ ,  $c = 13.3776(10) \text{ \AA}$ ,  $\beta = 97.054(5)^\circ$ ,  $V = 1684.8(2) \text{ \AA}^3$ ;  $Z = 4$ ,  $d_{\text{calc}} = 1.220 \text{ g cm}^{-3}$ ,  $\mu = 0.705 \text{ mm}^{-1}$ , 7520 measured reflections ( $4.83 < \theta < 57.41^\circ$ ), from them 2271 were independent, 1963 with  $I > 2\sigma(I)$ , 199 refined parameters, the final divergence factors  $R_1 = 0.0655$  and  $wR_2 = 0.1736$  on the reflections with  $I > 2\sigma(I)$ . The maximum and minimum values of electron density ( $\Delta\rho$ ) were equal to  $0.495/-0.279 \text{ e/\AA}^3$ .

**Compound 8**,  $\text{C}_{15}\text{H}_{26}\text{N}_4\text{O}_3$ ,  $M = 310.40$ , monoclinic crystals, the space group  $C2/c$ ,  $a = 43.572(3) \text{ \AA}$ ,  $b = 6.8063(5) \text{ \AA}$ ,  $c = 11.2344(9) \text{ \AA}$ ,  $\beta = 102.855(5)^\circ$ ,  $V = 3248.3(4) \text{ \AA}^3$ ;  $Z = 8$ ,  $d_{\text{calc}} = 1.269 \text{ g cm}^{-3}$ ,  $\mu = 0.731 \text{ mm}^{-1}$ , 7239 measured reflections ( $2.08 < \theta < 57.50^\circ$ ), from them 2180 were independent, 1742 with  $I > 2\sigma(I)$ , 200 refined parameters, the final divergence factors  $R_1 = 0.0676$  and  $wR_2 = 0.1949$  on the reflections with  $I > 2\sigma(I)$ . The maximum and minimum values of electron density ( $\Delta\rho$ ) were equal to  $0.226/-0.654 \text{ e/\AA}^3$ .

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