## STRUCTURE OF 2,4,4,5,5-PENTAMETHYL-2-IMIDAZOLINE-1-OXYL-3-OXIDE

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The crystal and molecular structures of the stable nitroxide radical 2,4,4,5,5-pentamethyl-2-imidazoline-1-oxyl-3-oxide was determined. The N—O bond lengths are 1.279(2) and 1.280(2) Å, respectively. The O<sup>-</sup>—N<sup>+</sup>=C—N—•O fragment is nearly planar with carbon atoms of the ethyl fragment that deviated from the O—N<sup>+</sup>=C—N—•O plane by -0.204(5) and +0.176(5) Å. The minimum intermolecular distance between the oxygen atoms of NO groups is 4.094 Å.

Key words: nitroxide radicals, nitroxides, structure.

Recently, we described synthesis and structure of the first nitronyl nitroxide radicals containing various Nalkylpyrazoles (NIT-Pz) [1] as substituents; these radicals were used to produce single crystals of chain polymer heterospin  $Cu(hfac)_2(NIT-Pz)$  complexes with unusual magnetic and mechanical properties [2]. As a continuation of these studies, we undertook an attempt to develop a method for synthesizing dinitronyl nitroxide radicals containing nitrogen unsubstituted pyrazole fragments whose structure favors the formation of high-dimension systems. At the first stage of these studies, we unexpectedly synthesized single crystals of a simple classical nitronyl nitroxide, 2,4,4,5,5-pentamethyl-2-imidazoline-1-oxyl-3-oxide (1). The structure of this compound is described in the present paper.

The crystals of 1 are monoclinic prisms: a = 6.235(1) Å, b = 13.135(2) Å, c = 11.844(2) Å,  $\beta = 101.82(2)^{\circ}$ , V = 949.4(3) Å<sup>3</sup>, Z = 4 for C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>,  $d_{calc} = 1.198$  g/cm<sup>3</sup>, and  $\mu(MoK_{\alpha}) = 0.087$  mm<sup>-1</sup>. A set of reflections was obtained on a Bruker AXS P4 autodiffractometer using a standard technique [239 K, Mo radiation,  $\theta/2\theta$  scan with a variable velocity of  $V_{min} = 3$  deg/min in the range  $2.34 < \theta < 25.02^{\circ}$ ; 1815  $I_{hkl}$  were measured, among which 1656 were independent ( $R_{int} = 0.0313$ )]. The structure was solved by direct methods and refined by a full-matrix least-squares method in an anisotropic approximation for non-hydrogen atoms and in an isotropic approximation for experimentally located hydrogen atoms up to  $R_1 = 0.0551$  and  $wR_2 = 0.1584$  for  $I_{hkl} > 2\sigma(I)$  and GOOF = 1.041. The structural solution and refinement were performed using the SHELX-97 software package. Table 1 shows atomic coordinates, and Table 2 lists the main bond lengths and angles.

TABLE 1

Atomic Coordinates (  $\times 10^4$ ) and Equivalent Thermal Parameters  $U_{eq} = (U_{11} + U_{22} + U_{33})/3$  (Å<sup>2</sup>  $\times 10^3$ )

Atom	x	y	z	$U_{\rm eq}$	Atom	x	y	z	$U_{\rm eq}$
O(1)	782(4)	3145(2)	5501(2)	82(1)	C(21)	389(5)	3085(3)	9536(3)	71(1)
N(1)	551(3)	3417(1)	6506(2)	52(1)	C(22)	3044(4)	4286(2)	9009(3)	72(1)
C(1)	1595(3)	2845(2)	7568(2)	49(1)	N(2)	-656(3)	4218(1)	7867(2)	53(1)
C(11)	3976(4)	2624(3)	7575(3)	78(1)	O(2)	-1764(3)	4839(2)	8353(2)	84(1)
C(12)	286(6)	1845(2)	7511(3)	78(1)	C(3)	-821(4)	4134(2)	6733(2)	54(1)
C(2)	1152(3)	3575(2)	8533(2)	45(1)	C(31)	-2345(7)	4736(3)	5865(3)	86(1)

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Bond Lengths [Å] and Angles [deg] in  ${\bf 1}$ 

