Magnetic Interactions in Hydrogen-Bonded Networks of Hydroxymethyl-Substituted Phenyl Nitronyl Nitroxides

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The *ortho-, meta-, and para*-Hydroxymethyl-substituted 4,4,5,5-tetramethyl-3-oxyl-2-phenylimidazoline 1-oxides (**1–3**) were synthesized and characterized by X-ray crystallography. The magnetic susceptibility was determined by temperature-dependent SQUID measurements. The nitronyl nitroxides **1** and **3** display a paramagnetic susceptibility which follows the Curie–Weiss law. Weak ferromagnetic interactions can be recognized at very low temperature. The nitronyl nitroxide **2** shows temperature-dependent antiferromagnetic behavior, which can be fitted perfectly with the Heisenberg linear-chain theory with an intrachain exchange interaction of -18.43 cm^{-1}.

Introduction

Crystal engineering is a tool for generating solid-state structures by design.[1] While the goal has been defined, its accomplishment still presents a challenge in most cases. In recent years we have been interested in the generation of hydrogen-bonded networks by co-crystallization of suitable hydrogen-bond donors and acceptors. Thus, it has been demonstrated that *meso*-1,2-diphenyl-1,2-ethanediol forms a co-crystal with a 1,4-diphenyl-substituted 1,4-bisimine.[2] The analysis of the crystal structure strongly implied that substitution of the aryl groups by electronically complementary substituents — for example, a dimethylamino group in the 4-positions of the aryl groups of *meso*-1,2-diphenyl-1,2-ethanediol and an acceptor group in the 4-positions of the diaryl-substituted 1,4-bisimine — should induce charge-transfer (CT) interactions. The fulfillment of this concept produced a new type of intermolecular photochromism based on a coupled electron-proton transfer.[3] Further studies on co-crystallization, replacing the 1,4-bisimine by heterocyclic compounds with two nitrogen atoms as acceptors, provided additional examples of a light-induced electron-proton transfer.[4]

In continuation of our efforts to create new solid-state structures with novel macroscopic functions, we report here on attempts to place stable organic radicals in definite locations of a crystal lattice by constructing hydrogen-bonded networks using hydroxymethyl groups as H-donors and oxygen atoms — either from the hydroxymethyl group or from nitronyl nitroxides — as acceptors.

Studies into imposing structural features on crystals of hydroxy-substituted 2-phenyl-nitronyl nitroxides through hydrogen bonding were begun shortly after the discovery of the first example of a low temperature, purely organic ferromagnetic material: 4-nitrophenyl-nitronyl nitroxide.[5] The crystal structures of mono- and dihydroxy-substituted 2-phenyl-nitronyl nitroxides have been determined, and their magnetic susceptibilities studied as a function of temperature.[6] Materials were discovered that exhibited ferromagnetic, antiferromagnetic, or paramagnetic behavior. Recently, a statistical analysis on the crystal structures of ferromagnetic and antiferromagnetic coupled nitronyl nitroxides was carried out in order to identify characteristic structural features for a certain type of magnetism.[7] It had to be concluded, however, that the analysis did not provide structural arguments for either type of magnetism. Magnetism is a three-dimensional property, which obviously cannot be explained by structural elements of component molecules, not even by one- or two-dimensional features.[8−10] It seems that more exploratory work must be performed before an understanding is reached and the rational design of molecular magnets becomes possible.

It is in that context that this study tries to broaden further the basis for an understanding of molecular magnetism, by presenting the syntheses, X-ray structural analyses, and magnetic susceptibilities of *ortho-, meta-,* and *para*-(hydroxymethyl)phenyl-substituted nitronyl nitroxide.

