DOI: 10.1002/ejoc.200600109

Synthesis of Alkynyl-Substituted Nitronyl Nitroxides through an Organosilicon Derivative

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Keywords: Alkynes / Diazo compounds / Cycloaddition / Nitrogen heterocycles / Radicals

4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol has been synthesized and oxidized to the corresponding nitronyl nitroxide (**1**). Further removal of the trimethylsilyl group gave the 2-ethynyl-substituted nitronyl nitroxide **2**. Both **1** and **2** are labile compounds. With certain precautions, however, they may be purified from admixtures and be obtained as single crystals, thanks to which X-ray diffraction study confirmed that molecules **1** and **2** each contain a triple bond. The accessibility of these spin-labeled acetylenes makes it possible to synthesize other derivatives of nitroxides, as was demonstrated in the case of 1,3-dipolar cycloaddition of CH_2N_2 to **1** and **2**, which gave the corresponding pyrazolyl-substituted nitronyl nitroxides. These were synthesized in a one-pot synthesis strategy, since the solutions of spin-labeled alkynes **1** and **2** formed in the course of synthesis are stable for a long time. The reaction between CH_2N_2 and **1**, containing the $(CH_3)_3Si$ substituent, was much more sluggish and mainly gave the 4-pyrazolyl-substituted nitronyl nitroxide, isolated as an individual compound and also identified by X-ray crystallography. In the same reaction with **2**, the product was the 3-pyrazolyl-substituted nitronyl nitroxide.

Introduction

Nitronyl nitroxides (NNs) and imino nitroxides (INs) attract intense interest as paramagnetic organic components for the design of molecule-based magnets,[1] because they offer the potential to vary the spatial and electronic structures of the compounds and thus selectively to change the magnitude and sign of exchange coupling energy inside heterospin exchange clusters.[2] This has stimulated the development of effective methods for the synthesis of nitroxides, resulting in a wide range of polyfunctional derivatives. Thus, although the spin-labeled nitrile NN–C≡N had long been a well defined compound,[3] only an effective production procedure[4] permitted the synthesis of a wide range of polyfunctional derivatives of nitroxides (Scheme 1), forming various molecular magnets by interaction with metal-containing matrices.[4,5]

This paper reports the syntheses and structures of 4,4,5,5-tetramethyl-2-[2-(trimethylsilyl)ethynyl]-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl (**1**) and 2-ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxide 1-oxyl (**2**) (Scheme 2), which can serve as substrates for the preparation of a family of new polyfunctional NNs and INs, including previously unavailable compounds.

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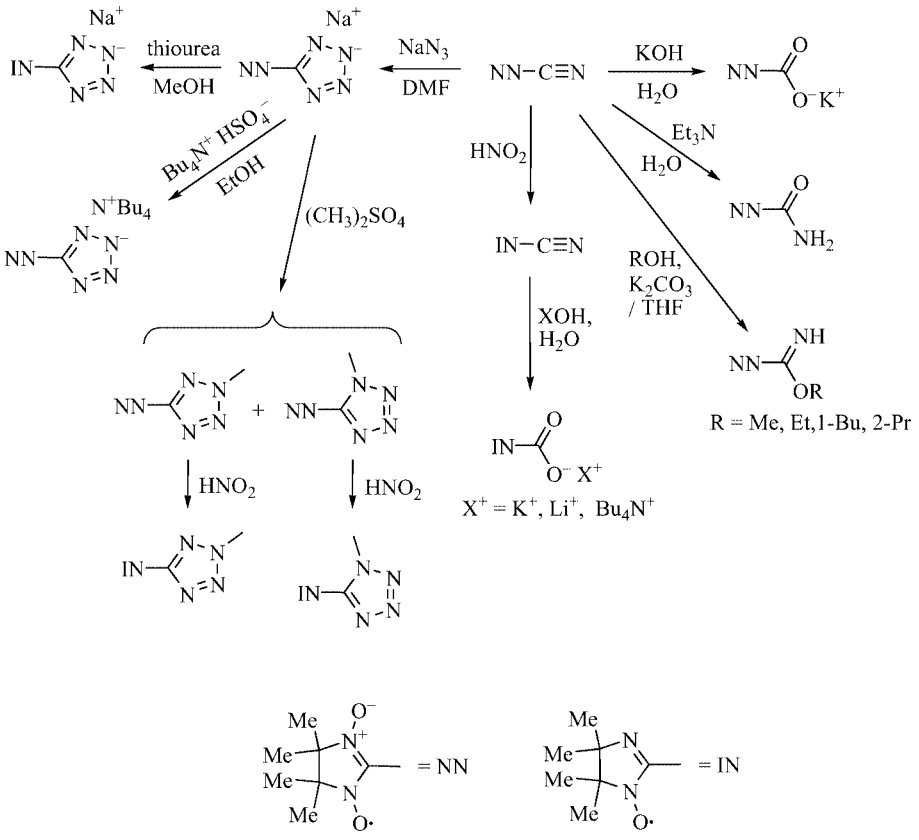
Results and Discussion

Attempts to obtain alkyne-substituted nitronyl nitroxides had been made previously: Ph–C≡C–NN, for example, was synthesized by dehydrobromination of Ph–CHBr–CHBr–NN.[6] The same compound (Ph–C≡C–NN) could not be synthesized by the classical Ullman procedure, because treatment of (4-R–C_6H_4)–C≡C–CHO with **3** formed 2-(1-hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)-1-arylethanones (**B**) (Scheme 3).[7]

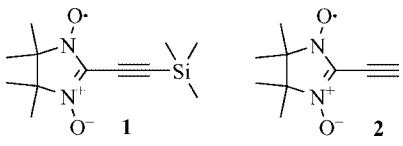
One can admit that there are several mechanisms leading to imidazolidin-2-ylidene **B**, one variant of which is presented in Scheme 3 (**A**). Any mechanism, however, should include a nucleophilic attack on the triple bond. In an effort to reduce the electrophilicity of the triple bond, we synthesized oct-2-ynal (**4**) and allowed it to react with **3**, but the product was once again the corresponding enamino ketone **5** (Scheme 4), obtained as perfect single crystals, on which we performed a molecular and crystal structure determination.

