Persistent vinylnitroxides

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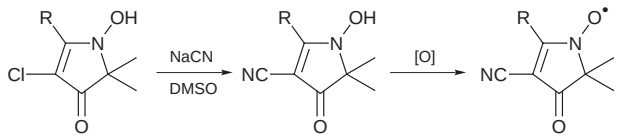
A method for the synthesis of persistent vinylnitroxides (vinylaminoxyls) has been developed and, for one of the radicals synthesized, an extremely high energy of intermolecular exchange interaction (−101 K) has been found.

Vinylnitroxides are traditionally considered transient radicals, since even EPR methods are often not powerful enough to detect them without using spin traps.[1] We succeeded in synthesizing persistent vinylnitroxides **1** and **2** and isolating them as individual solids (Scheme 1).†



3a R = Ph
b R = *m*-pyridyl

4a R = Ph
b R = *m*-pyridyl

1 R = Ph
2 R = *m*-pyridyl

Scheme 1

The vinylnitroxides isolated are similar to nitronyl nitroxides, whose synthesis was developed by Ullman *et al.*,[2] in that they have effective delocalization of spin density. The EPR data of solutions of **1** and **2** indicate that the spin density in **1** and **2** is significantly delocalized from the N–O• group to the nitrile group [$a_{N(N–O•)}$ = 6.0 G, $a_{N(CN)}$ = 1.0 G for **1** and $a_{N(N–O•)}$ = 6.0 G, $a_{N(CN)}$ = 1.2 G for **2**).

The magnetic properties‡ of solid **1** and **2** deserve special attention. Treatment of the experimental dependence $\chi(T)$ for **1** (Fig. 1) and **2** showed that the experimental curves perfectly fit the exchange chain model[3] with parameters g = 2.04, J/k = −101 K and x = 0.02 for **1** and g = 2.01, J/k = −55 K and x = 0.03 for **2**. Due to these strong exchange interactions in solid **1** and **2**, even at room temperature the μ_{eff} values of the compounds (1.49 μ_B for **1** and 1.58 μ_B for **2**) are considerably smaller than the theoretical value of 1.73 μ_B corresponding to the presence of one unpaired electron per molecule. The effective magnetic moments of **1** and **2** continuously decrease to 0.2 and 0.4 μ_B at 2 K, respectively. In $CHCl_3$ solutions of **1** and **2**, the magnetic moments equal the theoretical value within

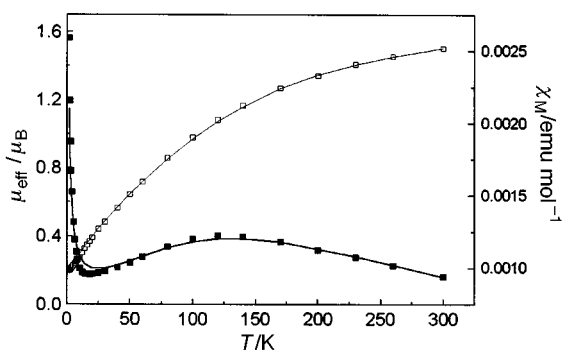


Fig. 1 Plots of effective magnetic moment (μ_{eff}) (□) and magnetic susceptibility (χ_M) (■) for **1**.

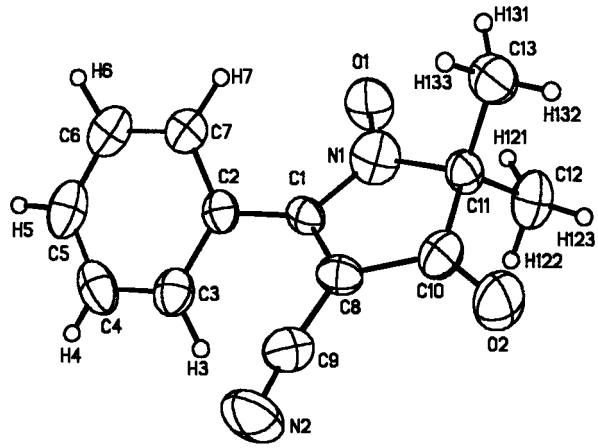


Fig. 2 ORTEP plot of the structure of **1**.

experimental error (1.70 μ_B for **1** and 1.73 μ_B for **2**) and do not change when the temperature decreases. Thus the experiment with vinylnitroxide solutions confirmed that strong spin–spin interactions are inherent in the solids. This prompted us to study the crystal structure of the vinylnitroxides. For **1** we succeeded in growing a single crystal of good quality (Fig. 2).§ In solid **1**, the shortest intermolecular contacts are at least 3 Å. Therefore, the structure of **1** should be considered molecular. However, the magnetic structure of **1**, as noted above, involves magnetic chains. The shortest intermolecular contacts in solid **1** are shown in Fig. 3. These are the nearly equal distances from the nitroxyl oxygen atom of one **1** molecule to both vinyl carbon atoms of the neighboring **1** molecule ($d_{O(N–O•)\cdots\beta\text{-}C(C=C)}$ = 3.183 Å and $d_{O(N–O•)\cdots\alpha\text{-}C(C=C)}$ = 3.296 Å). It is reasonable to assume that the 'magnetic chains' are formed by these contacts in solid **1** and are responsible for the strong exchange interactions (−101 K) in **1**.