Results and Discussion

The syntheses of *ortho-, meta-,* and *para*-(hydroxymethyl)-phenyl-substituted nitronyl nitroxide followed conventional procedures.[11] Condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane with *ortho-* and *meta*-phthalic dicarboxaldehydes in a 1:1 stoichiometric ratio provided the corresponding 1,3-dihydroxy-substituted imidazolidines. Reduction of the remaining formyl group by sodium borohydride and oxidation by sodium periodate yielded the

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two nitronyl nitroxides **1** and **2** in good yield. The *para*-substituted derivative was obtained after reduction of the free formyl group of terephthalic dicarboxaldehyde mono-diethylacetal with aluminum in the presence of potassium hydroxide, saponification of the acetal with phosphoric acid, condensation of the aldehyde with 2,3-bis(hydroxyl-amino)-2,3-dimethylbutane, and oxidation to nitronyl nitroxide **3** by lead dioxide.
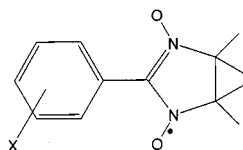
1: X = 2-hydroxymethyl
2: X = 3-hydroxymethyl
3: X = 4-hydroxymethyl

Single crystals of **1**−**3** were analyzed by X-ray crystallography.[12] The crystal packing of **1** (Figure 1) is characterized by head-to-tail dimers in which the nitronyl nitroxide units (interplanar separation 3.227 Å) and the phenyl rings are each coplanar. The planes of the nitronyl nitroxide unit and the phenyl ring are twisted by 53°. The hydroxymethyl groups on the phenyl moieties assume conformations that generate two intermolecular O−HO−N hydrogen bonds ($d_{O \cdots O}$ 2.788 Å, $d_{OH \cdots O}$ 1.757 Å, angle O−HO 173°). The O···O distances between oxygen atoms of the NO groups are 3.738 and 5.324 Å. The oxygen atoms of the four NO groups of the dimer form a parallelogram with N−O···O angles of 53 and 141°.

consequence of two different O−H···O bonds ($d_{O \cdots O}$ 2.770 and 2.830 Å, $d_{OH \cdots O}$ 2.268 and 2.447 Å, OH···O angles of 120 and 110°). The interplanar angle between the nitronyl nitroxide unit and the phenyl group is 23°, smaller than in **1**. Every second molecule in the string is positioned identically. The nitronyl nitroxide rings of neighboring molecules are almost orthogonal to each other (interplanar angle between the nitronyl nitroxide subunits 84°). The distances between an oxygen atom of an NO group of one radical to the oxygen atoms of the NO groups of a neighboring molecule are either 5.587 and 6.463 Å or 8.334 and 8.557 Å, depending on the NO group selected. Figure 3 shows the arrangement of three nitronyl nitroxide radicals, where the *m*-hydroxymethylphenyl group and the four methyl groups have been omitted for clarity. The arrangement of the hydroxymethyl substituents enforces a three dimensional, helical structure in individual strings.

The *para*-position of the hydroxymethyl group in **3** produces layers of nitronyl nitroxide molecules (Figure 4) in which zigzag infinite chains are bonded by two different O−HO−N bridges, due to disordering ($d_{O \cdots O}$ 2.755 or 2.781 Å, $d_{OH \cdots H}$ 1.879 Å, angle O−HO 166 or 129°). The nitronyl nitroxide radicals form the same chains in the layer below or above. However, these chains are rotated by 90° relative to the arrangement in the first layer. This leads to a pattern in which phenyl and nitronyl nitroxide groups lie above each other in different layers. In individual molecules, the phenyl and nitronyl nitroxide subunits show a twist angle of 32°. The closest O···O distances between NO group oxygen atoms are 4.627 and 4.958 Å (different layers), or
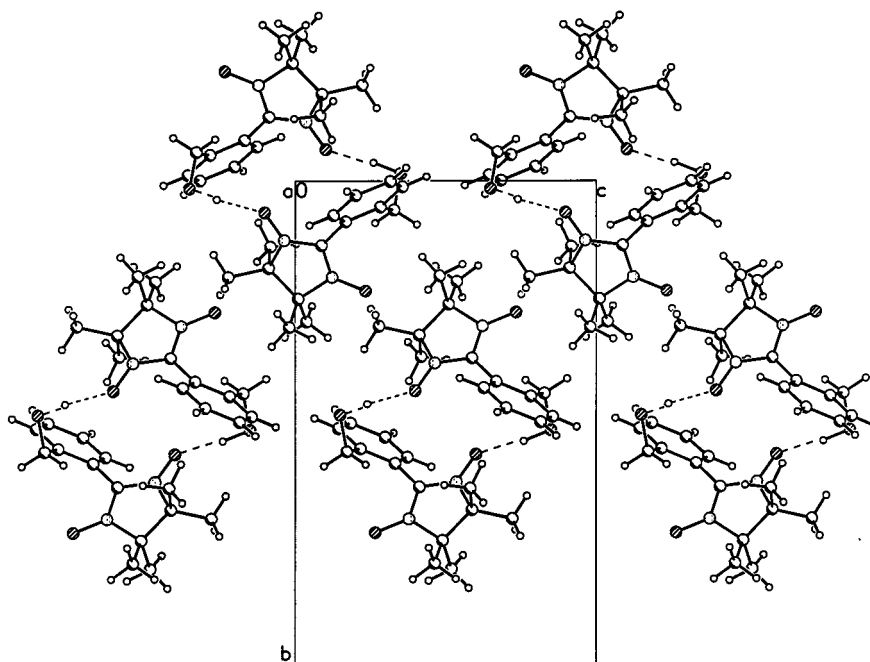