The N–O distance in molecule **5** is 1.406(5) Å, which is typical for hydroxyamines. The >NH group of the imidazoline ring forms an intramolecular H-bond with the O atom of the keto group [N–H 1.07(6) Å; H···O 2.06(5) Å; N···O 2.711(6) Å; ∠NHO 117(4)°]. The O(1)···O(2′) hydrogen bonds [2.603(5) Å] link molecules **5** into chains extending in the [001] direction; the chains are associated through N(2)···O(1′′) [3.106(6) Å] bonds into sheets parallel to the (011) plane (Figure 1).

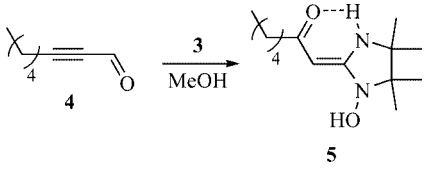
Seeking to reduce the electrophilicity of the triple bond further, while simultaneously making it less sterically ac-



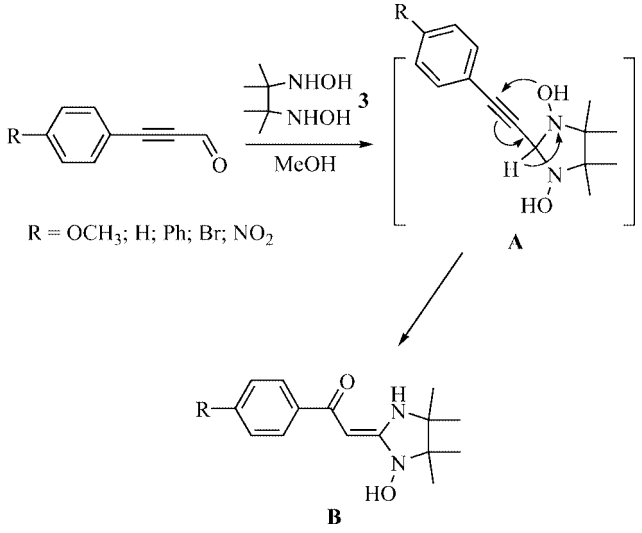
Scheme 1. Nitroxides derived from NN–C≡N.



Scheme 2.



Scheme 4.



Scheme 3.

cessible, we introduced a $(CH_3)_3Si$ group into propynal. Treatment of 3-(trimethylsilyl)propynal (**6**) with **3** was conducted under the same conditions as the reaction leading to compound **5**. The IR spectrum of product **7**, unlike that of **5**, showed a ν(C≡C) band, which was evidence in favor of the formation of a 2-alkynyl-1,3-dihydroxyimidazolidine (Scheme 5).

An X-ray diffraction study of **7** confirmed the molecular structure of the compound (Figure 2, a). In the solid compound, the molecules are linked by paired H-bonds [O–H···N 2.903(7) and 2.814(8) Å] into zigzag chains (Figure 2, b). Selected bond lengths for **7** are given in Table 1.

It is most important that use of **7** as a starting compound should yield the desired nitronyl nitroxide $Me_3Si–C≡C–NN$ (**1**) (Scheme 5). When **7** was oxidized with $NaIO_4$ in a $CHCl_3/H_2O$ (or CH_2Cl_2/H_2O) binary system, the organic phase quickly acquired a deep dark blue color due to the formation of nitronyl nitroxide **1**.[8] After the organic layer

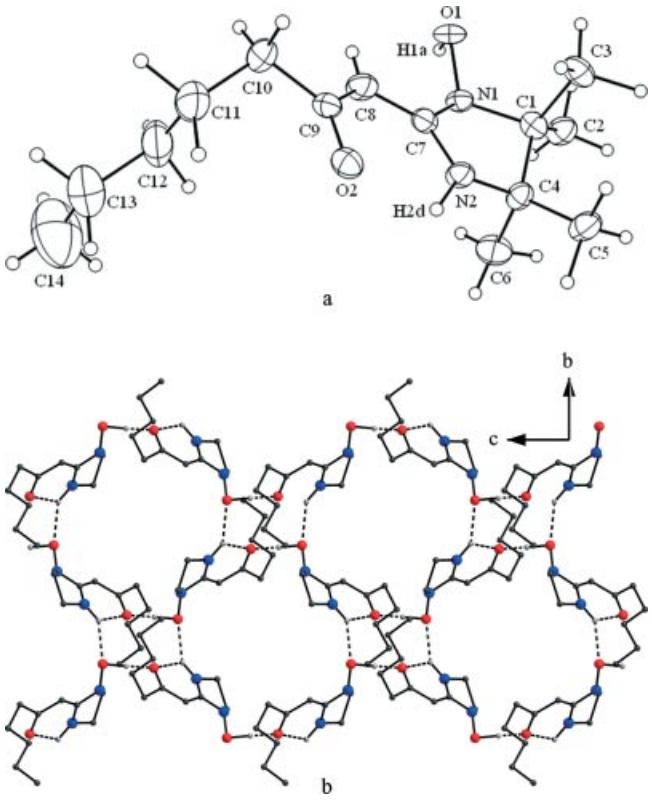
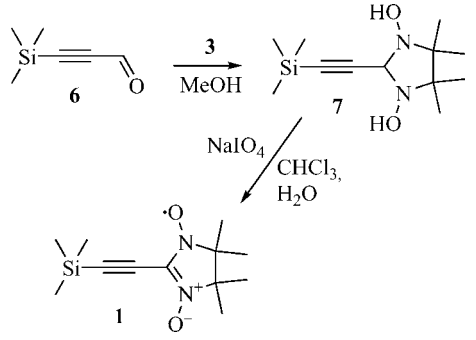


Figure 1. Molecule (a) and crystal packing (b) in **5**. Selected bond lengths [Å]: N–O 1.406(5), C(7)–N(1) 1.384(6), C(7)–N(2) 1.308(6), C(7)–C(8) 1.393(8), C(8)–C(9) 1.368(7), C=O 1.276(6).