5 []	0 [ 0]	
1.279(2)	N(2) - O(2)	1.280(2)
1.336(3)	N(2) - C(3)	1.331(3)
1.495(3)	C(2)— $N(2)$	1.497(3)
1.511(3)	C(2) - C(21)	1.511(3)
1.541(4)	C(2) - C(22)	1.520(3)
1.558(3)	C(3) - C(31)	1.478(3)
125.67(19)	O(2)— $N(2)$ — $C(3)$	124.70(19)
122.03(17)	O(2)— $N(2)$ — $C(2)$	122.73(17)
111.77(17)	C(3)— $N(2)$ — $C(2)$	112.30(17)
111.0(2)	N(2) - C(2) - C(21)	109.27(18)
104.83(19)	N(2)— $C(2)$ — $C(22)$	106.96(19)
110.3(2)	C(21)— $C(2)$ — $C(22)$	108.4(2)
101.34(15)	N(2)— $C(2)$ — $C(1)$	100.83(15)
115.83(19)	C(21)— $C(2)$ — $C(1)$	116.5(2)
112.6(2)	C(22)— $C(2)$ — $C(1)$	114.19(19)
109.93(18)	N(1)— $C(3)$ — $C(31)$	125.7(2)
124.3(2)		
	$\begin{array}{c} 1.279(2) \\ 1.336(3) \\ 1.495(3) \\ 1.511(3) \\ 1.541(4) \\ 1.558(3) \\ 125.67(19) \\ 122.03(17) \\ 111.77(17) \\ 111.0(2) \\ 104.83(19) \\ 110.3(2) \\ 101.34(15) \\ 115.83(19) \\ 112.6(2) \\ 109.93(18) \\ 124.3(2) \end{array}$	$\begin{array}{c ccccc} 1.27 & 0.27 & 0.27 & 0.27 \\ \hline 1.279(2) & N(2) &O(2) \\ 1.336(3) & N(2) &C(3) \\ 1.495(3) & C(2) &N(2) \\ 1.511(3) & C(2) &C(2) \\ 1.558(3) & C(3) &C(31) \\ 125.67(19) & O(2) &N(2) &C(3) \\ 122.03(17) & O(2) &N(2) &C(2) \\ 111.77(17) & C(3) &N(2) &C(2) \\ 111.0(2) & N(2) &C(2) &C(2) \\ 111.0(2) & N(2) &C(2) &C(2) \\ 104.83(19) & N(2) &C(2) &C(2) \\ 101.34(15) & N(2) &C(2) &C(1) \\ 115.83(19) & C(21) &C(2) &C(1) \\ 115.83(19) & C(21) &C(2) &C(1) \\ 112.6(2) & C(22) &C(2) &C(1) \\ 109.93(18) & N(1) &C(3) &C(31) \\ 124.3(2) & & \\ \end{array}$



Diagram 1.



Fig. 1. Molecular structure of 1 and a (100) projection of the structure.

As shown in Diagram 1, the synthesis of the dinitronyl nitroxide radical containing the nitrogen unsubstituted pyrazole fragment involved etherification of diacid 2, addition of diether 3 to vinyl ethyl ether, reduction of nitrogen substituted diether 4, oxidation of dialcohol 5 to dialdehyde 6, and condensation of the resultant dialdehyde with bishydroxylamine (BHA) by the classical Ulman procedure to the nitronyl nitroxide radical (NNR) and tetrahydroxy derivative 7 followed by its oxidation to 8. The final stage envisaged removal of acetal protection by an acid.

However, only trace amounts of dinitroxide 8 were detected. It was found that the main reaction product at the stage of production of 7, which was oxidized to 8 without isolation, was nitroxide 1. Its formation can be explained by acidic hydrolysis of 6 and/or 7 under the conditions of production of 7 and splitting of the alcohol molecule from the intermediate semiacetal followed by interaction of acetic aldehyde with BHA and its subsequent oxidation to 1 under the conditions of production of 8. This also explains the minor amounts of 8 in the competitive reactions of hydrolysis of N-acetal 6 and/or 7 and condensation of the carbonyl compound with BHA. The rate of the first reaction is obviously higher, and the aliphatic aldehyde formed by acidic hydrolysis is more reactive than the aromatic aldehyde. This explains why nitroxide 1 was obtained in the form of red crystals after recrystallization of the final product from hexane. Previously, **1** has been used in the synthesis of heterospin complexes [4–11] although its crystal structure remained unknown. The structure of **1** is molecular (see Fig. 1). As in most nitronyl nitroxide radicals, the N—O and N(2)—O(2), C(3)—N(1) and C(3)—N(2), and C(1)—N(1) and C(2)—N(2) bond lengths are close: 1.279(2) and 1.280(2), 1.336(3) and 1.331(3), and 1.495(3) and 1.497(3) Å, respectively. The O<sup>-</sup>—N<sup>+</sup>=C—N—oO fragment is nearly planar with carbon atoms of the ethyl fragments that deviated from the O<sup>-</sup>—N<sup>+</sup>=C—N—oO plane by -0.204(5) and +0.176(5) Å. The intermolecular distances between the oxygen atoms of the NO groups are rather large, the minimum of which is 4.094 Å. Hydrogen bonds are absent. We also note that the distance to the carbon atom of the methyl group at position **2** of the cycle is significantly shorter than the single bond length.

In metal complexes, the nitroxide structure differs significantly. In the examined complexes with 1, the deviation of the carbon atoms at positions 4 and 5 of the heterocycle from the  $CN_2O_2$  plane varies from 0.09 to 0.27 Å; the bond lengths in coordinated N—O groups lie in the interval 1.286–1.320 Å, whereas in uncoordinated N—O groups, they are within 1.268–1.282 Å. Correspondingly, the C—N bond lengths in the  $CN_2$  fragment are also different: the length is shorter for the coordinated group (1.310–1.335 Å) than for the uncoordinated group (1.328–1.363 Å). In all complexes, the C—C distance to the carbon atom of the methyl group at position 2 of the cycle is short (1.433–1.490 Å).

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