Figure 1. Crystal packing of 2-[*o*-(hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**1**)

The *meta* position of the hydroxymethyl group in **2** produces a crystal packing in which infinite strings of nitronyl nitroxide radicals are held together by OH···O bonds (Figure 2). The hydroxymethyl groups are disordered, with the

5.637 and 6.610 Å (same layer). The phenyl group in one layer is tilted relative to the nitronyl nitroxide unit in a second layer. Figure 5 displays the relative orientation and distances between nearest neighbors in two planes.
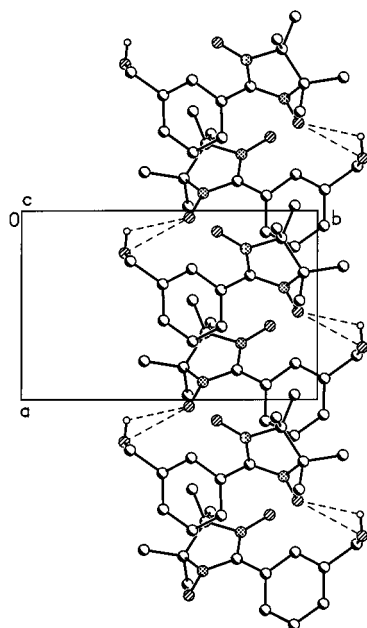
Figure 2. Crystal packing of 2-[*m*-(hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**2**)
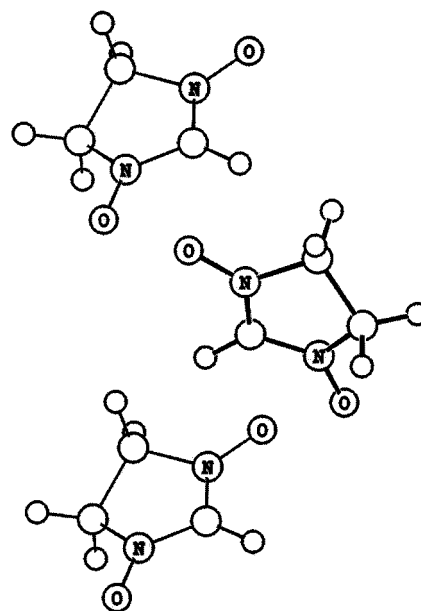

Figure 3. Arrangement of three molecules of **2** in the crystal lattice (simplified to the unsubstituted nitroxyl nitroxide rings)
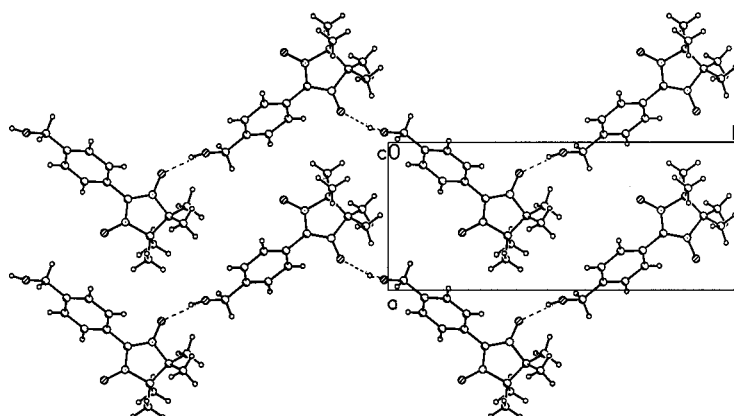

