

Synthesis and magnetic studies of 2-(pyrazolyl)imidazoline-derived iminonitroxides and nitronylnitroxides

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Dedicated to Professor Michail G. Voronkov on the occasion of his 80th birthday
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Abstract

The reaction of formylpyrazoles **1c,g** with 2,3-dimethyl-2,3-di(hydroxyamino)butane sulfate and followed by oxidation of the resulting 4,4,5,5-tetramethyl-2-(1*H*-pyrazolyl)imidazolidine-1,3-diols **2c,g** with sodium periodate afforded 4,4,5,5-tetramethyl-2-(1*H*-pyrazolyl)-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyls **3c,g**. Reduction of **3a–h** with sodium nitrite in the presence of acetic acid led to 4,4,5,5-tetramethyl-2-(1*H*-pyrazolyl)-4,5-dihydro-1*H*-imidazol-1-oxyls **4a–h**. For **3b**, **3c**, and **4f**, an anomalously large exchange coupling between the unpaired electrons of paramagnetic centers has been found.

Keywords: Pyrazolylnitronylnitroxides, pyrazolyliminonitroxides, organic radicals, magnetic properties

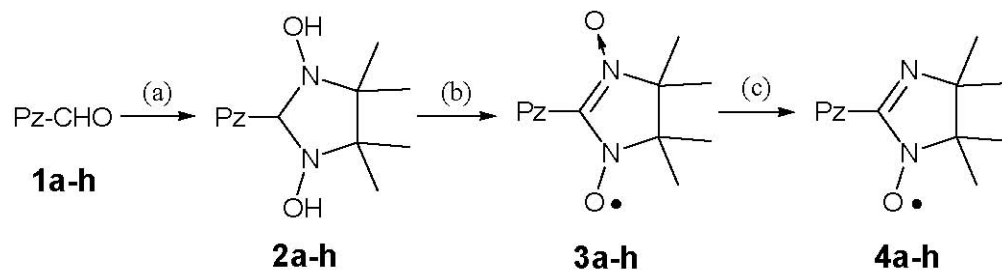
Introduction

In recent years, interest in creation of new classes of magnetically active materials has developed enormously. Syntheses of polyfunctional stable organic radicals and studies of their magnetostructural correlations have become an essential part of this research. Polyfunctional nitroxides are highly effective in design of n-dimensional heterospin systems capable of magnetic ordering.¹ Therefore we undertook this study to develop synthetic procedures and to study the structure and magnetic properties of pyrazolylimino- and pyrazolylnitronylnitroxides.²

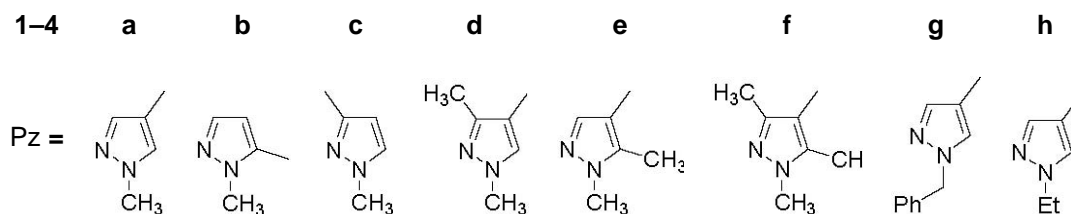
Results and Discussion

Iminonitroxides (IN) 4,4,5,5-tetramethyl-2-(1*H*-pyrazolyl)-4,5-dihydro-1*H*-imidazol-1-oxyls **4a–h** were synthesized by reduction of the corresponding nitronyl nitroxides (NN) 4,4,5,5-tetramethyl-2-(1*H*-pyrazolyl)-4,5-dihydro-1*H*-imidazol-3-oxide-1-oxyls **3a–h** with sodium nitrite in the presence of acetic acid. For the uncharacterized NN **3c** and **3g**, synthetic procedures are given here; other NNs were prepared by the procedures described previously.^{3,4} The general scheme of synthesis for these IN and NN, basically conforming with Ullman's classical approach,⁵ is presented below.

Since pyrazole carbaldehydes **1c** and **1g** are soluble in water, instead of 2,3-dimethyl-2,3-di(hydroxyamino)butane one can use its sulfate. This facilitates synthesis of adducts **2c** and **2g**, stabilizing the yields at 60–65%. Dihydroxyimidazolidines were then oxidized with sodium periodate to give NN **3c** and **3g** in 65–70% yields. Iminonitroxides **4a–h** were prepared in 70–75% yields by reduction of compounds **3a–h** with sodium nitrite in the presence of acetic acid at 60–65 °C.



(a) 2,3-Dimethyl-2,3-di(hydroxyamino)butane sulfate, H₂O; room temperature.
 (b) NaIO₄, CHCl₃, H₂O; 10–20 °C. (c) NaNO₂, AcOH, CHCl₃; 60–65 °C.



