

Crystal Structures and Magnetic Properties of Nitronyl Nitroxide Radicals

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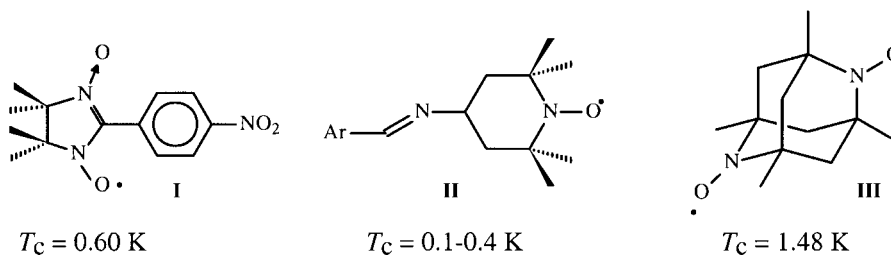
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Dedicated to Professor Jack D. Dunitz on the occasion of his 80th birthday

The crystal structures and magnetic properties of the nitronyl nitroxide radicals 4,5-dihydro-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**1**), 4,5-dihydro-2,4,4,5,5-pentamethyl-3-oxido(1*H*-imidazol-1-yloxy) (**2**), 2-(4-chlorophenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**3**), and 4,5-dihydro-2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**4**) are reported. Compound **1** has two polymorphic forms: the α phase is monoclinic ($P2_1/n$ space group), with a single molecule in the asymmetric unit, and the β phase is monoclinic ($P2_1/c$ space group), with four molecules in the asymmetric unit. In the two polymorphs, the molecules are arranged in dimers formed by hydrogen bonds of the type C–H \cdots O–N. The crystal structure of **3** contains layers of antiparallel ribbons of molecules. Compound **4** crystallizes with solvent molecules, and an intramolecular hydrogen bond is formed between the 2-OH group of the phenyl ring and the nitroxide O-atom. Compound **4** also loses the two O-atoms of the nitroxide moiety upon heating to 90°. Magnetic measurements showed that both α and β polymorphs of **1** exhibit antiferromagnetic coupling. The best fit to the experimental data was obtained using *Bleany–Bower's* singlet-triplet model ($H = -2JSaSb$): $J = -11.2$ K for the α phase and $J = -15.0$ K for the β phase. Compounds **3** and **4** show no evidence for spin coupling.

Introduction. – The quest for organic materials exhibiting technologically useful properties, such as electrical conductivity or ferromagnetism, started several decades ago. The goal was to create an assembly of organic molecules or macromolecules constructed from only light elements (C, H, N, O, S, *etc.*) and yet possessing the properties similar to those of pure metals, *e.g.*, to conduct electricity by electron mobility or some metals to enable spin alignment. The possibility of ferromagnetic coupling in organic radicals was theoretically predicted in 1963 by *McConnell* [1]. The first example of a purely organic bulk ferromagnet was reported in 1991 by *Kinoshita* and co-workers [2] for crystals of the β phase of the 2-nitrophenyl nitronyl nitroxide radical (**1**). The evidence for the existence of long-range ferromagnetic order for this compound was achieved by electric-susceptibility and heat-capacity measurements at low temperatures. The ferromagnetic behavior was detected below 0.60 K (T_c). It is interesting to note that the three other phases did not show ferromagnetic ordering, which verifies that it is not sufficient to search for stable organic radicals, as magnetism is a bulk property and, therefore, highly dependent on the solid-state structure.

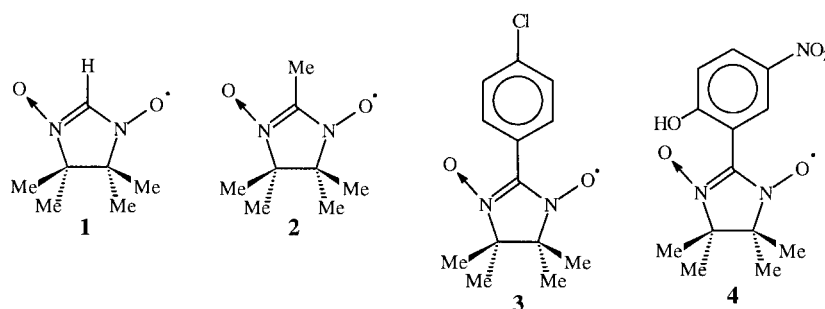
Since 1991, there has been a tremendous effort by many research groups worldwide to uncover the mystery of the dependence of spin coupling as a consequence of distinct relative molecular geometries. The belief that even the most-sophisticated properties