Figure 4. Crystal packing of 2-[*p*-(hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**3**)

It is expected that the relative positions of the radical units in crystals **1**−**3** will result in different magnetic properties. SQUID measurements were performed in the temperature range of 2 K to room temperature. Figure 6 displays a diagram of $\chi_{mol}T$ vs. the absolute temperature. Radicals **1** and **3** show paramagnetic behavior even at low temperature following the Curie−Weiss law ideally, with Curie and Weiss constants as given in Table 1. Only very weak intermolecular interactions are present. Close to the lowest experimentally accessible temperature, a slight increase in $\chi_{mol}T$ is observed, indicating ferromagnetic interactions of the radicals. The absolute value of $\chi_{mol}T$ for **1** is slightly lower than expected. This is an artifact due to slight impurities, and cannot be removed by recrystallization because the radical decomposes slowly during the recrystallization process. In contrast, radical **2** is characterized by an intermolecular antiferromagnetic coupling below 100 K. The data could be fitted using the Heisenberg linear-chain the-

ory.[13] An intrachain interaction of -18.43 cm^{-1} was obtained; intermolecular interactions, however, cannot be deduced from the experimental data.

What are the structure-determining features? In all of the crystal structures, the most important interaction is the CH$_2$O−H···O−N hydrogen bond. Molecular packing in the crystal has to take into account that the hydroxy group is attached to a tetrahedral carbon atom, which in turn is bonded to the phenyl ring. Free rotation about the latter bond allows fairly freely adjustable positioning of the OH group above or below the plane of the phenyl ring. Conformational flexibility also derives from rotation about the bond linking phenyl and nitronyl nitroxide. The two rings are in no case coplanar, adopting angles of 53° in **1**, 29° in **2**, and 32° in **3**. Radicals **1**−**3** differ in the attachment of the hydroxymethyl group at the phenyl group. *ortho*-Substitution places the nitronyl nitroxide oxygen in such a way relat-
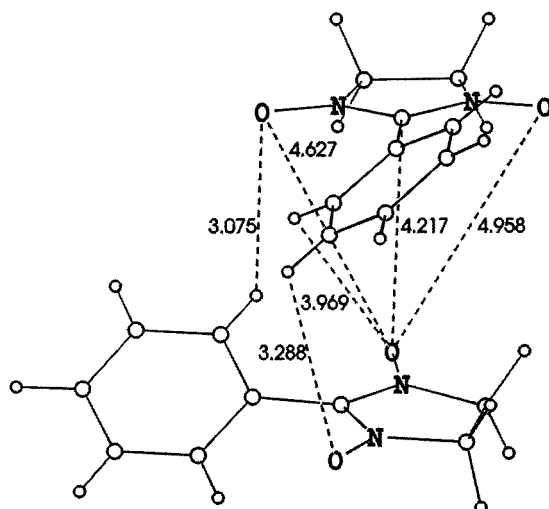
Figure 5. Relative orientation and important distances for nearest neighbors of **3** in two layers (hydroxymethyl group in *p*-position removed)
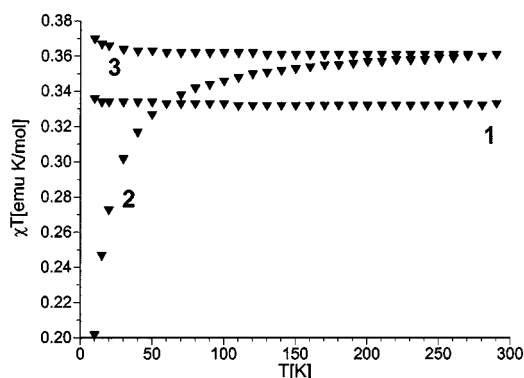

Figure 6. Temperature-dependent magnetic susceptibility of nitronyl nitroxides **1−3**

Table 1. Curie (C) and Weiss (Θ) constants for radicals **1−3** as obtained from temperature-dependent SQUID measurements

	1	**2**	**3**
C (emu K mol^{-1})	0.332 (0.376)[a]	0.368	0.361
Θ (K)	0.10 (0.12)[a]	−6.4	0.21

[a] Corrected to $g = 2.0$ for diamagnetic impurities.

ive to the hydroxy group that dimer formation is favored. The crystal packing of the dimers seems to be governed by van der Waals interactions and weak C−H (CH$_3$)···O (O−N) hydrogen bonds. If the hydroxymethyl group is linked in the *meta*-position, dimer formation is no longer possible for spatial reasons. The twist angle of 29° between the phenyl and nitronyl nitroxide units leads to an infinite string structure. In the case of the *para*-hydroxymethyl group, the molecular constraints produce a linear structure. The angle of ca. 90° between two molecules in the chain derives from the almost orthogonal position of the hydroxymethyl unit relative to the oxygen atom of the nitronyl nitroxide to which the hydrogen bond is formed.