Scheme 1

Nitronyl nitroxides **3c** and **3g** are dark blue crystals; iminonitroxides **4a–h** are dark red crystals. The compounds of both series are stable in the solid state and in solution for several weeks when stored at room temperature or for several months when stored in a refrigerator. Magnetic measurements were carried out on an MPMS-5s “Quantum Design” SQUID magnetometer (2–300 K, magnetic field 5 kOe). The results are presented in Figures 1 and 2. For nitroxides **4e**, **4g**, **3g**, and **4d** (Figure 1) the magnetic susceptibility is described by the Curie-

Weiss law $\chi = \frac{C}{T - \theta}$, with low Weiss constants θ over the whole temperature range under study (Table 1) suggesting weak exchange coupling between the odd electrons of nitroxide molecules. Characteristic exchange interaction energies for this group of nitroxides were estimated in a molecular field approximation⁶ using the expression $\theta = \frac{2zJS(S+1)}{3k}$ (J is the exchange parameter between nitroxide molecules, k is Boltzmann's constant, z is the number of the nearest neighbors of nitroxide molecules, and $S = 1/2$), relating the exchange coupling parameter to the Weiss constant. The resulting values, $|zJ| \sim 0.2\text{--}2.2 \text{ cm}^{-1}$ (Table 1) are typical for most nitroxides.

The C constants are close to the theoretical value of 0.375 for one odd electron per nitroxide molecule for all nitroxides from this group (Table 1). Notably, the exchange parameters differ between two groups of nitroxides, **4e**, **4g** and **3g**, **4d**, showing that exchange interactions are essentially antiferromagnetic for the former (zJ values are negative) and ferromagnetic for the latter (zJ values are positive). The latter property is extremely rare for nitroxides in general.

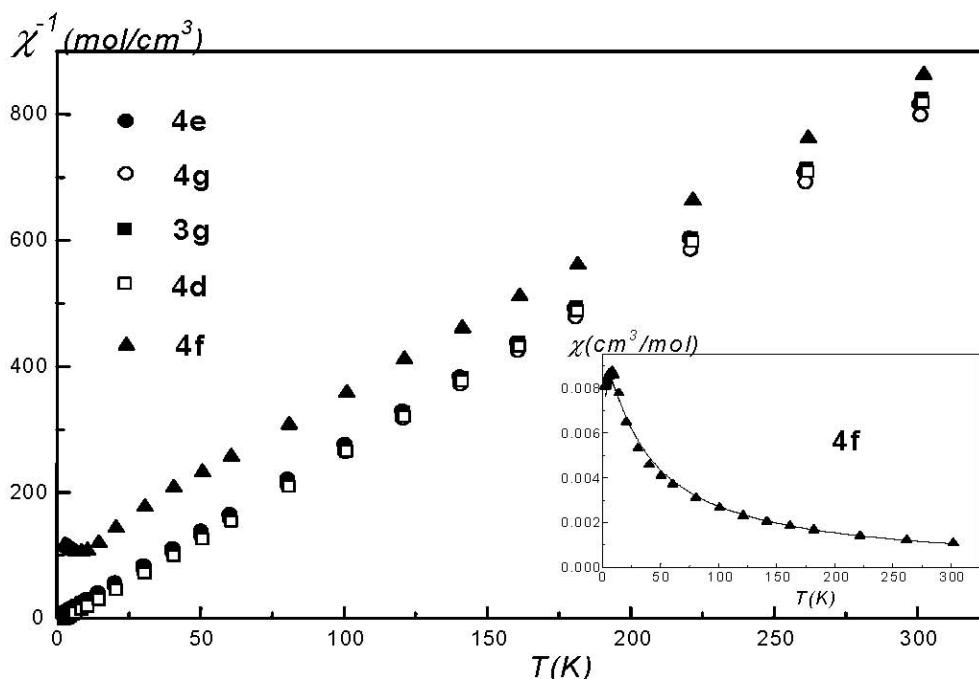


Figure 1. Temperature dependences $1/\chi(T)$ of nitroxides **3g**, **4d–g**. Insert: experimental (\blacktriangle) and theoretical curve (—) $\chi(T)$ for **4f**.

The next group of nitroxides under study includes **3b**, **3c**, **4a**, and **4f**. For **3b**, previous investigations² have shown that its magnetic properties are well approximated by the dimer exchange cluster model, despite the anomalously long ($>3 \text{ \AA}$) distances between the paramagnetic centers. The exchange interaction energy in the dimer was found to be -27 cm^{-1} . For **3c** and **4a**, the temperature dependences of magnetic susceptibility $\chi(T)$ are analogous to $\chi(T)$ of **3b** and are also defined in terms of the dimer exchange cluster model (Figure 2), in which

magnetic susceptibility is given by Bleaney-Bowers' relation:⁷

$$\chi = \frac{N\beta^2 g^2}{3kT} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{kT}\right) \right]^{-1} \quad \text{Eq. 1}$$

J is the exchange parameter in the dimer, and g is the g -factor of the nitroxide. The parameters obtained by optimization procedures for **3c** and **4a** are listed in Table 2. The $z'J'$ (z' is the number of the nearest neighbors of dimmers) value defines the intercluster (interdimer) exchange interaction, which is calculated by the molecular field method.⁸