Scheme 5.

had been separated and dried, compound **1** was stable (one spot on a TL chromatogram) in solution for a few days under normal conditions. However, addition of heptane and subsequent concentration of the solution resulted in compound **1** being isolated with a small amount of impurity products (impurity spots on a TL chromatogram). Because of this, slightly inconsistent element analysis data and an underestimated effective magnetic moment (ca. 1.4 B.M.) were obtained for **1**. The coating of impurities detected under a microscope on the thin, greenish-blue needles of compound **1** did not, however, hinder the X-ray diffraction study of the product (Figure 3, Table 1), which confirmed the results of structure determination. Note that

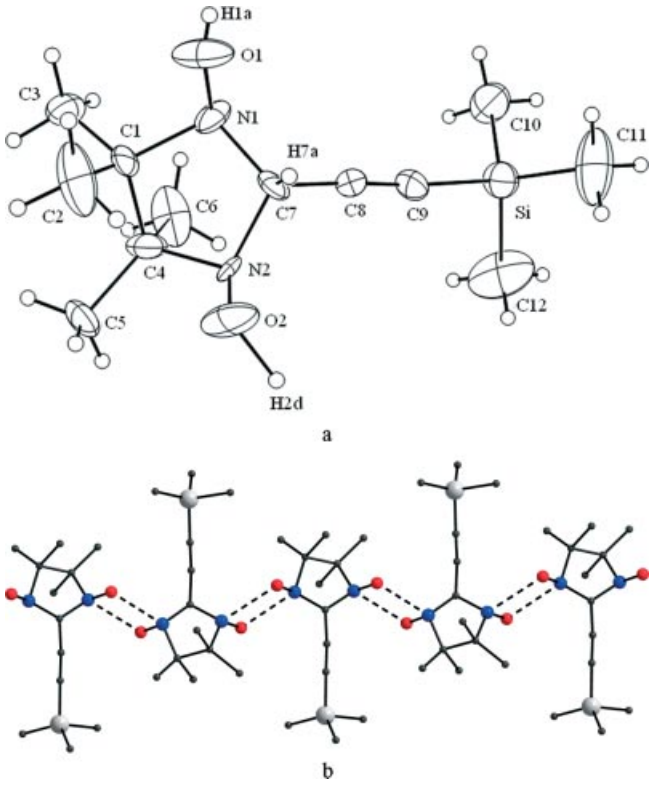


Figure 2. Molecule **7** (a) and chain motif (b).

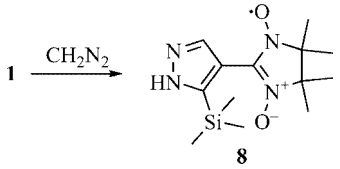
Table 1. Selected bond lengths *d* [Å] in molecules **1**, **2**, **7**, **8**.

d	**1**			**2**	**7**	**8**
	A[a]	**B**	**C**			
N(1)–O(1)	1.282(5)	1.258(5)	1.283(5)	1.259(2)	1.402(7)	1.287(2)
N(2)–O(2)	1.279(5)	1.286(5)	1.281(6)	1.274(2)	1.439(7)	1.270(2)
N(1)–C(7)	1.340(6)	1.355(6)	1.343(6)	1.353(3)	1.484(8)	1.340(3)
N(2)–C(7)	1.352(6)	1.332(6)	1.340(6)	1.319(2)	1.461(7)	1.342(3)
C(7)–C(8)	1.427(7)	1.408(7)	1.406(8)	1.420(3)	1.454(6)	1.432(3)
C(8)–C(9)	1.199(7)	1.203(7)	1.203(7)	1.106(3)	1.216(6)	1.399(3)
C(9)–Si	1.860(6)	1.860(6)	1.841(6)		1.834(5)	1.841(3)
Si–C	1.823(8)	1.836(8)	1.615(14)		1.832(9)	1.845(4)
	1.828(7)	1.841(6)	1.617(17)		1.825(8)	1.862(4)
	1.862(7)	1.840(8)	1.790(12)		1.862(9)	1.888(2)

[a] Crystallographically independent molecules.

this was the first structure determination of an alk-1-ynyl derivative in the family of nitronyl nitroxides.

Because of its stability in solution over prolonged periods of time, compound **1** could be subjected to further transformations. Treatment of **1** with CH_2N_2 for 96 h thus resulted in the formation of spin-labeled pyrazole **8** (48%) (Scheme 6), also grown as perfect single crystals, on which a structure determination was performed (part a of Figure 4, Table 1).



Scheme 6.

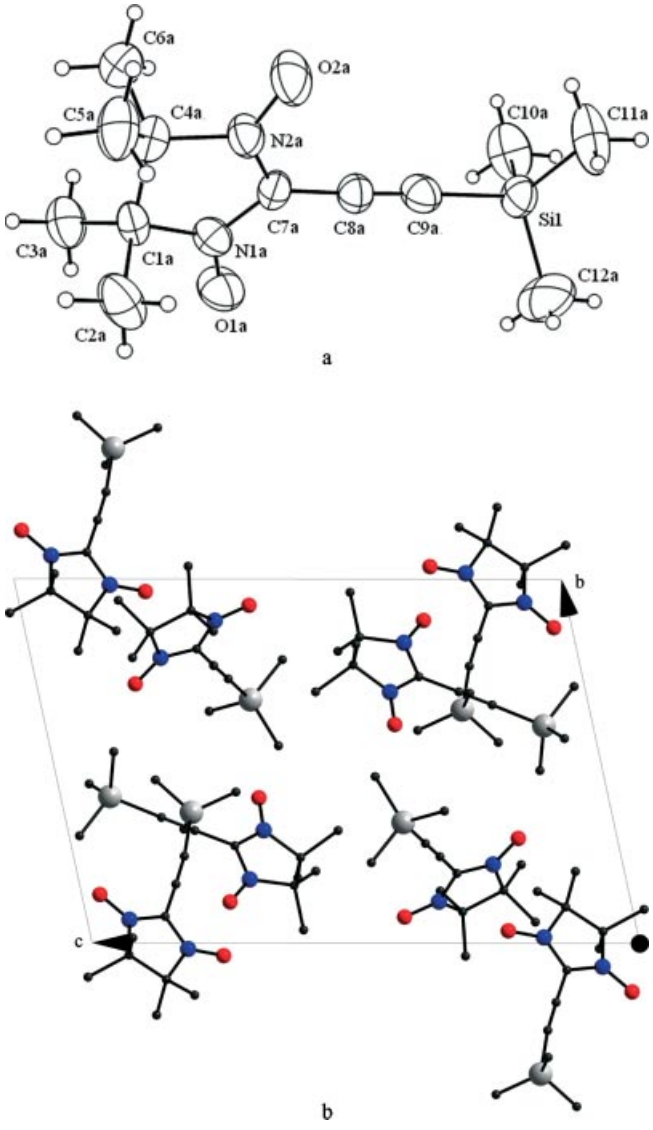


Figure 3. Molecule (a) and crystal packing in **1** (b).