How does the molecular packing influence the magnetic properties? The three molecules can be separated into two classes. Compounds **1** and **3** display paramagnetic behavior even at very low temperatures. In radical **2**, in contrast, antiferromagnetic interactions dominate at low temperature. It does not seem to be easy to relate the observed magnetic susceptibility to the crystal structure features. Systematic differences in the NO···NO distances, which might be indicative of different intermolecular spin-spin interactions, cannot be identified. It can only be guessed that the special behavior of **2** is related to the helical strings of nitronyl nitroxide radicals, leading to strong intrachain exchange interactions. Similar chains exist neither for **1** nor for **3**. In the latter case, the nitronyl nitroxide units which come closest stem from molecules in different layers of the crystal

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra: Varian Gemini-200 and Bruker AMX-300. Internal standard TMS. − High resolution MS: Fisons Instruments VG Pro Spec 300 (70 eV). − ESR Bruker ER-420 X-band spectrometer (9.4 GHz) equipped with a double cavity and a variable temperature unit. − ESR data acquisition: Pentium PC equipped with a Microstar DAP 1200/4 data acquisition board and DigiS (GfS Aachen, Germany) software. − Quantum Design MPMS SQUID magnetometer. − Melting points (uncorrected) Büchi 510.

Materials: Most starting materials were commercially available. 2,3-Bis(hydroxylamino)-2,3-dimethylbutane was prepared according to a published procedure.[14]

2-[*o*-(Hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-Oxide (1). − Step a) Preparation of 2-(*o*-Formylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine: A mixture of *o*-phthalic dicarboxaldehyde (2.50 g, 18.6 mmol) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2.80 g, 19.0 mmol) in 250 mL of methanol was stirred for 24 h at room temperature. The precipitate was filtered and washed thoroughly with water. Yield 3.45 g (13.1 mmol, 70%). The material is a mixture of two isomers, formed by addition of a 1,3-dihydroxyimidazolidine *N*-hydroxy group to the free aldehyde function, forming a half-acetal. − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.10−1.28 (12 H, 4 × CH$_3$), 4.79 and 4.88 [2 s, 1 H, H-2 (imidazolidine)], 5.77 (d, ^3J = 7.8 Hz, 1 H, half-acetal CH), 6.71 (d, ^3J = 7.8 Hz, 1 H, half-acetal OH), 7.24−7.52 (m, 4 H, aromatic-H). − C$_{14}$H$_{20}$N$_2$O$_3$ (264.3): calcd. C 63.62, H 7.63, N 10.60; found C 63.65, H 7.74, N 10.75.

Step b) Preparation of 1: A suspension of 2-(*o*-formyl)phenyl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (1.80 g, 6.80 mmol) and sodium borohydride (1.70 g, 44.9 mmol, in 20 mL water) in 400 mL of 2-propanol was stirred for 24 h, then neutralized with acetic acid, and filtered. Isopropanol was removed in vacuo and the residue dissolved in 350 mL of chloroform. At $T < 3$ °C, the solution was treated twice with a solution of sodium periodate (1.5 g, 7.0 mmol) in 30 mL water for 5 min in a separation funnel. After washing with water and drying over magnesium sulfate, the solvent was removed in vacuo. The residue was extracted with diethyl ether. After partially removing diethyl ether 0.58 g (2.20 mmol, 33%) of the product was isolated. Single crystals were obtained from diethyl ether. M.p. 92−93°. − ESR (CHCl$_3$): quintet 1:2:3:2:1, a_N = 0.75 mT. − C$_{14}$H$_{19}$N$_2$O$_3$ (263.3): calcd. C 63.86, H 7.27, N 10.64; found

C 63.02, H 7.17, N 10.58. − HR-MS (70 eV) $C_{14}H_{19}N_2O_3$: calcd. 263.1396; found 263.1394.