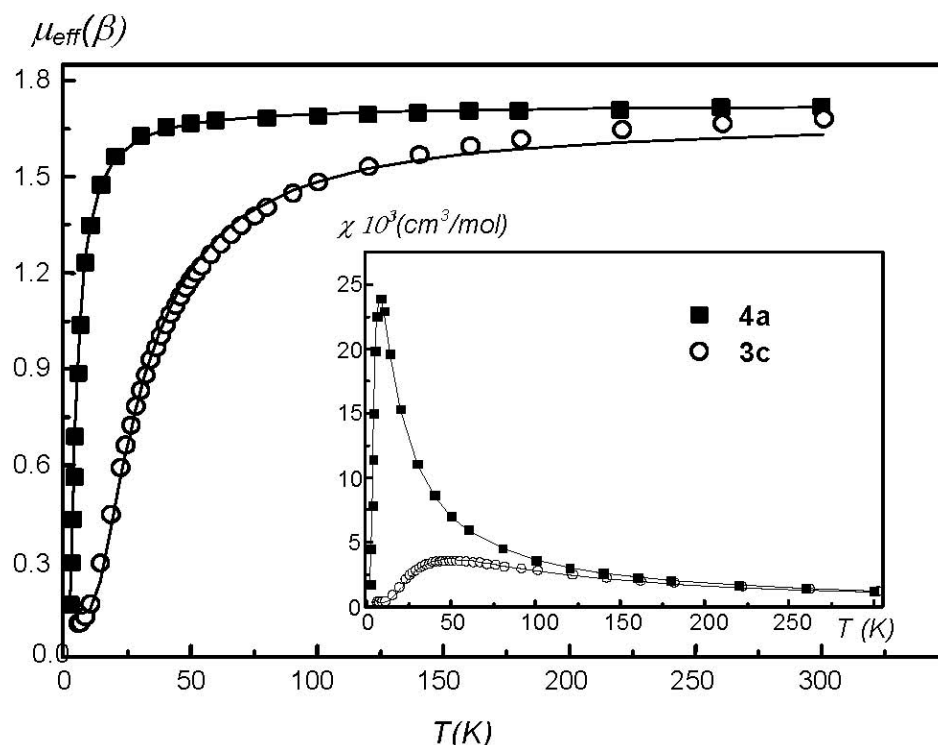


Figure 2. Temperature dependences $\mu_{\text{eff}}(T)$ and $\chi(T)$ for **3c** and **4a**. Lines (—) theoretical curves.

The magnetic behavior of nitroxide **4f** was found to be unusual (Figure 1). The dependence $1/\chi(T)$ is linear above 30 K subject to the Curie-Weiss equation with a Weiss constant θ (Table 1) distinctly higher than the values obtained for **4e**, **4g**, **3g**, and **4d**. This suggests much stronger exchange interactions in **4f**. On the other hand, the observed maximum on the $\chi(T)$ curve at 8 K is indicative of rather weak antiferromagnetic exchange interactions. Seeking possible channels of exchange interactions in solid **4f**, we have studied its crystal structure.

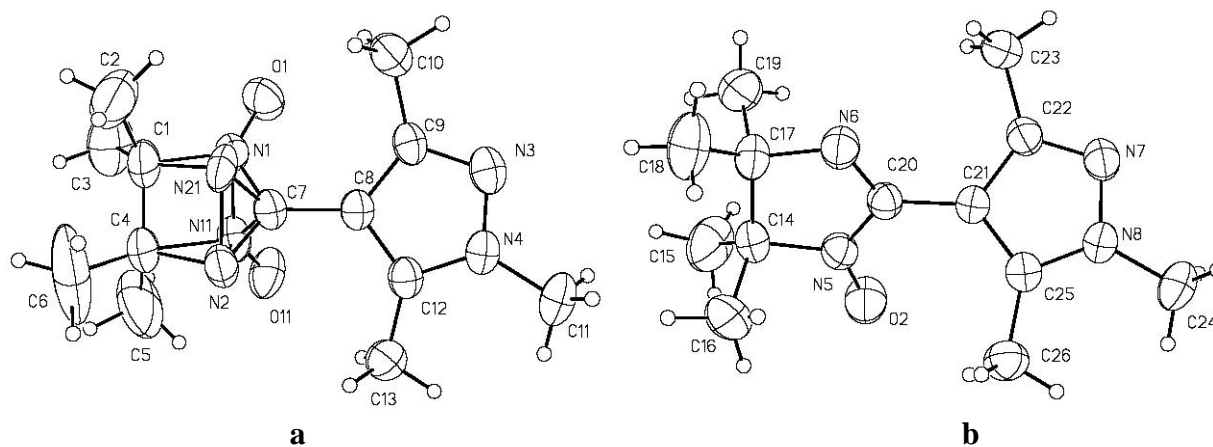
Table 1. Parameters of the temperature dependence of magnetic susceptibility for **3g**, **4d–g**

Compound	C [$\text{cm}^3 \text{K/mol}$]	θ [K]	zJ [cm^{-1}]
4e	0.367	-1.6	-2.2
4g	0.373	-0.23	-0.3
3g	0.364	0.13	0.2
4d	0.360	0.74	1.0
4f	0.378	-44.7	

Table 2. Exchange Parameters

Compound	g	J [cm^{-1}]	$z'J'$ [cm^{-1}]
3b	2.0 ± 0.01	-27.1 ± 0.5	
3c	2.0 ± 0.01	-26.1 ± 1.0	-3.0 ± 1.0
4a	2.0 ± 0.01	-4.3 ± 0.1	-0.4 ± 0.1
4f	2.0 ± 0.01	-0.6 ± 0.1	

Crystals **4f** (Figure 3) are dark red, monoclinic; unit cell parameters are: $a = 7.735(2)$, $b = 32.776(7)$, $c = 15.555(3)$ Å, $\beta = 132.64(3)^\circ$, $V = 2901.0(11)$ Å³, space group $P2_1/n$, $Z = 8$ of $\text{C}_{13}\text{H}_{21}\text{N}_4\text{O}$, $d_{\text{calc}} = 1.149$ g/cm³. The structure was solved using 5002 independent reflections (Bruker AXS P4, Mo radiation, $3 < 2\theta < 50^\circ$, $V_{\text{min}} = 3$ deg/min, absorption correction applied empirically) with SHELX97 program package. The least-squares refinement was performed anisotropically for nonhydrogen atoms. Hydrogen atoms were located from difference electron density maps and refined isotropically together with nonhydrogen atoms in a rigid group approximation. The final R indices are $R_1 = 0.0973$, $wR_2 = 0.2746$ for $I_{hkl} > 2\sigma(I)$. The positional and thermal parameters of nonhydrogen atoms are listed in Table 3; selected bond lengths and angles are given in Table 4.