can be rationally designed by a systematic modification of organic molecular structures, motivated and fueled by increased synthetic capabilities, enlarged the number of groups working in this field. New stable organic radicals that undergo ferromagnetic ordering were prepared, *e.g.*, compounds of type **II** [3] and **III** [4]. However, the goal of easily preparing compounds that display ferromagnetic properties at ambient temperatures is yet to be realized.

Ferro- or antiferromagnetic coupling of stable radicals depends on the spin density on each atom and the interactions between them [5]. Since no correlation was found between relative orientation of O–N=C–N–O groups and the types of coupling [6][7], it appears that ferro- or antiferromagnetic coupling in the nitronyl nitroxide radicals depends on the shortest contacts between atoms (*i.e.*, hydrogen and *Van der Waals* bonds) and their spin densities.

H-Bonds play a crucial role in controlling the structural dimensionality of open-shell molecules as a crystal-design element for organic molecular solids with intermolecular ferromagnetic coupling [8][9]. Moreover, H-bonds have been proved to transmit ferromagnetic coupling between spins in the different hydroxy- and alkyne-substituted, ferromagnetically ordered nitroxide radicals [9–11]. Also, there are some reports about magnetic coupling *via* H-bonds in transition-metal complexes [12].



In the present work, we describe and discuss the crystal structures of four stable nitronyl nitroxides radicals: 4,5-dihydro-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**1**), 4,5-dihydro-2,4,4,5,5-pentamethyl-3-oxido(1*H*-imidazol-1-yloxy) (**2**), 2-(4-chlorophenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**3**), and 4,5-dihydro-2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazol-1-yloxy) (**4**), as well as the magnetic properties of three of these compounds (**1**,

3, and 4). The crystal structure of the product obtained by heating compound 4 is also discussed.

Results and Discussion. – *Crystal Structures.* Compound 1 crystallizes in two polymorphic forms (α and β). The crystal structures of both forms were solved [13], but have never been published in detail. The α form crystallizes in the monoclinic crystal system in space group $P2_1/n$, with a single molecule in the asymmetric unit. The β form crystallizes in the monoclinic crystal system in space group $P2_1/c$, with four independent molecules in the asymmetric unit. In both polymorphs, the molecules are arranged in dimers formed through H-bonds of the type $N-O\cdots H-C$. In the α polymorph, there is a single type of dimer formed between identical molecules related by an inversion center (Fig. 1). Comparison of the H-bond geometries is given in Table 1. In the β polymorph, there are three different dimers. There are two dimers at $z = 0.0$, each is made up from two identical molecules related by inversion centers (Fig. 2, left). The third dimer at $z = 0.25$ is made of two nonidentical molecules related *via* a pseudo inversion center (Fig. 2, right).

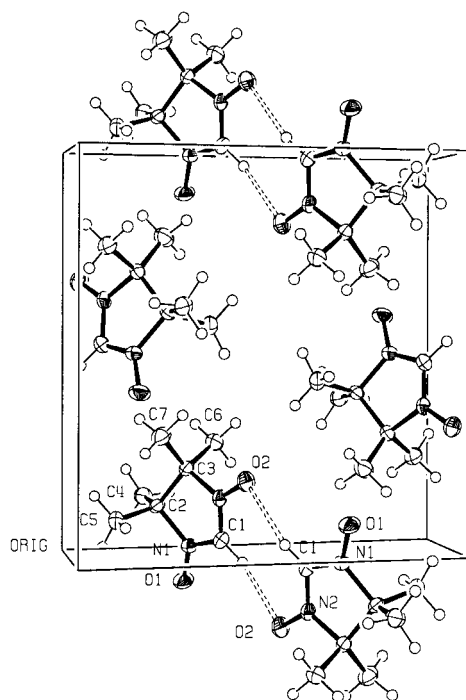


Fig. 1. Packing of molecules of the α polymorph of 1

The different structures of the two polymorphs, and, in particular, the unique structure of the β polymorph, were probed by crystal-structure prediction. The crystal structure of the α phase was among the most stable ones produced by the polymorph predictor [14]. Since it was suggested [15] that the β phase is metastable, its crystal structure was not considered in such a prediction.