2-[*m*-(Hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-Oxide (2). − Step a) Preparation of 2-(*m*-Formyl)phenyl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine: Water (100 mL) was added to a solution of *m*-phthalic dicarboxaldehyde (2.68 g, 20.0 mmol) in 50 mL of methanol. A solution of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (2.96 g, 20.0 mmol) in 50 mL of water was added dropwise. After 12 h, the precipitate was isolated, washed with water, and dried in vacuo. In order to remove biscondensation product, the product was treated with hot ethyl acetate and filtered after cooling to room temperature. A product (2.94 g, 11.0 mmol, 56%) with m.p. 156° was isolated. − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.05 and 1.08 (2 s, 12 H, 4 × CH$_3$), 4.59 [s, 1 H, H-2 (imidazolidine)], 7.36−8.02 (m, 4 H, aromatic H), 7.86 (s, 2 H, N−OH), 10.02 (s, 1 H, CH=O). − ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 17.43 and 24.58 (4 × CH$_3$), 66.48 [C-4, C-5 (imidazolidine), 89.91 [C-2 (imidazolidine)], 128.74, 129.19, 129.26, 135.02, 136.12, 143.42 (aromatic C), 193.50 (CH=O). − $C_{14}H_{20}N_2O_3$ (264.3): calcd. C 63.62, H 7.63, N 10.60; found C 62.90, H 7.63, N 10.60.

Step b) Conversion into *m*-(1,3-Dihydroxy-4,4,5,5-tetramethylimidazolidine-2-yl)benzyl Alcohol: A solution of sodium borohydride (1.00 g, 26.4 mmol) in 20 mL of water was added slowly to a solution of the aldehyde (2.90 g, 11.0 mmol) in 250 mL of 2-propanol. After 12 h, the solution was neutralized with acetic acid, filtered, and the solvent evaporated in vacuo to dryness. The alcohol (2.14 g, 8.00 mmol, 73%) was isolated and recrystallized from water. M.p. 174−176 °C. − ^{1}H NMR (500 MHz, CD$_3$OD): δ = 1.12 and 1.16 (s, 12 H, 4 × CH$_3$), 4.60 (s, 2 H, CH$_2$), 4.68 (s, 1 H, H-2), 4.87 (s, 3 H, N−OH, OH), 7.26−7.55 (m, 4 H, aromatic H). − ^{13}C NMR (125 MHz, CD$_3$OD): δ = 17.76 and 24.95 (4 × CH$_3$), 65.44 (CH$_2$), 68.00 (C-4, C-5), 91.64 (C-2), 127.39, 128.31, 128.70, 128.96, 142.18, 142.82 (aromatic C). − $C_{14}H_{22}N_2O_3$ (266.3): calcd. C 63.13, H 8.33, N 10.52; found C 62.98, H 8.37, N 10.53.

Step c) Conversion to 2: Sodium periodate (1.00 g, 4.70 mmol) in 20 mL of water was added at less than 5 °C to a solution of the benzyl alcohol (1.05 g, 3.90 mmol) in 220 mL of chloroform/methanol (10:1). The solution was vigorously shaken for 5 min, then the organic layer was separated, washed with water three times, and dried over magnesium sulfate. After removal of the solvent in vacuo, the residue was recrystallized from diethyl ether (0.64 g, 2.40 mmol, 62%) as dark blue crystals, m.p. 105 °C. − $C_{14}H_{19}N_2O_3$ (263.3): calcd. C 63.86, H 7.27, N 10.64; found C 63.58, H 7.17, N 10.37. − ESR (CHCl$_3$): quintet 1:2:3:2:1, a_N = 0.75 mT.