To understand the magnetic behavior of **1** we carried out *ab initio* calculations on the electronic structure and intermolecular exchange interaction parameters in a two-radical model system [Fig. 4(*a*)]. It was found that the traditional HF (ROHF, UHF) and post-HF (direct CI, CASSCF) methods failed to give the

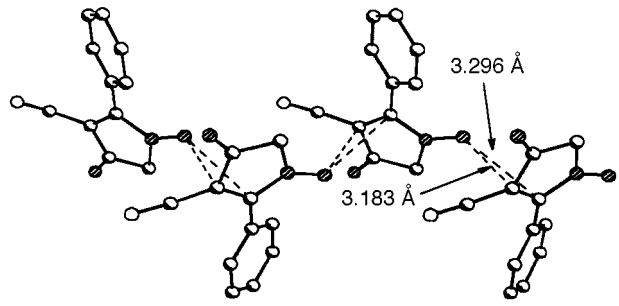


Fig. 3 Structure of the exchange chain in solid **1** (H atoms and CH_3 groups are omitted for clarity).

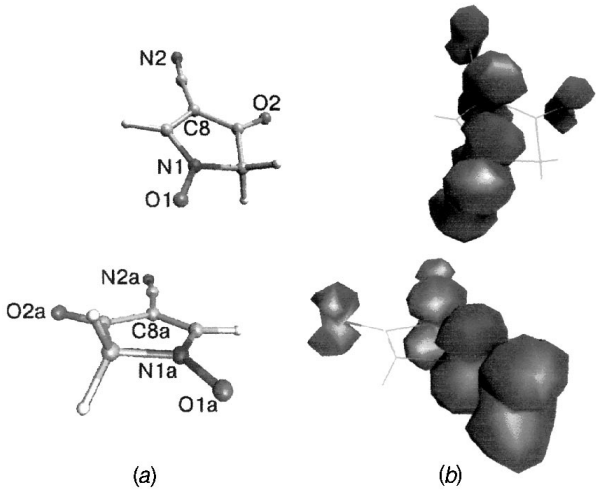


Fig. 4 Truncated (two-radical) model system (*a*) and general view of the spin density distribution for the model system (*b*).

Table 1 Exchange interaction parameters calculated in the framework of HF and DFT methods

Method	Basis set[a]	(*J*/*k*)/K
ROHF UHF	BG	$> 10^4$
CASSCF (4,6)	BG	1.5
ROHF CI(2,2)	BG	2.4
ROHF CI(2,4)	BG	2.8
ROHF CI(4,6)	BG	40.3
VWN	BG	−98.6
BP86	BG	−50.2
VWN	DZVP	−190.0
BP86	DZVP	−108.9
Experiment		−101

[a] BG: see ref. 4. DZVP: see ref. 5.

Table 2 Main calculated atomic spin densities (VWN approach)

	Basis set	
Atom	DZVP	BG
O1	0.420	0.547
N1	0.214	0.124
O2	0.101	0.107
C8	0.237	0.212
N2	0.093	0.074
O1a	0.437	0.548
N1a	0.201	0.119
O2a	0.098	0.106
C8a	0.235	0.211
N2a	0.088	0.074

sign of the exchange interaction parameter, whereas DFT/Broken Symmetry methods gave the same sign and order of the *J* parameter as in the experiment (Table 1). Analyzing the spin density distribution [Table 2 and Fig. 2(*b*)] calculated by the VWN method, one can assume that the most preferable intermolecular exchange channel passes through the vinyl β-carbon atom (C8a). The part (0.21–0.24) of the unpaired electron spin density localized on the C8a atom in one molecule contacts the spin density localized on the nitroxyl group of the neighboring molecule, causing an effective intermolecular exchange interaction between the neighboring radicals.

