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Esters of 4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidic acid*

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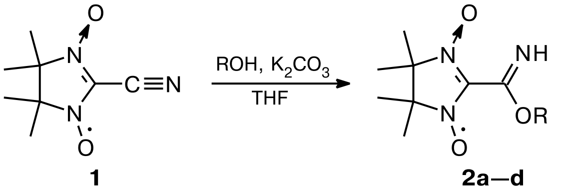
Esters of 4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidic acid were synthesized. Their structures and magnetic properties were investigated.

Key words: free radicals, nitronyl nitroxides, imino esters, X-ray diffraction analysis.

Recently,[1] we have developed a procedure for the preparation of 2-cyano-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (**1**) (Scheme 1) in amounts sufficient for its use in subsequent synthesis of derivatives. For example, the reaction with **1** as the starting compound afforded nitronyl nitroxide containing the tetrazole substituent, which appeared to be an efficient component for the self-assembly of the cage diamond-type heterospin structure.[2] Evidently, the transformation into spin-labeled tetrazole is only one of numerous possibilities of functionalization of **1**. In the present study, we describe the synthesis and structure of an original group of the corresponding esters of 4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidic acid (**2a—d**) derived from compound **1**.

Scheme 1



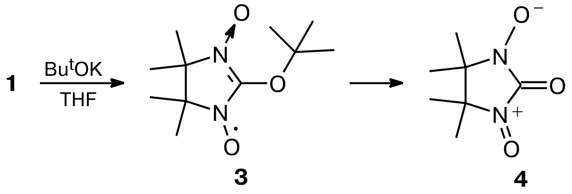
R = Me (**2a**), Et (**2b**), Bu^n (**2c**), Pr^i (**2d**)

Results and Discussion

Esters **2** are among nitroxyls, whose synthesis has recently been impossible[3] because compounds **1** were inaccessible. Compounds **2** were prepared according to Scheme 1.

The reaction in MeOH or EtOH afforded compounds **2a** and **2b**, respectively, in high yields; the results being reproducible. Since compound **1** is insoluble in Bu^nOH and Pr^iOH, THF was added to the reaction mixture. The mixture was heated to ~50 °C with stirring for 2 h to prepare compounds **2c** and **2d**, respectively, in high yields. Under analogous conditions, the reaction of Bu^tOH with **1** did not give the corresponding imino ester. An attempt to perform the addition under more severe conditions with the use of Bu^tOK instead of the addition of alcohol led to the replacement of the nitrile group with the *tert*-butoxy group (Scheme 2). The resulting nitroxyl **3** is poorly stable. It decomposes on silica gel on heating to 109—115 °C as well as upon storage at 0 °C for several months to give orange 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-one 1,3-dioxide (zwitterion **4**).[3] A solution of **3** in AcOEt applied to a column with Al_2O_3 gives a stationary blue layer. Subsequent elution with ethanol affords only zwitterion **4**.

Scheme 2



X-ray diffraction study of the crystals of **2a—d** demonstrated that there is an intramolecular NH...O—N hydrogen bond in all these compounds (Fig. 1). The geometric characteristics of this hydrogen bond are given in Table 1. The structures of the molecules differ most substantially in the angle between the planes of the CN_2 fragment of the imidazoline ring and the C(=N)O fragment, which varies from 3.3° in molecule **2c** to 27.6° in molecule **2d**. Other structural features of molecules **2a—d** are similar. For example, the N(1)—O(1) distance in the