In solid compound **8**, one of the NO groups forms an H-bond with the NH fragment of the pyrazole ring of the adjacent molecule [N–H 0.85(3), H···O 2.03(3), N···O 2.833(3) Å], resulting in the formation of chains (Figure 4, b).

The successful synthesis of **1** stimulated our interest in the synthesis of nitronyl-nitroxyl-containing acetylene HC≡C–NN (**2**). An attempted synthesis of **2** described in the literature was based on treatment of HC≡C–CHO with **3**.[9] Firstly, as mentioned above, dehydrocondensation may be accompanied by a rearrangement, forming a compound of structural type **B** along with the compound of type **A** (Scheme 3). Secondly, oxidation of the product obtained from treatment of HC≡C–CHO with **3** resulted in a deep red color of the solution, which was a very unusual result.[9] This prompted us to reproduce the reported synthesis[9] of "2-ethynyl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine". X-ray diffraction analysis of the resulting pale yellow crystals indicated that the actual product formed in the reaction between HC≡C–CHO and **3** was the imidazo[1,2-*b*]-isoxazole-1,6-diol **9** (yield 20%, Scheme 7). In molecule **9**, both heterocycles are shaped like envelopes, with the C(1) atom deviating by –0.73 Å and C(9) by –0.47 Å from the planes through the C(4)N(2)C(7)N(1) and O(2)N(2)C(7)-C(8) atoms, respectively (Figure 5). The angle between the planes is 60.2(1)°. In the structure, the molecules are linked by H-bonds similar to those found for **7** [O···N 2.853(2) Å]; the resulting dimers are associated into layers [O···N 2.837(2) Å].

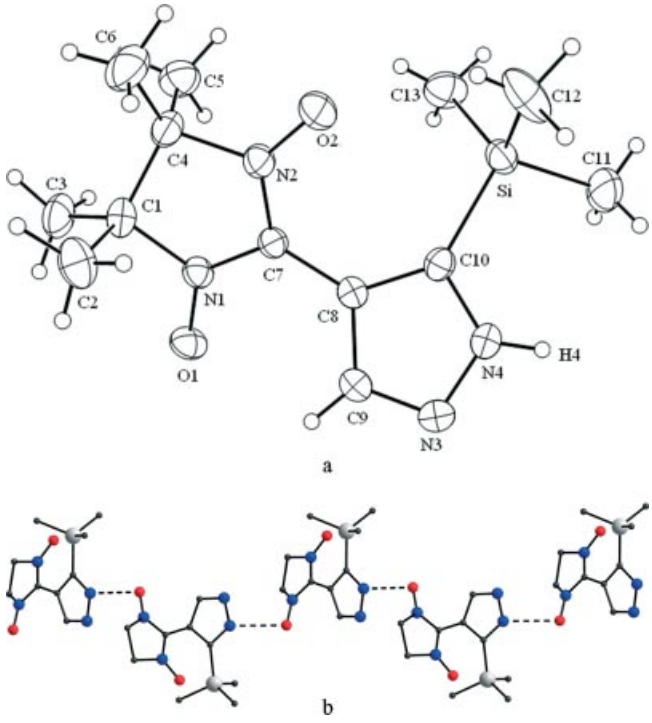
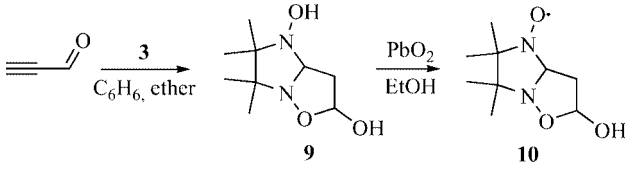


Figure 4. Molecule **8** (a) and motif of chain (b).



Scheme 7.

Indeed, oxidation of **9** resulted in a characteristic deep red color of the solution. However, it would be reasonable to assume that the product was nitroxide **10** and not compound **2**, and the low stability of this product prevented it from being isolated in pure form. We therefore attempted to synthesize HC≡C–NN from **1** or **7**, since methods of Si–C bond cleavage in Me_3Si-substituted acetylenes are well developed and achievable under mild conditions.[10] Indeed, after treatment of **1** with a methanol solution of NH_3, the dark blue spot of **1** with R_f = 0.8 gradually vanished from a TLC plate, while a bluish violet spot with R_f = 0.65 appeared. Addition of excess CH_2N_2 to the solution and subsequent stirring of the reaction mixture for 20 min resulted in the formation of 4,4,5,5-tetramethyl-2-(pyrazol-3-yl)-4,5-