**Figure 3.** Structure of two crystallographically independent molecules **4f**.

The structure of **4f** is rather unusual. The molecule in general has a nonplanar structure because of the maximal possible number of substituents in the pyrazole ring. In one of the two crystallographically independent molecules, the CN₂O fragment is disordered over two mutually orthogonal positions [the angle between the planes is 88.7(6)°] (Figure 3).

The angle between the plane of the pyrazole rings and the CN₂O fragment of the imidazoline does not change: 42.4(3) and 46.7(5)°. In the other molecule, this angle is 45.1(2)°. The C-N bond lengths in the CN₂O fragment differ: C-N(-O•) is much longer (1.389(5) Å) than C-N (1.289(5) Å); the N-O distance is 1.263(4) Å (in the ordered molecule). All these distances are intermediate between double and single bond lengths.

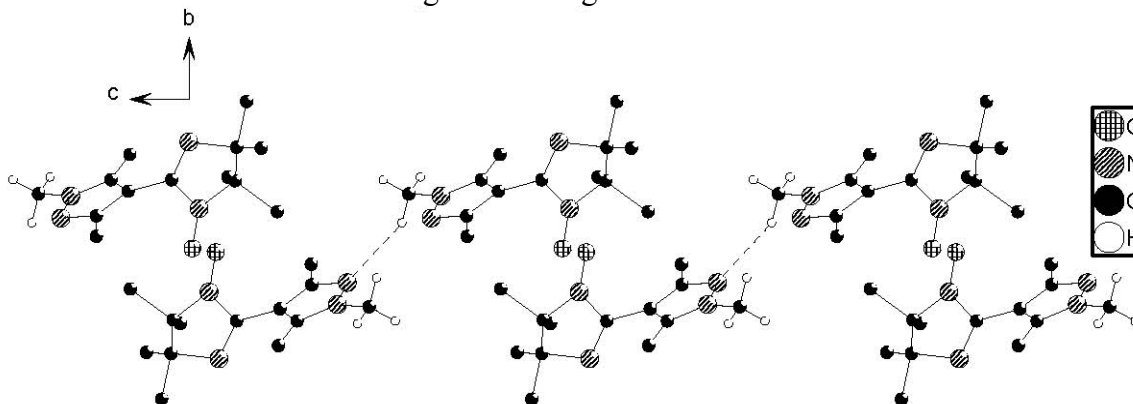


Figure 4. Chain structure in **4f**.

The structure in general is molecular. Note the rather short distances of 3.376(10) Å between the disordered nitroxyl oxygens arranged in pairs, which, in turn, are linked by N_{Pz}...Me-N_{Pz} type hydrogen bonds (N...H(-C) distance is 2.61 Å) in chains (Figure 4). Thus in the crystal structure of **4f**, one can isolate pairs of paramagnetic centers {>N•O...O•N<} with a short contact of 3.376 Å between the O atoms of the nitroxyl groups. However, as in the case of nitroxides **3c**, **4a**, and **3b**, an attempt to describe the magnetic behavior of **4f** using Equation (1) has shown that this model does not adequately fit the experiment. This result suggests that strong antiferromagnetic exchange interactions take place along with pair-wise interactions.

To estimate the exchange parameter in pairs, we used a modified Bleaney-Bowers Equation (Eq. 2), in which the exchange interactions other than pair-wise interactions are specified by the parameter θ :

$$\chi = \frac{N\beta^2 g^2}{3k(T-\theta)} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{kT}\right) \right]^{-1} \quad \text{Eq. 2.}$$