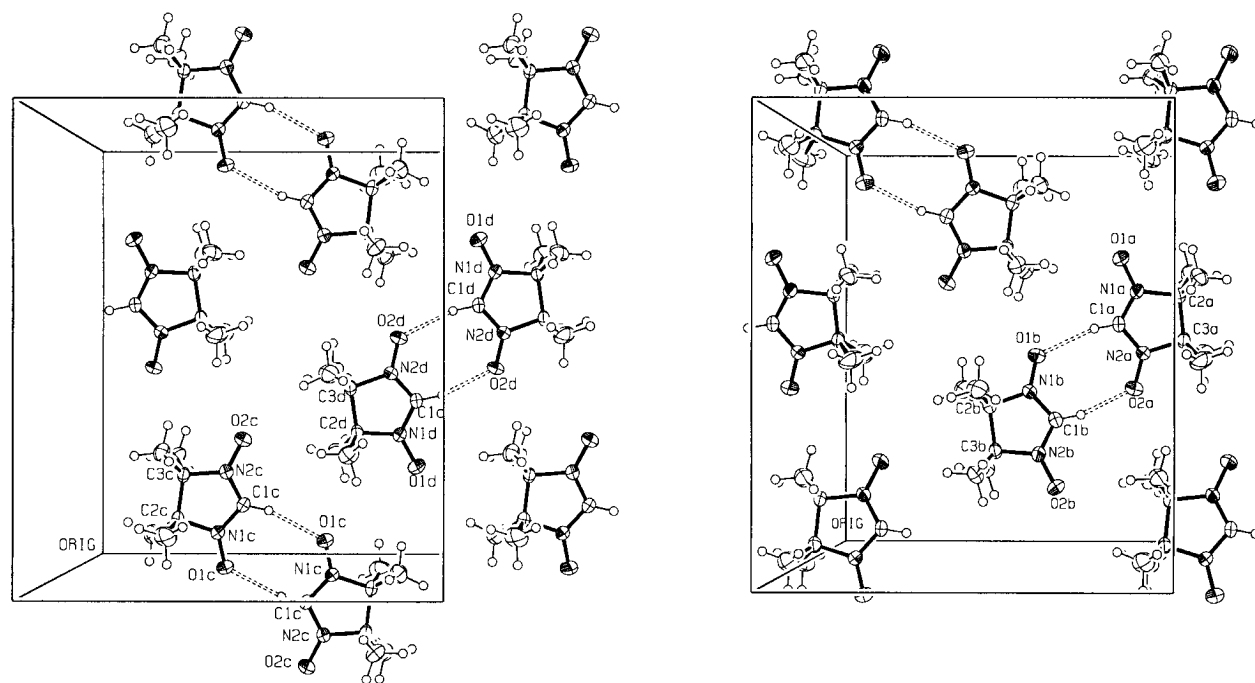


Fig. 2. View of a layer of molecules of the β polymorph of **1** for $z = 0.0$ (left) and $z = 0.25$ (right)

Table 1. Comparison of H-Bonding Geometries in the Two Polymorphs of **1**. 'D' stands for 'donor', 'A' for 'acceptor'; bond lengths in Å, bond angles in degrees.

D–H...A	D–H	H...A	D...A	D–H...A
<i>α-1</i>				
C(1)–H(1)···O(2)	0.94(3)	2.438(4)	3.347(4)	163.3(18)
<i>β-1</i>				
C(1a)–H(1a)···O(1b)	0.87(3)	2.241(4)	3.094(4)	164.4(18)
C(1b)–H(1b)···O(2a)	0.89(3)	2.365(4)	3.197(4)	154.4(18)
C(1c)–H(1c)···O(1c)	0.90(3)	2.255(4)	3.135(4)	164.3(18)
C(1d)–H(1d)···O(2d)	0.93(3)	2.296(4)	3.187(4)	159.7(18)

Table 2. Comparison of Selected Bond Lengths [Å] and Angles [°]