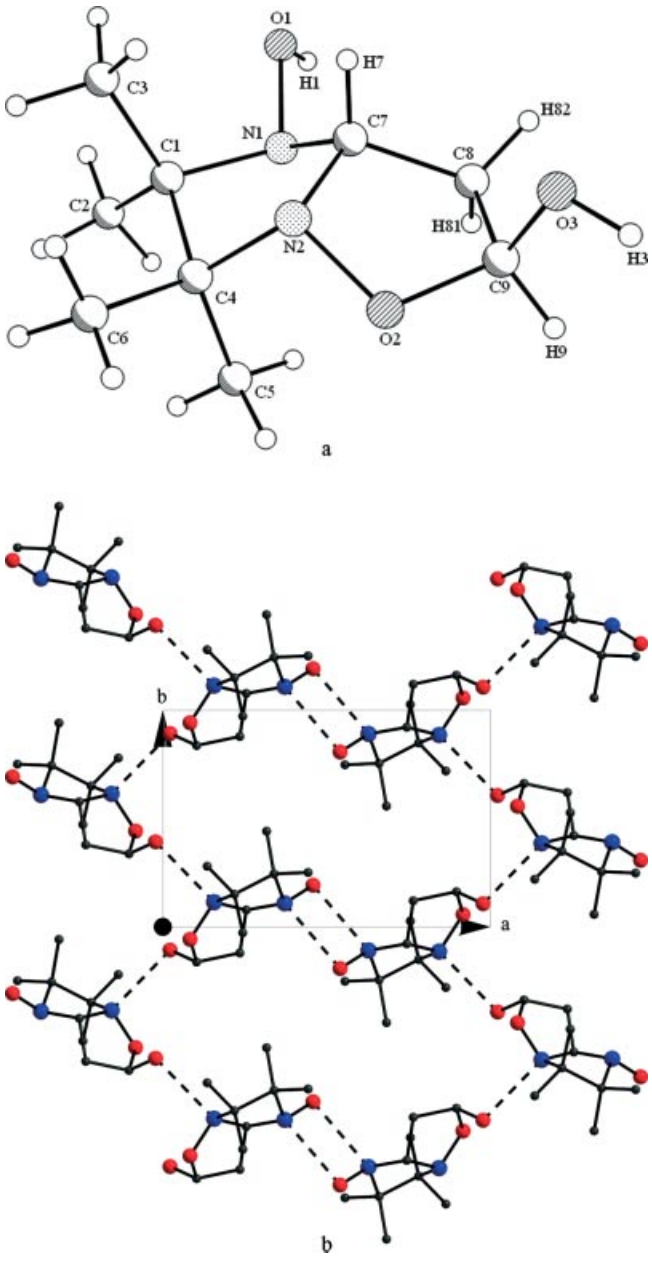
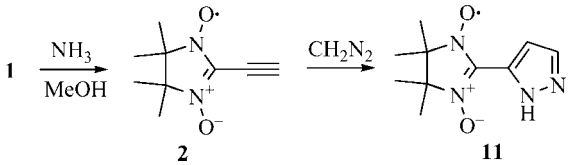


Figure 5. Molecule (a) and H-bonded layer (b) formed in the crystal structure of **9**. Selected bond lengths [Å]: O(H)–N 1.447(2), N–O 1.461(2), (N)O–C 1.421(3), C–O 1.389(2), N–C 1.472(2)–1.507(2), C–C 1.505(3)–1.554(3).

dihydro-1*H*-imidazole 3-oxide 1-oxyl (**11**) (identified by comparison with an authentic sample[11]) in 39% yield, which confirmed that the reaction mixture had contained compound **2** (Scheme 8).



Scheme 8.

After a few days of storage at ca. 0 °C, TLC of the reaction mixture indicated only a spot corresponding to **2**. However, evaporation of the reaction mixture and further dissolution of the residue gave a solution in which TLC also revealed other products in addition to **2**. Further manipulations with this solution resulted in complete decomposition of **2**. We believed that subsequent chemical transformations of **2** were caused by the presence of organosilicon compounds in the residue left after evaporation of the reaction mixture. Benzene was therefore added to the reaction mixture, and evaporation of this with pressure control allowed the substitution of MeOH by benzene. The resulting solution was then placed on a chromatographic column, and a fraction containing **2** was collected; evaporation of this fraction gave stable crystalline compound **2**. After recrystallization of the residue we isolated **2** in the form of single crystals and determined its structure (Figure 6).

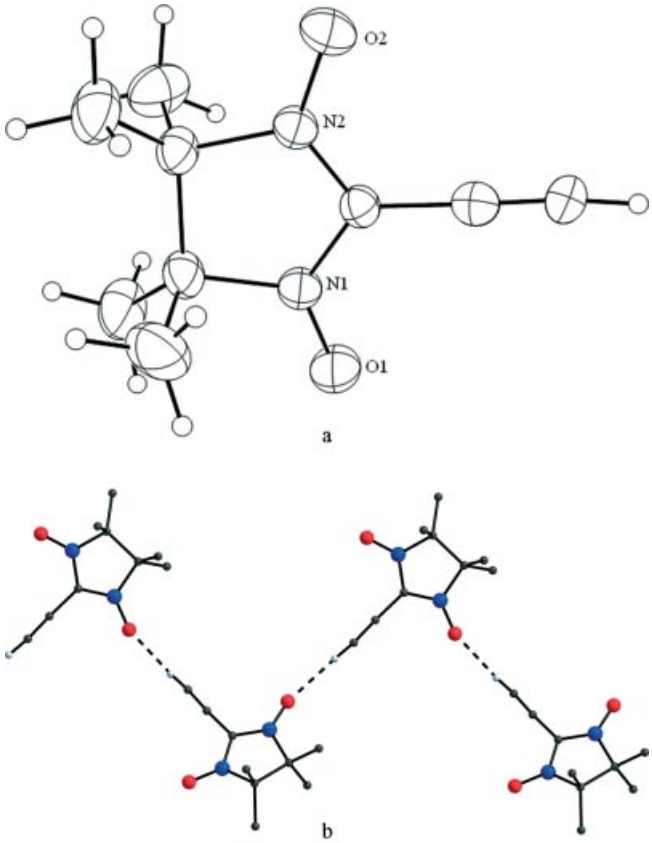


Figure 6. Molecule (a) and H-bonded chains (b) formed in the crystal structure of **2**.

The distances in the NO groups in molecule **2** differ: N(1)–O(1) is 1.259(2), while N(2)–O(2) is 1.274(2) Å. The latter bond is longer because the O atom of this group is involved in the hydrogen bond to the H atom of the –C≡C–H group of the neighboring molecule [C≡C 1.106(3) Å, C–H 0.88(3) Å, H···C 2.22(3) Å, C···O 3.097(3) Å, ∠CHO 172(2)°]; due to these bonds one can formally distinguish chains in the structure (Figure 6).