In the insert of Figure 1, the solid line represents the theoretical curve (2) with parameters $J = -0.6 \text{ cm}^{-1}$ and $\theta = 35 \text{ K}$.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4f**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atom	x	y	z	U(eq)
O(1)	7752(6)	16(1)	9682(4)	87(1)
O(11)	11479(14)	460(4)	10213(9)	92(3)
N(1)	8086(6)	393(1)	9868(4)	62(1)
N(11)	9906(16)	602(4)	10136(9)	73(3)
C(1)	7684(7)	652(2)	10841(4)	104(2)
C(2)	5797(9)	687(3)	10640(6)	154(3)
C(3)	8246(10)	360(2)	11987(5)	132(2)
C(4)	9040(7)	966(2)	10886(4)	97(2)
C(5)	10830(11)	958(3)	11548(7)	194(4)
C(6)	8176(16)	1396(2)	11147(6)	211(4)
N(2)	9042(7)	1016(1)	9590(4)	67(1)
N(21)	7115(14)	785(4)	9266(8)	68(3)
C(7)	8638(5)	662(1)	9119(3)	57(1)
C(8)	8834(5)	551(1)	7956(3)	55(1)
C(9)	7661(5)	323(1)	7087(3)	58(1)
C(10)	5934(6)	130(2)	7100(4)	84(1)
N(3)	8299(4)	302(1)	6129(3)	68(1)
N(4)	9881(4)	508(1)	6399(2)	63(1)
C(11)	10939(7)	530(2)	5535(4)	86(1)
C(12)	10254(5)	663(1)	7491(3)	59(1)
C(13)	11891(6)	895(1)	7988(4)	76(1)
O(2)	7064(4)	2328(1)	6939(3)	90(1)
N(5)	8704(4)	2245(1)	7242(3)	61(1)
C(14)	9969(6)	2442(1)	8239(3)	73(1)
C(15)	9647(8)	2897(2)	8218(7)	133(2)
C(16)	9520(9)	2248(2)	9333(4)	142(3)
C(17)	11773(6)	2300(1)	8001(3)	70(1)
C(18)	13169(8)	2189(2)	9050(5)	117(2)
C(19)	12524(7)	2612(1)	7280(5)	96(2)
N(6)	11272(4)	1940(1)	7223(3)	66(1)
C(20)	9583(5)	1935(1)	6804(3)	54(1)
C(21)	8637(5)	1656(1)	5915(3)	53(1)
C(22)	9191(5)	1546(1)	4890(3)	59(1)
C(23)	10812(6)	1683(1)	4512(4)	76(1)
N(7)	8035(4)	1288(1)	4247(3)	66(1)
N(8)	6744(4)	1232(1)	4854(3)	61(1)
C(24)	5295(6)	956(1)	4372(4)	84(1)

Table 3. Continued

C(25)	7063(5)	1448(1)	5862(3)	56(1)
C(26)	5906(6)	1424(1)	6694(4)	76(1)

Table 4. Bond lengths [Å] and angles [deg] for **4f**

O(1)-N(1)	1.270(5)	N(3)-N(4)	1.367(4)	C(14)-C(17)	1.558(6)
N(1)-C(7)	1.385(6)	N(4)-C(12)	1.349(4)	C(17)-C(18)	1.480(6)
N(1)-C(1)	1.518(6)	N(4)-C(11)	1.452(5)	C(17)-N(6)	1.488(5)
C(1)-C(2)	1.427(8)	C(12)-C(13)	1.474(6)	C(17)-C(19)	1.531(7)
C(1)-C(3)	1.628(8)	O(11)-N(11)	1.286(14)	N(6)-C(20)	1.282(5)
C(1)-C(4)	1.462(7)	N(11)-C(7)	1.370(11)	C(20)-C(21)	1.449(5)
C(4)-C(5)	1.419(9)	C(1)-N(21)	1.855(10)	C(21)-C(25)	1.383(5)
C(4)-N(2)	1.536(6)	N(11)-C(4)	1.715(12)	C(21)-C(22)	1.421(5)
C(4)-C(6)	1.618(8)	N(21)-C(7)	1.296(11)	C(22)-N(7)	1.329(4)
N(2)-C(7)	1.291(5)	O(2)-N(5)	1.263(4)	C(22)-C(23)	1.495(6)
C(7)-C(8)	1.460(5)	N(5)-C(20)	1.389(5)	N(7)-N(8)	1.372(5)
C(8)-C(12)	1.388(5)	N(5)-C(14)	1.486(5)	N(8)-C(25)	1.354(4)
C(8)-C(9)	1.410(5)	C(14)-C(15)	1.512(7)	N(8)-C(24)	1.447(5)
C(9)-N(3)	1.337(5)	C(14)-C(16)	1.549(7)	C(25)-C(26)	1.478(6)
C(9)-C(10)	1.482(6)				
O(1)-N(1)-C(7)	126.2(4)	C(12)-N(4)-N(3)	112.6(3)	C(15)-C(14)-C(17)	116.3(4)
O(1)-N(1)-C(1)	127.2(5)	C(12)-N(4)-C(11)	128.4(4)	C(16)-C(14)-C(17)	114.5(4)
C(7)-N(1)-C(1)	105.9(4)	N(3)-N(4)-C(11)	119.0(3)	C(18)-C(17)-N(6)	110.6(4)
C(2)-C(1)-C(4)	130.3(6)	N(4)-C(12)-C(8)	105.5(3)	C(18)-C(17)-C(19)	109.2(4)
C(2)-C(1)-N(1)	107.7(5)	N(4)-C(12)-C(13)	122.8(4)	N(6)-C(17)-C(19)	105.5(3)
C(4)-C(1)-N(1)	98.5(4)	C(8)-C(12)-C(13)	131.7(3)	C(18)-C(17)-C(14)	115.4(4)
C(2)-C(1)-C(3)	104.2(6)	O(11)-N(11)-C(7)	125.7(9)	N(6)-C(17)-C(14)	103.6(3)
C(4)-C(1)-C(3)	109.7(4)	O(11)-N(11)-C(4)	134.0(9)	C(19)-C(17)-C(14)	112.0(4)
N(1)-C(1)-C(3)	103.6(4)	C(7)-N(11)-C(4)	93.7(7)	C(20)-N(6)-C(17)	109.8(3)
C(5)-C(4)-C(1)	127.2(6)	C(2)-C(1)-N(21)	79.9(5)	N(6)-C(20)-N(5)	113.1(3)
C(5)-C(4)-N(2)	108.4(5)	C(4)-C(1)-N(21)	82.4(5)	N(6)-C(20)-C(21)	125.4(3)
C(1)-C(4)-N(2)	102.0(4)	C(3)-C(1)-N(21)	157.1(5)	N(5)-C(20)-C(21)	121.4(3)
C(5)-C(4)-C(6)	107.8(6)	C(5)-C(4)-N(11)	79.7(5)	C(25)-C(21)-C(22)	106.1(3)
C(1)-C(4)-C(6)	107.2(6)	C(1)-C(4)-N(11)	81.7(5)	C(25)-C(21)-C(20)	129.1(3)
N(2)-C(4)-C(6)	101.3(4)	C(6)-C(4)-N(11)	159.0(6)	C(22)-C(21)-C(20)	124.8(3)
C(7)-N(2)-C(4)	106.0(4)	C(7)-N(21)-C(1)	93.0(6)	N(7)-C(22)-C(21)	110.3(3)
N(2)-C(7)-N(1)	112.2(4)	N(21)-C(7)-C(8)	120.3(5)	N(7)-C(22)-C(23)	121.2(3)
N(2)-C(7)-C(8)	124.0(4)	N(11)-C(7)-C(8)	124.9(6)	C(21)-C(22)-C(23)	128.4(3)