2-[*p*-(Hydroxymethyl)phenyl]-4,4,5,5-tetramethyl-3-oxylimidazoline 1-Oxide (3). − Step a) Preparation of *p*-(Hydroxymethyl)benzaldehyde:[15] In a 500 mL three-necked round-bottomed flask with reflux condenser, argon gas inlet and stopper were placed finely powdered potassium hydroxide (16.8 g, 0.30 mol) and terephthalic dicarboxaldehyde (20.8 g, 0.10 mol) in 40 mL dry ethanol. At 5−10 °C, aluminum powder (8.10 g, 0.30 mol) was added slowly. The mixture was stirred overnight at room temperature. After addition of 40 mL of ethanol, the solution was filtered and then 600 mL of water were added. Phosphoric acid was added until pH 1 was reached, the solution was stirred overnight at room temperature and then neutralized with sodium hydroxide. After extraction with dichloromethane and evaporation of the solvent, *p*-(hydroxymethyl)benzaldehyde (9.24 g, 70.0 mmol, 68%) was isolated as a white solid, which was recrystallized from petroleum ether to yield colorless needles of m.p. 42 °C. − ^{1}H NMR (200 MHz, CDCl$_3$): δ =

2.47 (br. 1 H, OH), 4.75 (s, 2 H, CH$_2$), 7.48 and 7.82 (d, 4 H, ^3J = 8.2 Hz, aromatic H), 9.94 (s, 1 H, CHO). − ^{13}C NMR (50 MHz, CDCl$_3$): δ = 64.41 (CH$_2$), 126.93 (C-3), 129.98 (C-2), 135.56 (C-1), 147.94 (C-4), 192.16 (CHO).

Step b). Conversion to 3: 2,3-Bis(hydroxylamino)-2,3-dimethylbutane (1.20 g, 8.10 mmol) was added to *p*-(hydroxymethyl)benzaldehyde (1.50 g,11.0 mmol) in 70 mL of water. After 24 h at room temperature, the mixture was extracted with ethyl acetate, the organic layer was dried over sodium sulfate, and the solvent was evaporated. The remaining solid was dissolved in 200 mL of water and treated with lead(IV) oxide (10.0 g, 41.8 mmol) for 2 h. After filtration, the dark blue solution was extracted with trichloromethane. After drying with magnesium sulfate, the solvent was removed in vacuo yielding 1.97 g (7.50 mmol, 93%) of the nitronyl nitroxide which was recrystallized from diethyl ether (m.p. 137 °C). − $C_{14}H_{19}N_2O_3$ (263.3): calcd. C 63.86, H 7.27, N 10.64; found C 63.67, H 7.34, N 10.84. − ESR (CHCl$_3$): quintet 1:2:3:2:1, a_N = 0.75 mT.

X-ray Crystallographic Data
Crystal Structure of 1: $C_{14}H_{19}N_2O_3$, crystal size 0.43 × 0.39 × 0.26 mm, red, monoclinic space group $P2_1/n$, Z = 4, a = 7.7292(12), b = 17.057(3), c = 10.6318(14) Å, β = 92.002(6)°, V = 1400.8(4) Å^3, Mo-$K_α$ radiation, P4-Siemens diffractometer, ρ = 1.249 gcm^{-3}, Θ_{max} = 25°, intensities measured 2604, independent 2415 (R_{int} = 0.0382), of which 1710 with [$I > 2\sigma(I)$], Siemens SHELXTL 5.03 program suite, refinement on F^2, riding model for hydrogen atoms with the 1.2-fold (1.5-fold for methyl groups) isotropic U of the corresponding C-atom, 173 parameters, $R1$ = 0.0716, $wR2$ (all data) = 0.2320, Gof = 1.054, residual electron density +0.721/−0.248 eÅ^{-3}.

Crystal Structure of 2: $C_{14}H_{19}N_2O_3$, crystal size 0.38 × 0.34 × 0.17 mm, dark blue, orthorhombic space group $P2_12_12_1$, Z = 4, a = 7.0311(4), b = 10.9230(7), c = 18.0616(11) Å, V = 1387.1(2) Å^3, Mo-$K_α$ radiation, Siemens SMART-1000 CCD diffractometer, ρ = 1.261 gcm^{-3}, Θ_{max} = 28.28°, intensities measured 11329, independent 2838 (R_{int} = 0.0448), of which 2185 with $I > 2\sigma(I)$, Siemens SHELXTL 5.03 program suite, refinement on F^2, riding model for hydrogen atoms with the 1.2-fold (1.5-fold for methyl groups) isotropic U of the corresponding C-atom, 181 parameters, max/min transmission 1.00/0.70, $R1$ = 0.0554, $wR2$ (all data) = 0.1420, Gof = 1.069, absolute structure not reliably determined, residual electron density +0.300/−0.134 eÅ^{-3}.