Conclusions

As a result of our study we isolated alk-1-ynyl-substituted nitronyl nitroxides **1** and **2**, and X-ray analyses of these compounds confirmed that their molecular structures contain acetylene fragments. The synthesis of **1** and **2** demanded an experimental approach that would allow preservation of the triple bond near the nitronyl nitroxide fragment in the course of the reactions. In the case of **2**, an effective approach was a chain of transformations that involved condensation of 3-(trimethylsilyl)propanal with 2,3-bis(hydroxyamino)-2,3-dimethylbutane, oxidation of the resulting dihydroxyimidazolidine, and further removal of the protecting $(CH_3)_3Si$ group. Special precautions taken to purify the solutions of nitroxides **1** and **2** from impurities in the course of synthesis allowed us to obtain these compounds as single crystals and to determine their molecular structures.

The synthetic potential of **1** and **2** includes the synthesis of various spin-labeled derivatives of these compounds. Importantly, for realization of this potential, **1** and **2** need not be preliminarily isolated as individual solids, because the synthetic procedures provide for the use of solutions of alkynes **1** and **2** that are formed during synthesis and are stable within a few days. This was demonstrated in the case of 1,3-dipolar cycloadditions of CH_2N_2 to **1** and **2**, which afforded the corresponding pyrazolyl-substituted nitronyl nitroxides. While investigating the products of the reactions between CH_2N_2 and **1** or **2**, we encountered the known effect of steric factors, which may become dominant over electronic effects in cycloaddition orientations.[12] Indeed, the bulky trimethylsilyl substituent in **1** affected the steric accessibility of the triple bond so much that the major reaction product was the 4-pyrazolyl-substituted nitronyl nitroxide. The reaction between CH_2N_2 and **2**, however, was much faster than that with **1**, in accordance with Auwers's rule,[13] and gave the 3-pyrazolyl-substituted nitronyl nitroxide as the sole reaction product. This shows that **1** may be used not only as a precursor for the synthesis of **2**, but also for incorporation of the 2-imidazoline fragment at a particular position in the heterocycle being constructed.

Experimental Section

General Methods: All the solvents used were reagent quality. The solvents were removed under reduced pressure, and all commercial reagents were used without additional purification. The reactions were monitored by TLC on silica gel (60 F_{254}) aluminium sheets (Merck). IR spectra were obtained with KBr pellets with use of a Bruker VECTOR 22 infrared spectrometer. Melting points were obtained with a "Boetius" melting point apparatus. Microanalyses were obtained with a Carlo–Erba 1106 analyzer. Mass spectra were recorded on a Finnigan MAT-8200 instrument by the electron-impact ionization technique (70 eV). ^{1}H NMR spectra were recorded with a Bruker Avance 300 spectrometer locked to the deuterium resonance of the solvent. The ESR spectra were registered on a Bruker EMX CW ESR spectrometer in liquid toluene (10^{-5}–10^{-4} M solutions) at room temperature with use of solid *N*,*N*-diphenyl-*N*′-(2,4,6-trinitrophenyl)hydrazyl (DPPH) as standard to determine *g*-values.

General Procedure for the Reactions between Propargyl Aldehydes and 3: 2,3-Bis(hydroxyamino)-2,3-dimethylbutane[14,15] (**3**, 1.20 g, 8.1 mmol) was added at –30 °C to a stirred solution of oct-2-ynal (**4**) or 3-(trimethylsilyl)propynal (**6**) (8.1 mmol) in MeOH (25 mL). The reaction mixture was stirred for 2 h, while the temperature was gradually raised to room temperature. Evaporation of the solvent gave the crude product, which was ground with hexane, filtered, and recrystallized from a mixture of ethyl acetate and hexane.

(*E*)-1-(1-Hydroxy-4,4,5,5-tetramethylimidazolidin-2-ylidene)heptan-2-one (5): Yield 1.36 g (63%). White powder, m.p. 143–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, 3 H, CH_2CH_3), 1.1–1.4 [14 H, s $C(CH_3)_2$, s $C(CH_3)_2$ and m $(CH_2)_2$], 1.61 [pent, 2 H, $C(=O)CH_2CH_2$], 2.28 [t, 2 H, $C(=O)CH_2$] ppm. IR: $\tilde{\nu}_{max}$ = 713, 750, 907, 951, 1042, 1121, 1153, 1178, 1268, 1303, 1323, 1365, 1455, 1484, 1512, 1606, 2858, 2941, 3317 cm^{-1}. $C_{15}H_{26}N_2O_2$ (266.38): calcd. C 66.1, H 10.3, N 11.0; found C 66.2, H 10.1, N 11.1.

4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]imidazolidine-1,3-diol (7): Yield 1.07 g (45%). Yellowish powder, m.p. 156–157 °C. ^{1}H NMR (300 MHz, [D_6]acetone, 25 °C): δ = 0.13 [s, 9 H, $Si(CH_3)_3$], 1.04 [s, 6 H, $C(CH_3)_2$], 1.07 [s, 6 H, $C(CH_3)_2$], 4.51 (s, 1 H, CH) ppm. IR: $\tilde{\nu}_{max}$ = 701, 761, 808, 841, 907, 984, 1028, 1098, 1162, 1252, 1319, 1370, 1391, 1461, 2179, 2961, 3251 cm^{-1}. $C_{12}H_{24}N_2O_2Si$ (256.42): calcd. C 56.2, H 9.4, N 10.9; found C 55.7, H 9.5, N 10.4.