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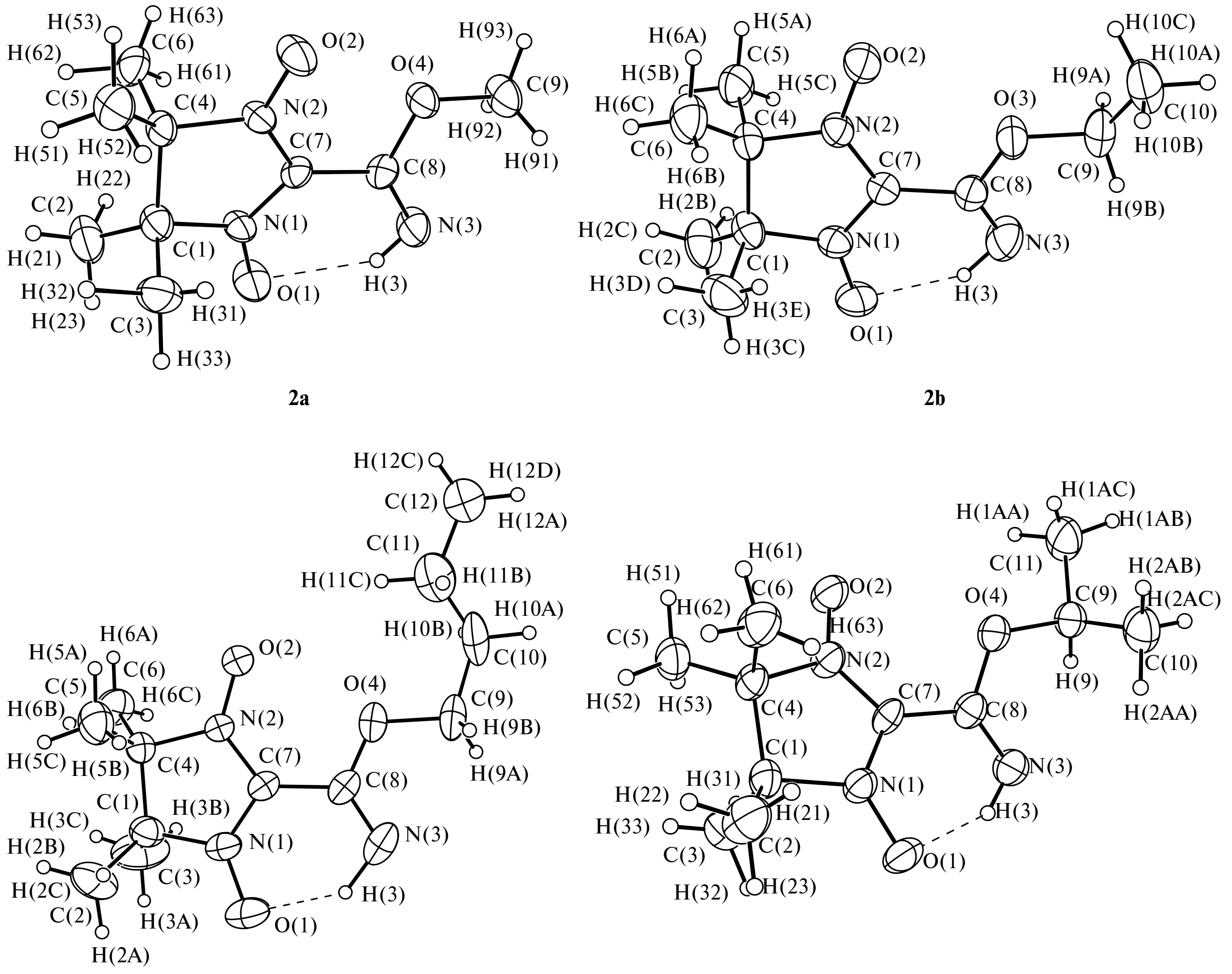

2a **2b**

2c **2d**

Fig. 1. Molecular structures of nitroxyls **2a—d**.

fragment whose O atom is involved in hydrogen bonding is always longer than the analogous N(2)—O(2) distance in the fragment, which is not involved in H bonds (Table 2). The fact that the N(1)—C(7) bond length is similar to the N(2)—C(7) bond length is indicative of the electron density delocalization in the nitroxyl molecules along the conjugated $O^{\bullet}$—N—C—N→O fragment. The presence of conjugation in the carboximido group is confirmed by the C(8)—N(3) and C(8)—O(4) bond lengths.