Thus, we succeeded in synthesizing persistent vinylnitroxides and revealed their surprising ability to form magnetic chains with strong interchain exchange interactions at long intermolecular distances (> 3 Å) in formally molecular solids. The quantum-chemical calculations adequately explain these strong exchange interactions in solid vinylnitroxides. It appeared that these strong interactions are favored by localization of the spin density of the N–O$^{\bullet}$ group of one nitroxide near the β-carbon of the vinyl group bonded to the nitroxyl group of the neighboring nitroxide.

Notes and references

† The starting 2-phenylpyrroline **3a** was obtained according to V. A. Reznikov, L. A. Vishnivetskaya and L. B. Volodarsky, *Izv. Akad. Nauk., Ser. Khim.*, **1990**, 390. The pyridine derivative was synthesized in a similar manner.

Synthesis of **4a**: 0.5 g (2 mmol) of chloropyrroline **3a** was added over 15 min to a solution of 0.2 g of NaCN (4 mmol) in 5 ml of anhydrous DMSO with stirring and cooling. The mixture was stirred further for 30 min at 20 °C and then diluted with 15 ml of water with cooling. The solution was acidified with 5% HCl to pH 3. The product precipitate was filtered off, washed with water and a 1 : 1 EtOAc–hexane mixture, and dried (80%); mp 213–216 °C (from EtOAc–MeOH); ν_{max}(KBr)/cm^{-1} 2200 (C≡N), 1675 (C=O); λ_{max}(EtOH)/nm (log ε) 245 (4.27), 346 (3.88); δ_H([$^2H_6$]DMSO) 1.35 [s, 6H, 5-(CH$_3$)$_2$], 7.64 (m, 3H), 7.84 (m, 2H, Ph); δ_C([$^2H_6$]DMSO) 20.75 [5-(CH$_3$)$_2$], 71.08 (C-5), 77.96 (C-3), 115.41 (C≡N), 125.82, 128.45, 128.84, 132.64 (Ph), 170.92 (C-2), 194.96 (C-4). The pyridine derivative **4b** was obtained in a similar manner.

Synthesis of **1**: A suspension of 0.2 g of the hydroxy compound **4b** and 2 g of MnO_2 in 10 ml of $CHCl_3$ was stirred for 30 min at 20 °C. The excess of the oxidant was filtered off, the solution was evaporated, and the residue was chromatographed on silica gel, with $CHCl_3$ as eluent (60%), mp 143–145 °C (from hexane); ν_{max}(KBr)/cm^{-1} 2200 (C≡N), 1700 (C=O), 1540, 1600 (C=C); λ_{max}(hexane)/nm (log ε) 250 (4.17), 270 (4.11), 313 (3.73), 334 (3.93), 397 (3.68), 578 (3.26) [Found (calc.): C, 68.5 (68.7); H, 4.8 (4.8); N, 12.1% (12.1%)]. An analogous procedure with the pyridine derivative **4b** afforded the corresponding radical **2** in 40% yield, mp 113–115 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1705 (C=O), 1590 (C=C), 2200 (C≡N); λ_{max}(hexane)/nm (log ε) 246 (4.14), 308 (3.48), 333 (3.67), 395 (3.48), 564 (3.05) [Found (calc.): C, 55.7 (55.6); H, 4.2 (4.5); N, 15.3% (15.6%)].

‡ Magnetic susceptibility was measured with an MPMS-5S SQUID magnetometer over 2–300 K.

§ *Crystal data* for **1**: $C_{13}H_{11}N_2O_2$, M = 227.24, orthorhombic, space group *Aba*2, a = 15.334(3), b = 18.203(4), c = 8.414(2) Å, V = 2348.6(9) Å^3, Z = 8, D_c = 1.285 g cm^{-3}, λ(Mo-Kα), Enraf-Nonius CAD 4, θ region 2.60 ≤ θ ≤ 23.48°, T = 293 K, 1512 reflections collected, 847 independent (R_{int} = 0.0265), full-matrix least-squares on F^2 (SHELX 97), GOF = 0.506, final R values [847 $I_1 > 2\sigma(I)$ R_1 = 0.0204, wR_2 = 0.0251], extinction coefficient 0.0056(4). CCDC 182/1172. Crystallographic data are available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/CC/1999/539/

1 H. G. Aurich, K. Hahn and K. Stock, *Chem. Ber.*, 1979, **112**, 2776.
2 E. F. Ullman, J. H. Osiecki, D. G. B. Boocock and R. Darcy, *J. Am. Chem. Soc.*, 1972, **94**, 7049.
3 J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, 1964, **135**, 640.
4 R. Poirier, R. Kari and I. G. Csizmadia, *Handbook of Gaussian Basis Sets*, Elsevier, Netherlands, 1985.
5 E. R. Davidson and D. Feller, *Chem. Rev.*, 1986, **86**, 681; N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.

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