Crystal Structure of 3: $C_{14}H_{19}N_2O_3$, crystal size 0.26 × 0.23 × 0.14 mm, colorless, monoclinic space group $P2_1/c$, Z = 4, a = 8.1860(5), b = 18.9486(11), c = 9.3799(5) Å, V = 1376.28(14) Å^3, Mo-$K_α$ radiation, Siemens SMART-1000 CCD diffractometer, ρ = 1.271 gcm^{-3}, Θ_{max} = 22.5°, intensities measured 5780, independent 1641 (R_{int} = 0.0347), of which 1261 with $I > 2\sigma(I)$, Siemens SHELXTL 5.03 program suite, refinement on F^2, riding model for hydrogen atoms with the 1.2-fold (1.5-fold for methyl groups) isotropic U of the corresponding C-atom, 185 parameters, max/min transmission 1.00/0.81, $R1$ = 0.0611, $wR2$ (all data) = 0.1775, Gof = 1.057, residual electron density +0.292/−0.152 eÅ^{-3}, O(3) and the attached hydroxy atoms disordered and given occupation factors of 1/3 and 2/3, respectively.

[1] [1a] G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, **1989**. − [1b] G. R. Desiraju, *Angew. Chem.* **1995**, *107*, 2541−2558; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328.

[2] A. Reyes-Arellano, R. Boese, I. Steller, R. Sustmann, *Struct. Chem.* **1995**, *6*, 391−396.

[3] [3a] M. Felderhoff, I. Steller, A. Reyes-Arellano, R. Boese, R. Sustmann, *Adv. Mater.* **1996**, *8*, 402−405. − [3b] M. Felderhoff, T. Smolka, R. Sustmann, I. Steller, H.-C. Weiss, R. Boese, *J. Prakt. Chem.* **1999**, *341*, 639−648.

[4] T. Smolka, R. Sustmann, R. Boese, *J. Prakt. Chem.* **1999**, *341*, 378−383.

[5] [5a] K. Awaga, T. Inabe, U. Nagashima, Y. Maruyama, *J. Chem. Soc., Chem. Commun.* **1989**, 1617−1618. − [5b] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, M. Kinoshita, *Chem. Phys. Lett.* **1991**, *186*, 401−404.

[6] [6a] E. Hernandez, M. Mas, E. Molins, C. Rovira, J. Veciana, *Angew. Chem.* **1993**, *105*, 919−921; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 882. − [6b] J. Cirujeda, L. E. Ochando, J. M. Amigo, C. Rovira, J. Rius, J. Veciana, *Angew. Chem.* **1995**, *107*, 99−102; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 55. − [6c] J. Cirujeda, M. Mas, E. Molins, F. Lafranc de Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, J. Veciana, *J. Chem. Soc., Chem. Commun.* **1995**, 709−710. − [6d] T. Suga-wara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, M. Ishikawa, *J. Chem. Soc., Chem. Commun.* **1994**, 1723−1724. − [6e] M. M. Matsumoto, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, *J. Am. Chem. Soc.* **1997**, *119*, 4369−4379.

[7] M. Deumal, J. Cirujeda, J. Veciana, J. J. Novoa, *Chem. Eur. J.* **1999**, *5*, 1631−1641.

[8] M. Kinoshita, *Jpn. J. Appl. Phys.* **1994**, *33*, 5718−5733.

[9] V. I. Ovcharenko, R. Z. Sagdeev, *Russ. Chem. Rev.* **1999**, *68*, 345−363.

[10] B. Pilawa, *Ann. Phys. (Leipzig)* **1999**, *8*, 191−254.

[11] E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, R. Darcey, *J. Am. Chem. Soc.* **1972**, *94*, 7049−7059.

[12] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-141623 (**1**), CCDC-141624 (**2**), and CCDC-141624 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CD2 IEZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[13] M. E. Fisher, *Am. J. Phys.* **1964**, *32*, 343−346.

[14] M. Lamchen, T. W. Mittag, *J. Chem. Soc. (C)* **1966**, 2300−2303.

[15] J. W. Baker, J. A. L. Brieux, D. G. Saunders, *J. Chem. Soc.* **1956**, 404−411.