Table 1. Parameters of hydrogen bonds in nitroxyls **2a—d**

Compound	Fragment	*d*/Å			Angle N—H—O /deg
		N—H	H...O	N...O	
2a	N(3)—H(3)...O(1)	0.68(8)	2.40(9)	2.881(10)	129(10)
2b	N(3)—H(3)...O(1)	0.99(3)	1.93(3)	2.797(3)	145(2)
2c	N(3)—H(3)...O(1)	1.16(6)	1.82(7)	2.761(7)	135(5)
2d	N(3)—H(3)...O(1)	0.88(5)	2.16(5)	2.871(7)	137(4)

Table 2. Selected bond lengths (Å) in nitroxyls **2a—d**

Bond	**2a**	**2b**	**2c**	**2d**
O(1)—N(1)	1.280(7)	1.289(2)	1.286(4)	1.270(4)
N(2)—O(2)	1.299(6)	1.272(2)	1.271(4)	1.249(5)
N(1)—C(7)	1.361(7)	1.339(2)	1.332(4)	1.320(6)
N(2)—C(7)	1.363(8)	1.349(2)	1.335(4)	1.323(5)
N(1)—C(1)	1.515(8)	1.503(2)	1.474(4)	1.483(6)
C(1)—C(4)	1.571(9)	1.541(3)	1.562(5)	1.503(7)
C(4)—N(2)	1.512(8)	1.511(2)	1.499(4)	1.492(6)
C(7)—C(8)	1.465(10)	1.477(2)	1.477(5)	1.468(7)
C(8)—N(3)	1.266(10)	1.256(3)	1.209(6)	1.231(6)
C(8)—O(4)	1.346(8)	1.337(2)	1.286(5)	1.320(6)
O(4)—C(9)	1.449(9)	1.457(2)	1.439(4)	1.447(6)

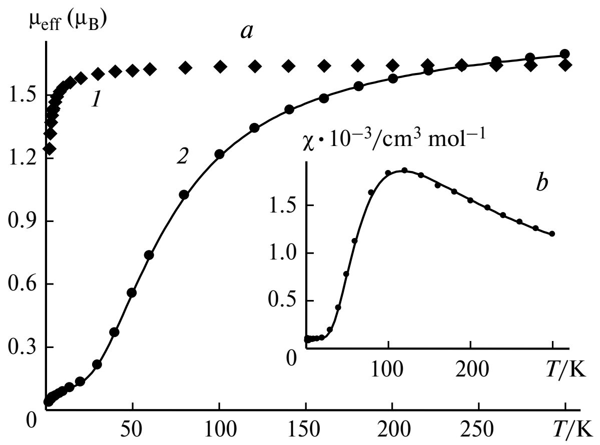

Fig. 2. *a*, Dependence $\mu_{eff}(T)$ for compounds **2a—c** (*1*) and **2d** (*2*); *b*, the dependence $\chi(T)$ for compound **2d**. Points correspond to the experimental data, and the solid lines indicate the calculated data.

In the structures of **2a—c**, the shortest distances between the O atoms of the NO groups of the adjacent molecules are in the range of 4.255—4.628 Å, which is responsible for the similarity of their magnetic behavior. At room temperature, the effective magnetic moments μ_{eff} of **2a—c** are close to the theoretical value of 1.73 μ_B (Fig. 2). This parameter changes only slightly with decreasing temperature. The packing of **2d** is formed by pairs of molecules, the distance between the O atoms of the NO groups in these pairs being short (3.422 Å). Hence, the dependence $\mu_{eff}(T)$ for **2d** is adequately described by the Bleaney—Bowers equation[4,5] (see Fig. 2) with the exchange parameter of -64.5 cm^{-1}.