N(1)-C(7)-C(8)	123.7(3)	O(2)-N(5)-C(20)	126.9(3)	C(22)-N(7)-N(8)	105.2(3)
C(12)-C(8)-C(9)	106.7(3)	O(2)-N(5)-C(14)	123.9(3)	C(25)-N(8)-N(7)	112.5(3)
C(12)-C(8)-C(7)	124.9(3)	C(20)-N(5)-C(14)	108.9(3)	C(25)-N(8)-C(24)	129.3(4)
C(9)-C(8)-C(7)	128.4(4)	N(5)-C(14)-C(15)	109.9(4)	N(7)-N(8)-C(24)	118.1(3)
N(3)-C(9)-C(8)	109.7(3)	N(5)-C(14)-C(16)	104.2(4)	N(8)-C(25)-C(21)	105.8(3)
N(3)-C(9)-C(10)	120.1(3)	C(15)-C(14)-C(16)	110.5(5)	N(8)-C(25)-C(26)	122.7(3)
C(8)-C(9)-C(10)	130.2(4)	N(5)-C(14)-C(17)	100.2(3)	C(21)-C(25)-C(26)	131.4(3)
C(9)-N(3)-N(4)	105.5(3)				

In summary, a number of pyrazolyl-substituted iminonitroxides and nitronylnitroxides has been obtained. Anomalously strong exchange interactions between the odd electrons of paramagnetic centers have been found in solid **3b**, **3c**, and **4f**. Investigation of the reasons for high-energy exchange interactions in molecular crystals of nitroxides **3b**, **3c**, and **4f** requires a special quantum-mechanical study.

Experimental Section

General Procedures. The reactions were monitored and the products were identified by TLC on Silufol UV-254 plates using a chloroform/ethyl acetate mixture (3:1) as eluent and aqueous NaIO₄ as a developer for **2c** and **2g**; ethyl acetate was used as eluent for **3c**, **3g**, **4a–h**. The IR-spectra were recorded (KBr) on a Bruker IFS 66 instrument. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C. ¹H-NMR signals were referenced to the solvent (DMSO-*d*₆, δ_H 2.50). The electronic absorption spectra of the benzene (reagent-grade) solutions of the radicals were recorded on a Specord UV VIS (Carl Zeiss) spectrophotometer using quartz cells with an optical thickness of 0.1–1 cm. The concentrations of the radicals were varied from 10⁻⁴ to 10⁻³ M. The maxima of absorption bands were determined to an accuracy of ±50 cm⁻¹; extinction coefficients, to an accuracy of ±5%.

Unless otherwise stated, commercially available samples were used. All organic solvents were analytical quality and used as purchased. Solvent mixtures are defined by volume ratios (v/v). 2,3-Bis(hydroxyamino)-2,3-dimethylbutane monosulfate monohydrate was prepared by the procedure described.⁹ Aldehydes **1a**, **1d–f**,¹⁰ **1b**, **1c**,¹¹ **1g**,¹² and **1h**,³ adducts **2a**, **2h**,³ and **2b**, **2d–f**,⁴ and nitronylnitroxides **3a**, **3h**³ and **3b**, **3d–f**⁴ were synthesized according to known procedures.

4,4,5,5-Tetramethyl-2-(1H-pyrazolyl)imidazolidine-1,3-diols **2c** and **2g**. General procedure

An equimolar mixture of 2,3-dimethyl-2,3-di(hydroxyammonium)butane sulfate monohydrate (3.96 g, 0.015 mol), formylpyrazole **1c** or **1g** (0.015 mol), and water (10 mL) was stirred at room temperature until **1c** or **1g** was consumed (monitored by TLC). NaHCO₃ (1.39 g, 0.0165 mol) was added to the reaction mixture, and the precipitate formed was filtered off and recrystallized.

4,4,5,5-Tetramethyl-2-(1-methyl-1H-pyrazol-3-yl)imidazolidine-1,3-diol (2c). Colorless crystals (3.046 g, 96%), mp 170–171 °C (ethyl acetate). IR (KBr): $\tilde{\nu}$ [cm⁻¹] 787, 843, 920, 934, 1028, 1121, 1143, 1218, 1273, 1374, 1435, 2980, 3172; ¹H NMR (DMSO-*d*₆): δ 0.93 (6H, s, 2 CH₃), 0.97 (6H, s, 2 CH₃), 3.75 (3H, s, CH₃N), 4.67 (1H, s, 2-H_{Im}), 6.15 (1H, s, 4-H_{Pz}), 7.19 (1H, s, 5-H_{Pz}), 7.92 (2H, br s, 2 HON). Anal. Calcd for C₁₁H₂₀N₄O₂ (240.30): C, 54.48; H, 8.39; N, 23.31. Found: C, 54.60; H, 8.43; N, 23.29.