Atoms	1 (<i>α</i>)	1 (<i>β</i>)a	1 (<i>β</i>)b	1 (<i>β</i>)c	1 (<i>β</i>)d	2	3	4
O(1)–N(1)	1.272(3)	1.281(3)	1.280(3)	1.276(3)	1.278(3)	1.285(4)	1.279(2)	1.312(6)
O(2)–N(2)	1.276(3)	1.294(3)	1.282(3)	1.287(3)	1.279(3)	1.276(4)	1.285(2)	1.292(5)
N(1)–C(1)	1.327(4)	1.316(3)	1.329(3)	1.330(3)	1.325(3)	1.324(4)	1.351(3)	1.319(7)
N(2)–C(1)	1.327(4)	1.328(3)	1.333(3)	1.326(3)	1.325(3)	1.327(5)	1.343(3)	1.376(7)
N(1)–C(2)	1.508(4)	1.501(3)	1.490(3)	1.490(3)	1.505(3)	1.506(4)	1.494(3)	1.508(7)
N(2)–C(3)	1.512(4)	1.485(3)	1.505(3)	1.509(3)	1.494(3)	1.487(4)	1.496(3)	1.501(7)
C(2)–C(3)	1.559(4)	1.563(3)	1.567(3)	1.560(3)	1.576(3)	1.559(5)	1.555(3)	1.568(8)
O(1)–N(1)–C(1)	126.3(3)	125.6(2)	125.9(2)	126.0(2)	125.3(2)	125.8(3)	126.3(2)	124.4(4)
O(2)–N(2)–C(1)	126.2(3)	125.3(2)	125.8(2)	125.9(2)	125.8(2)	125.5(3)	126.1(2)	124.9(4)
O(1)–N(1)–C(2)	122.4(2)	122.2(2)	121.3(2)	121.8(2)	121.8(2)	122.1(3)	120.3(2)	119.8(4)
O(2)–N(2)–C(3)	122.4(2)	121.9(2)	122.6(2)	122.5(2)	122.1(2)	122.1(3)	120.1(2)	120.6(4)
C(1)–N(1)–C(2)	110.9(2)	112.2(2)	122.4(2)	112.0(2)	112.9(2)	111.8(3)	113.2(2)	115.7(4)
C(1)–N(2)–C(3)	111.1(2)	112.8(2)	111.3(2)	111.3(2)	112.1(2)	113.0(3)	113.6(2)	114.1(4)
N(1)–C(1)–N(2)	110.9(3)	111.0(2)	110.8(2)	110.7(2)	111.1(2)	109.9(3)	108.3(2)	106.9(4)
N(1)–C(2)–C(3)	100.5(2)	101.9(2)	101.0(2)	101.0(2)	101.6(2)	101.1(2)	102.0(2)	101.1(4)
N(2)–C(3)–C(2)	100.2(2)	101.7(2)	101.4(2)	101.0(2)	101.3(2)	100.5(2)	101.7(2)	101.2(4)

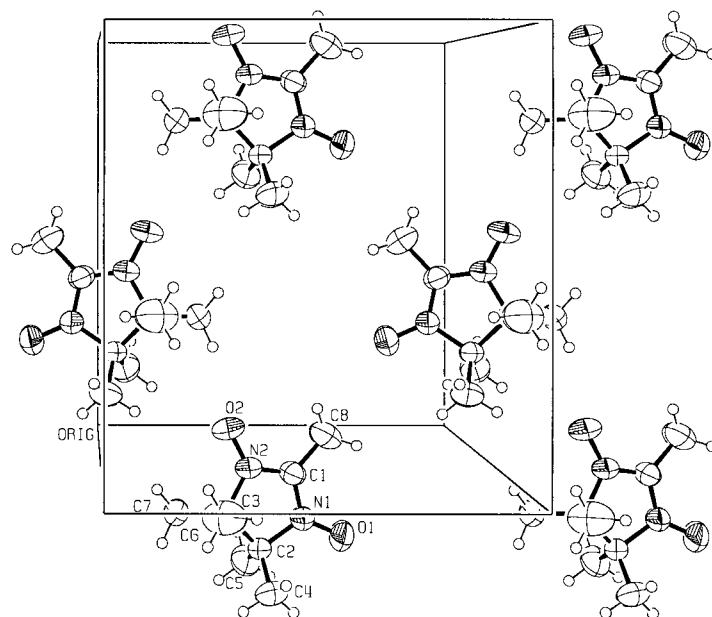
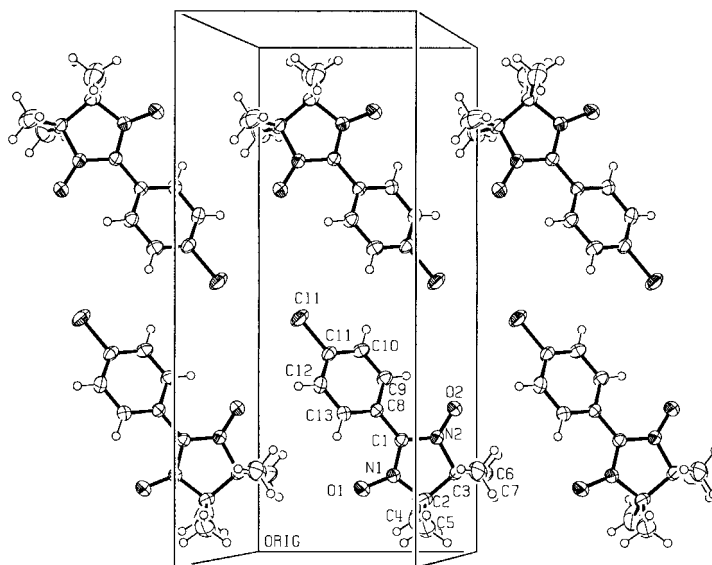
The packing of molecules in the crystal of compound **2** is shown in Fig. 3. Selected bond lengths and angles are given in Table 2.