Experimental

The IR spectra were recorded on a Bruker Vector 22 spectrometer in KBr pellets. Elemental analysis was carried out on a Carlo—Erba C,H,N-analyzer at the Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The magnetic measurements were performed on a SQUID MPMS-5S (Quantum Design) magnetometer in the temperature range of 2—300 K at 5 kOe. Spin-labeled nitrile **1** was prepared according to a procedure described earlier.[1]

Methyl 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidate (2a). A mixture of **1** (182 mg, 1.0 mmol), Na_2CO_3 (0.2 g), and MeOH (6 mL) was stirred at ~20 °C for 15 min and filtered. The filtrate was concentrated on a rotary evaporator. The residue was dissolved in Et_2O (15 mL), filtered, and again concentrated. The residue was triturated with cold light petroleum and the solvent was decanted. The crystals were dissolved in CH_2Cl_2 (3 mL), heptane (4 mL) was added to the solution, and the solution was kept in an open flask at ~5 °C. The blue-violet needle-like crystals thus formed were filtered off. The yield was 130 mg (61%), m.p. 75—76 °C. IR, ν/cm^{-1}: 569, 709, 853, 883, 959, 995, 1014, 1114, 1135, 1168, 1184, 1221, 1323, 1372, 1403, 1421, 1463, 1480, 1633, 2946, 2985, 3037, 3275, 3442 br. Found (%): C, 50.0; H, 7.5; N, 19.5. $C_9H_{16}N_3O_3$. Calculated (%): C, 50.5; H, 7.5; N, 19.6.

Ethyl 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidate (2b) was prepared analogously to **2a**. The yield was 110 mg (48%), m.p. 93—95 °C. IR, ν/cm^{-1}: 708, 847, 876, 897, 1030, 1122, 1172, 1217, 1322, 1373, 1411, 1456, 1622, 2936, 2988, 3253. Found (%): C, 52.6; H, 8.2; N, 18.5. $C_{10}H_{18}N_3O_3$. Calculated (%): C, 52.6; H, 8.0; N, 18.4.

***n*-Butyl 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidate (2c).** Potassium carbonate (200 mg) was added to a solution of compound **1** (90 mg, 0.49 mmol) in a mixture of THF (4 mL) and *n*-butyl alcohol (2 mL). The reaction mixture was stirred at 50—55 °C for 2 h. Then EtOH (10 mL) was added and the mixture was filtered. The filtrate was concentrated. The residue was chromatographed on a column (SiO_2, 1.5×15 cm) using $CHCl_3$ as the eluent. The blue fraction was collected and concentrated. The residue was recrystallized from heptane. Crystals of **2d** suitable for X-ray diffraction analysis were prepared analogously to **2a**. The yield was 85 mg (66%), m.p. 66—68 °C. IR, ν/cm^{-1}: 709, 825, 872, 940, 1020, 1059, 1118, 1171, 1211, 1319, 1372, 1390, 1409, 1456, 1630, 2874, 2958, 3278. Found (%): C, 55.9; H, 8.9; N, 16.2. $C_{12}H_{22}N_3O_3$. Calculated (%): C, 56.2; H, 8.7; N, 16.4.

Isopropyl 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3-oxide-carboximidate (2d) was prepared analogously to **2c**. The yield was 33 mg (50%), m.p. 119—120 °C. IR, ν/cm^{-1}: 711, 815, 847, 870, 890, 927, 972, 1102, 1144, 1171, 1215, 1308, 1333, 1346, 1373, 1387, 1411, 1461, 1631, 1734, 2932, 2987, 3291. Found (%): C, 54.9; H, 8.6; N, 17.5. $C_{11}H_{20}N_3O_3$. Calculated (%): C, 54.5; H, 8.3; N, 17.3.