2-(1-Benzyl-1H-pyrazol-4-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (2g). Colorless crystals (3.99 g, 84%), mp 175–176 °C (ethyl acetate/THF 10:1). IR (KBr): $\tilde{\nu}$ [cm⁻¹] 845, 917, 939, 1000, 1027, 1169, 1204, 1305, 1363, 1373, 1386, 1417, 1456, 1497, 1570, 2928, 2983, 3223; ¹H NMR (DMSO-*d*₆): δ 1.01 (6H, s, 2 CH₃), 1.04 (6H, s, 2 CH₃), 4.54 (1H, s, 2-H_{Im}), 5.28 (2H, s, CH₂N), 7.25–7.40 (5H, m, C₆H₅), 7.42 (1H, s, 3-H_{Pz}), 7.69 (1H, s, 5-H_{Pz}), 7.76 (2H, s, 2 HON). Anal. Calcd for C₁₇H₂₄N₄O₂ (316.40): C, 64.53; H, 7.65; N, 17.71. Found: C, 64.35; H, 7.67; N, 17.55.

4,4,5,5-Tetramethyl-2-(1H-pyrazolyl)imidazoline-3-oxide-1-oxyls 3c and 3g. General procedure

NaIO₄ (1.71 g, 0.008 mol) was added in portions with stirring and cooling with ice water to a mixture of adduct **2c** or **2g** (0.005 mol), chloroform (30 mL), and water (30 mL) for 30 min. Stirring was continued at room temperature for 1–4 h. The organic phase was separated, and the aqueous layer was extracted with chloroform. The combined extracts were dried over MgSO₄, the solvent was removed, and the residue was chromatographed on silica gel using chloroform as an eluent. The products were **3c**, **3g** (major) and **4c**, **4g** (minor).

4,4,5,5-Tetramethyl-2-(1-methyl-1H-pyrazol-3-yl)-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (3c). Dark blue crystals (0.88 g, 74%), mp 179.5–180.5 °C (hexane/benzene 10:1). UV (benzene): λ_{\max} [nm] (ϵ) 340 sh (9400), 356 (12800), 560 (420), 606 (540), 660 sh (340); IR (KBr): $\tilde{\nu}$ [cm⁻¹] 811, 868, 928, 1020, 1049, 1136, 1167, 1194, 1223, 1272, 1367, 1385, 1399, 1415, 1453, 1476, 1586, 1788, 2944, 2987, 3000, 3107, 3124. Anal. Calcd for C₁₁H₁₇N₄O₂ (237.28): C, 55.68; H, 7.22; N, 23.61. Found: C, 55.91; H, 7.26; N, 23.82.

2-(1-Benzyl-1H-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (3g). Dark blue crystals (1.08 g, 69%), mp 136–137 °C (hexane/benzene 5:1); UV (benzene): λ_{\max} [nm] (ϵ) 322 sh (2900), 336 (8900), 352 (19400), 508 sh (130), 559 sh (470), 602 (1000), 658 (1100); IR (KBr): $\tilde{\nu}$ [cm⁻¹] 994, 1015, 1129, 1173, 1202, 1310, 1323, 1356, 1399, 1436, 1456, 1483, 1498, 1543, 1601, 2934, 2983, 3146. Anal. Calcd for C₁₇H₂₁N₄O₂ (313.37): C, 65.16; H, 6.75; N, 17.88. Found: C, 64.66; H, 6.67; N, 18.09.

4,4,5,5-Tetramethyl-2-(1H-pyrazolyl)-4,5-dihydro-1H-imidazol-1-oxyls 4a-h. General procedure. A mixture of nitronyl nitroxide **3a-h** (0.005 mol), NaNO₂ (0.52 g, 0.0075 mol), and glacial acetic acid (a few drops) in chloroform (30 mL) was stirred with boiling for 30 min until the reaction mixture changed its color from dark blue to red. The mixture was filtered through a silica gel layer, the solvent was distilled off in vacuo; the residue recrystallized three times with charcoal from hexane.

4,4,5,5-Tetramethyl-2-(1-methyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4a).

Dark red crystals (0.70 g, 63%), mp 81.5–82.0 °C (hexane). UV (benzene): λ_{max} [nm] (ϵ) 310 (1900), 424 sh (470), 452 sh (650), 472 (690), 508 sh (400); IR (KBr): $\tilde{\nu}$ [cm^{-1}] 901, 935, 953, 981, 1001, 1014, 1069, 1114, 1133, 1183, 1216, 1240, 1299, 1374, 1387, 1422, 1447, 1484, 1520, 1612, 2931, 2979, 2995, 3009, 3095, 3153. Anal. Cald for $\text{C}_{11}\text{H}_{17}\text{N}_4\text{O}$ (221.28): C, 59.71; H, 7.74; N, 25.32. Found: C, 59.75; H, 7.66; N, 24.96.

4,4,5,5-Tetramethyl-2-(1-methyl-1H-pyrazol-5-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4b).