4,4,5,5-Tetramethyl-2-[2-(trimethylsilyl)ethynyl]-4,5-dihydro-1*H*-imidazole 3-Oxide 1-Oxyl (1): $NaIO_4$ (0.2 g, 9 mmol) was added to an ice-cooled, stirred mixture of **7** (0.13 g, 0.44 mmol), CH_2Cl_2 (6 mL), and water (3 mL). The reaction mixture was then stirred for 2 h, while the temperature was gradually raised to room temperature. The organic layer was separated, dried with Na_2SO_4, and filtered. The filtrate was concentrated to ca. 3 mL, and heptane (5 mL) was added. The solvent was then distilled off on a rotary evaporator at a bath temperature of ca. 30 °C and at a pressure of 130 Torr until a tawny film started to form on the walls of the flask. The resulting blue solution was decanted into a flat-bottomed flask and stored at 0 °C for a few days. The resulting thin greenish blue needles, covered with a yellow amorphous substance, were filtered off. (After the maximum possible amount of mechanical cleaning of the crystals and repeated recrystallization, greenish blue needles with small amounts of the sticky yellow amorphous substance formed again. The yield had decreased to 22%.) Yield 60 mg (47%). M.p. 130–135 °C with decomposition; R_f = 0.8 (EtOAc). ESR: g_{iso} = 2.0067; $A_N(2N)$ = 7.25 G, $A_{H(CH3)}(12H)$ = 0.2 G, $A_{H(C\equiv C-H)}(1H)$ = 1.38 G. IR: $\tilde{\nu}_{max}$ = 663, 764, 848, 941, 1025, 1169, 1250, 1372, 1418, 1630, 2113, 2981 cm^{-1}. $C_{12}H_{21}N_2O_2Si$ (253.39): calcd. C 56.9, H 8.4, N 11.1; found C 56.4, H 8.7, N 11.5.

4,4,5,5-Tetramethyl-2-[5-(trimethylsilyl)pyrazol-4-yl]-4,5-dihydro-1*H*-imidazole 3-Oxide 1-Oxyl (8): A solution of CH_2N_2 in diethyl ether (30 mL), prepared from *N*-nitroso-*N*-methylurea (77 mg, 0.75 mmol), was added to a solution of **1** in CH_2Cl_2 (15 mL) obtained from 1,3-dihydroxyimidazolidine **7** (0.13 g, 0.51 mmol). The reaction mixture was kept at room temperature for 72 h. The same amount of CH_2N_2 was then again added to the reaction mixture, and the mixture was allowed to stand for 24 h. The solvent was evaporated; heptane (5 mL) and the smallest possible amount of CH_2Cl_2 necessary for complete solution were added to the residue. The solution was filtered into a flat-bottomed flask and slowly evaporated. This gave perfect blue crystals of nitroxide **8**. The crystals were filtered off, and the filtrate was evaporated and chromatographed on an Al_2O_3 column. The residual compound **1** and the orange products were eluted with chloroform, and the additional amount of **8** was eluted with ethyl acetate. Yield 70 mg (48%). M.p.

200–204 °C with decomposition; R_f = 0.35 (EtOAc). IR: $\tilde{\nu}_{max}$ = 758, 848, 865, 937, 1089, 1137, 1178, 1218, 1250, 1296, 1352, 1370, 1392, 1451, 1531, 1578, 2977, br. 3177 cm^{-1}. $C_{13}H_{23}N_4O_2Si$ (295.43): calcd. C 52.9, H 7.9, N 19.0; found C 53.1, H 8.2, N 18.8.

2,2,3,3-Tetramethyl-1,2,3,6,7,7a-hexahydroimidazo[1,2-*b*]isoxazole-1,6-diol (9): Propanal diethyl acetal (1.28 g, 10 mmol) was added dropwise at 80 °C to a stirred mixture of H_2SO_4 (0.2 N, 4 mL) and hydroquinone (8 mg). Diethyl ether (10 mL) was then added slowly. The resulting azeotrope of propanal and diethyl ether was distilled off through a Liebig condenser into a stirred suspension of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**3**, 1.0 g, 6.8 mmol). The reaction mixture was stirred for 14 h, the solvent was distilled off, and the residue was recrystallized from a mixture of ethyl acetate and MeOH. The resulting pale yellow crystals were filtered off. Yield 0.28 g (20%). The product decomposes at 170–173 °C with evolution of gas bubbles and formation of a pale green liquid phase. IR: $\tilde{\nu}_{max}$ = 721, 797, 900, 916, 943, 966, 988, 1039, 1103, 1146, 1202, 1248, 1293, 1308, 1352, 1372, 1392, 1435, 1476, 2920, 2976, br. 3171 cm^{-1}. $C_9H_{18}N_2O_3$ (202.25): calcd. C 53.5, H 9.0, N 13.9; found C 53.2, H 8.8, N 13.9.

2-Ethynyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-Oxide 1-Oxyl (2): A solution of NH_3 in MeOH (14%, 2 mL) was added to a solution of **1** in CH_2Cl_2, prepared from the dihydroxyimidazolidine **7** (60 mg, 0.23 mmol). This solution was evaporated on a rotary evaporator to a volume of ca. 1 mL. A solution of NH_3 in MeOH (14%, 2 mL) was added, and the resulting mixture was stirred at room temperature. A TLC analysis of the reaction mixture indicated that after 30 min, the dark blue spot with R_f = 0.8 (EtOAc) had vanished completely, while a bluish violet spot with R_f = 0.65 (EtOAc) had formed. The solution was concentrated to a volume of ca. 2 mL. It was then diluted with benzene (10 mL) and placed on a column [Merck silica gel (0.063–0.100 mm for column chromatography), 15 × 1.5 cm, wetted with benzene]. The column was eluted with ethyl acetate, and a bluish violet fraction was collected; the fraction was evaporated. The solvent was distilled off, the residue was ground with petroleum ether, and the solvent was decanted. The resulting crystals were dissolved in CH_2Cl_2 (2 mL), *n*-heptane (2 mL) was then carefully added, and the mixture was kept in an open flask at ca. 5 °C to give dark blue violet crystals suitable for an X-ray investigation. Yield 20 mg (47%). M.p. 102 °C with decomposition. ESR: g_{iso} = 2.0067; A_N(2N) = 7.17 G, $A_{H(CH3)}$ (12H) = 0.2 G, $A_{H(C\equiv C-H)}$(1H) = 1.38 G. IR: $\tilde{\nu}_{max}$ = 704, 756, 870, 1136, 1170, 1216, 1375, 1418, 1448, 2116, 2985, 3210 cm^{-1}. $C_9H_{13}N_2O_2$ (181.21): calcd. C 59.7, H 7.2, N 15.5; found C 59.7, H 7.3, N 15.5.