2-*tert*-Butoxy-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (3). Potassium *tert*-butoxide (31 mg, 32 mmol) was added to a stirred solution of **1** (50 mg, 0.27 mmol) in THF (2 mL), which was accompanied by a change in the color of the reaction mixture from blue-green to violet. The solvent was distilled off and light petroleum (15 mL) was added to the residue. The reaction mixture was kept in an ultrasonic bath for ~2 min and then filtered. The filtrate was concentrated to ~2 mL on a rotary evaporator and kept at −10 °C for 16 h. The violet needle-like crystals that formed were filtered off. The yield was 30 mg (48%). IR, ν/cm^{-1}: 729, 776, 820, 877, 955, 1089, 1150, 1175, 1223, 1269, 1353, 1373, 1397, 1456, 1566, 2986. Found (%): C, 57.1; H, 9.3; N, 12.3. $C_{11}H_{21}N_2O_3$. Calculated (%): C, 57.6; H, 9.2; N, 12.2.

X-ray diffraction data sets were collected from single crystals on an automated Bruker AXS SMART APEX diffractometer (Mo radiation) at ~20 °C according to a standard procedure. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic thermal parameters for nonhydrogen and hydrogen atoms, respectively. (It should be noted that crystals of **2c** were of poor quality, which was reflected in the accuracy of the experimental data.) The positions of the H atoms in the structures of **2a**, **2b**, and **2d** were revealed from difference electron density syntheses. The positions of the H atoms in the structure of **2c** were calculated geometrically and refined in the rigid-body approximation, except for the position of the imine H atom, which was revealed from the difference electron density synthesis and refined without restrictions. The carbon atoms of the butyl group in molecule **2c** are, apparently, disordered. However, neither

Table 3. Crystallographic characteristics of nitroxyls **2a—d** and details of X-ray diffraction study

Parameter	**2a**	**2b**	**2c**	**2d**
Formula	$C_9H_{16}N_3O_3$	$C_{10}H_{18}N_3O_3$	$C_{12}H_{22}N_3O_3$	$C_{11}H_{20}N_3O_3$
Molecular weight	214.25	228.27	256.33	242.30
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2/c$	$P2_1/c$	$C2/c$
a/Å	12.410(8)	10.3708(17)	9.027(3)	24.44(2)
b/Å	12.238(8)	10.7678(17)	13.021(5)	7.063(6)
c/Å	7.554(5)	11.3375(18)	12.456(5)	17.412(16)
α/deg	90	90	90	90
β/deg	90	105.239(2)	91.049(7)	124.47(3)
γ/deg	90	90	90	90
V/Å^3	1147(13)	1221.5(3)	1463.8(9)	2478(4)
Z	4	4	4	8
d_{calc}/g cm^{-3}	1.240	1.241	1.163	1.299
μ/mm^{-1}	0.0984	0.093	0.084	0.095
θ/deg	2.34—23.35	2.04—23.26	2.26—23.40	2.84—23.55
Number of measured reflections	4222	4232	6183	4771
Number of independent reflections (N*)	1599	1751	2117	1796
R_{int}	0.1787	0.0174	0.1267	0.1534
Number of reflections with $I > 2\sigma_I$ (N**)	1078	1554	1515	825
Number of parameters in refinement	197	218	189	235
GOOF	1.021	1.189	1.165	0.829
R_1 (for N**)	0.0812	0.0430	0.1103	0.0647
wR_2	0.1956	0.1391	0.2982	0.1299
R_1 (for N*)	0.1144	0.0478	0.1353	0.1550
wR_2	0.2224	0.1442	0.3164	0.1718

the consideration of disorder nor lowering of the symmetry led to a decrease in the R factor. All calculations associated with the structure solution and refinement were carried out using the SHELX97 program package. The parameters of main hydrogen and interatomic bonds are given in Tables 1 and 2, respectively. Selected crystallographic characteristics of nitroxyls **2a—d** and details of X-ray diffraction study are listed in Table 3.

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