Dark red crystals (0.61 g, 55%), mp 114–115 °C (hexane). IR (KBr): $\tilde{\nu}$ [cm^{-1}] 781, 801, 877, 908, 932, 956, 1022, 1048, 1116, 1153, 1220, 1255, 1302, 1316, 1369, 1379, 1391, 1427, 1451, 1476, 1601, 2934, 2978, 2992, 3103. Anal. Cald for $\text{C}_{11}\text{H}_{17}\text{N}_4\text{O}$ (221.28): C, 59.71; H, 7.74; N, 25.32. Found: C, 59.90; H, 7.90; N, 25.54.

4,4,5,5-Tetramethyl-2-(1-methyl-1H-pyrazol-3-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4c).

Dark red crystals (0.51 g, 46%), mp 108.0–108.5 °C (hexane). UV (benzene): λ_{max} [nm] (ϵ) 313 (1950), 351 (155), 407 sh (405), 450 (640), 469 (650), 505 sh (380), 559 sh (60); IR (KBr): $\tilde{\nu}$ [cm^{-1}] 801, 877, 933, 957, 1022, 1048, 1116, 1153, 1220, 1255, 1302, 1316, 1369, 1379, 1391, 1427, 1451, 1476, 1601, 1807, 2934, 2978, 2992, 3103. Anal. Cald for $\text{C}_{11}\text{H}_{17}\text{N}_4\text{O}$ (221.28): C, 59.71; H, 7.74; N, 25.32. Found: C, 59.84; H, 7.70; N, 25.64.

4,4,5,5-Tetramethyl-2-(1,3-dimethyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4d).

Dark red crystals (0.61 g, 52%), mp 108.0–108.5 °C (hexane). UV (benzene): λ_{max} [nm] (ϵ) 320 (1950), 365 (165), 409 sh (400), 450 (640), 470 (660), 505 sh (390), 560 sh (60); IR (KBr): $\tilde{\nu}$ [cm^{-1}] 829, 859, 881, 953, 998, 1071, 1105, 1138, 1153, 1219, 1257, 1365, 1429, 1485, 1523, 1610, 2931, 2977, 3147. Anal. Cald for $\text{C}_{12}\text{H}_{19}\text{N}_4\text{O}$ (235.31): C, 61.25; H, 8.14; N, 23.81. Found: C, 61.02; H, 8.20; N, 23.73.

4,4,5,5-Tetramethyl-2-(1,5-dimethyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4e).

Dark red crystals (0.71 g, 60%), mp 71–72 °C (hexane); UV (benzene): λ_{max} [nm] (ϵ) 313 (1950), 351 (155), 407 sh (405), 450 (640), 469 (650), 505 sh (380), 559 sh (60). IR (KBr): $\tilde{\nu}$ [cm^{-1}] 831, 878, 896, 946, 1080, 1146, 1184, 1219, 1249, 1292, 1367, 1389, 1407, 1450, 1497, 1537, 1600, 1678, 2937, 2982, 3126. Anal. Cald for $\text{C}_{12}\text{H}_{19}\text{N}_4\text{O}$ (235.31): C, 61.25; H, 8.14; N, 23.81. Found: C, 61.39; H, 8.59; N, 23.31.

4,4,5,5-Tetramethyl-2-(1,3,5-trimethyl-1H-pyrazol-4-yl)-4,5-dihydro-1H-imidazol-1-oxyl (4f).

Dark red crystals (0.80 g, 64%), mp 81.0–81.5 °C (hexane). UV (benzene): λ_{max} [nm] (ϵ) 310 (1900), 350 (120), 410 sh (415), 460 (650), 470 (650), 505 sh (390), 560 sh (65); IR (KBr): $\tilde{\nu}$ [cm^{-1}] 935, 957, 995, 1041, 1106, 1151, 1179, 1224, 1259, 1309, 1367, 1389, 1434, 1450, 1503, 1541, 1616, 2929, 2979. Anal. Cald for $\text{C}_{13}\text{H}_{21}\text{N}_4\text{O}$ (249.33): C, 62.62; H, 8.49; N, 22.47. Found: C, 62.85; H, 8.50; N, 22.90.

2-(1-Benzyl-1H-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (4g).

Dark red crystals (1.04 g, 70%), mp 83–84 °C (hexane). UV (benzene): λ_{max} [nm] (ϵ) 311 (2600), 422 sh (370), 450 sh (540), 472 (600), 500 sh (330); IR (KBr): $\tilde{\nu}$ [cm^{-1}] 825, 848, 877, 955, 992, 1016, 1030, 1077, 1115, 1134, 1191, 1216, 1244, 1385, 1451, 1481, 1498, 1518, 1618, 2929, 2975, 3033, 3154. Anal. Cald for $\text{C}_{17}\text{H}_{21}\text{N}_4\text{O}$ (297.37): C, 68.66; H, 7.12; N, 18.84. Found: C,

68.40; H, 7.32; N, 18.82.

2-(1-Ethyl-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (4h). Dark red crystals (0.68 g, 58%), mp 109–110 °C (hexane). UV (benzene): λ_{\max} [nm] (ϵ) 315 (1950), 420 sh (480), 460 sh (670), 480 (700), 510 sh (390); IR (KBr): $\tilde{\nu}$ [cm⁻¹] 876, 893, 956, 989, 1015, 1079, 1105, 1131, 1179, 1213, 1251, 1321, 1373, 1389, 1446, 1462, 1482, 1518, 1613, 2935, 2972, 3096, 3152. Anal. Calcd for C₁₂H₁₉N₄O (235.31): C, 61.25; H, 8.14; N, 23.81. Found: C, 61.10; H, 8.32; N, 23.82.

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