X-ray Structure Analysis: The single-crystal diffraction data for the compounds were collected on a SMART APEX CCD (Bruker AXS) automatic diffractometer (Mo-K_α, λ = 0.71073 Å, room temperature); an absorption correction was applied by use of the Bruker SADABS program, version 2.03. The structures were solved by direct methods and refined by full-matrix, least-squares in an anisotropic approximation for non-hydrogen atoms. The positions of the H atoms were mostly calculated theoretically. The methyl H atoms were refined as a rigid group with isotropic thermal parameters. All structure solution and refinement calculations were carried out with SHELX-97 and Bruker Shelxtl Version 6.12 program packages.

Compound 1: $C_{12}H_{21}N_2O_2Si$; *FW* = 253.40; triclinic, $P\bar{1}$; a = 10.850(6), b = 12.433(7), c = 18.070(10) Å, α = 77.444(11), β = 86.832(12), γ = 81.093(11)°; V = 2350(2) $Å^3$; Z = 6, D_C = 1.074 $g{\cdot}cm^{-3}$; μ = 0.144 mm^{-1}; 1.70 < θ < 23.31°; 8584 collected, 6383 unique, R_{int} = 0.0787; 524 parameters; *Goof* = 1.032; R indices for $I > 2\sigma$ R_1 = 0.0811, wR_2 = 0.2108; R indices (all data) R_1 = 0.1295, wR_2 = 0.2544.

Compound 2: $C_9H_{13}N_2O_2$; *FW* = 181.21; orthorhombic, *Pbca*; a = 11.055(3), b = 11.691(3), c = 15.436(4) Å; V = 1995.1(8) $Å^3$; Z = 8; D_C = 1.207 $g{\cdot}cm^{-3}$; μ = 0.087 mm^{-1}; 2.64 < θ < 29.56°; 20845 collected, 2683 unique, R_{int} = 0.2554; 171 parameters; *Goof* = 0.917; R indices for $I > 2\sigma$ R_1 = 0.0780, wR_2 = 0.1602; R indices (all data) R_1 = 0.1431, wR_2 = 0.1882.

Compound 5: $C_{14}H_{26}N_2O_2$; *FW* = 254.37; monoclinic, *C*2/*c*; a = 22.512(6), b = 11.653(3), c = 12.170(3) Å, β = 91.459(6)°; V = 3191.6(14) $Å^3$; Z = 8, D_C = 1.059 $g{\cdot}cm^{-3}$; μ = 0.071 mm^{-1}; 2.57 < θ < 23.29°; 6737 collected, 2288 unique, R_{int} = 0.1557; 259 parameters; *Goof* = 0.950; R indices for $I > 2\sigma$ R_1 = 0.0902, wR_2 = 0.1600; R indices (all data) R_1 = 0.1882, wR_2 = 0.2008.

Compound 7: $C_{12}H_{24}N_2O_2Si$; *FW* = 256.42; orthorhombic, *Pna*2_1; a = 21.735(4), b = 6.9151(14), c = 10.741(2) Å; V = 1614.3(6) $Å^3$; Z = 4, D_C = 1.055 $g{\cdot}cm^{-3}$; μ = 0.141 mm^{-1}; 1.87 < θ < 23.53°; 11563 collected, 2297 unique, R_{int} = 0.1059; 184 parameters; *Goof* = 0.998; R indices for $I > 2\sigma$ R_1 = 0.0672, wR_2 = 0.1592; R indices (all data) R_1 = 0.0998, wR_2 = 0.1813.

Compound 8: $C_{13}H_{23}N_4O_2Si$; *FW* = 295.44; monoclinic, $P2_1/c$; a = 7.3636(10), b = 12.8684(18), c = 17.045(2) Å, β = 91.576(3)°; V = 1614.5(4) $Å^3$; Z = 4; D_C = 1.215 $g{\cdot}cm^{-3}$; μ = 0.153 mm^{-1}; 1.98 < θ < 29.61°; 14156 collected, 4202 unique, R_{int} = 0.0852; 274 parameters; *Goof* = 0.884; R indices for $I > 2\sigma$ R_1 = 0.0617, wR_2 = 0.1240; R indices (all data) R_1 = 0.1134, wR_2 = 0.1451.

Compound 9: $C_9H_{18}N_2O_3$; *FW* = 202.25; monoclinic, $P2_1/c$; a = 11.963(3), b = 7.1389(18), c = 13.626(3) Å, β = 115.563(4)°; V = 1049.7(5) $Å^3$; Z = 4; D_C = 1.280 $g{\cdot}cm^{-3}$; μ = 0.096 mm^{-1}; 1.89 < θ < 29.49°; 9578 collected, 2706 unique, R_{int} = 0.0741; 200 parameters; *Goof* = 0.803; R indices for $I > 2\sigma$ R_1 = 0.0549, wR_2 = 0.1339; R indices (all data) R_1 = 0.0936, wR_2 = 0.1556.

CCDC-277835 (for **1**), -277836 (for **2**), -277837 (for **5**), -277838 (for **7**), -277839 (for **8**), and -277840 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: The magnetochemical experiment was run on an MPMS-5S ("Quantum Design") SQUID magnetometer at temperatures from 2 K to 300 K in a homogeneous external magnetic field of up to 49.5 kOe. The molar magnetic susceptibility χ was calculated by Pascal's additive scheme, including diamagnetic corrections. It was shown for compounds **2** and **8** that the values of μ_{eff} in the range 30–300 K are close to 1.73 B.M. and are practically independent of temperature.

Supporting Information (see also the footnote on the first page of this article): Experimentally measured and simulated EPR spectra of **1** and **2**.

Acknowledgments

We are grateful to the Fund for Support of Research in Russia, to the Russian Academy of Sciences, to the Siberian Branch of the Russian Academy of Sciences, to RFBR (grants 03-03-32518, 05-03-32305), NSh-2298.2003.3, and to the Bruker Company for financial support. The authors also thank Dr. D. V. Stass for ESR experimental assistance.

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Received: February 8, 2006
Published Online: May 10, 2006