The structure of compound **3** is shown in Fig. 4, and selected bond lengths and angles are also given in Table 2.

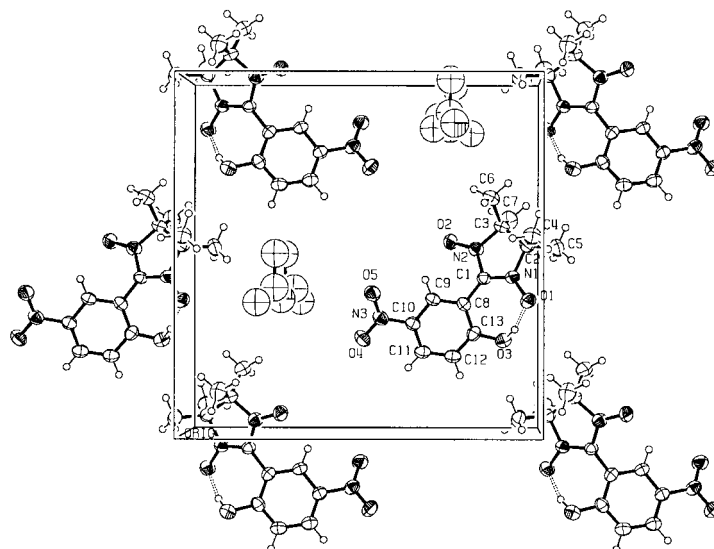
The molecular structure of **3** was known before from the crystal-structure determination of its complex with copper [16] and gadolinium [17]. The molecules are packed in layers perpendicular to the *c*-axis. A layer consists of ribbons related by an inversion center. As a result of the packing, the intermolecular distance between two Cl-atoms related by the inversion center is 3.360(2) Å, *i.e.*, shorter than the sum of *Van der Waals* radii (3.50 Å). The 4-chlorophenyl moiety is rotated by 25.2° with respect to the imidazole ring.

Compound **4** crystallized with disordered solvent molecules from ethyl acetate. The molecular packing in the unit cell is shown in Fig. 5, and selected bond lengths and angles are given in Table 2.

Intramolecular H-bonding between the phenyl OH group and the nitroxide O-atom determines the conformation of the molecule with respect to the rotation of the phenyl ring relative to the plane formed by nitronyl nitroxide. The torsion angle

Fig. 3. Packing of molecules of **2**Fig. 4. A layer in the crystal structure of **3**

$\text{N}(1)-\text{C}(1)-\text{C}(8)-\text{C}(13)$ is $-35.7(9)^\circ$, and the $\text{O}(1)\cdots\text{H}(3)$ distance is $1.58(8)$ Å. The molecular structure may be compared with that of 2-(2,5-dihydroxyphenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido(1*H*-imidazolyl-1-oxyl) [10]. The conformations of

Fig. 5. Packing of molecules of **4**

the two polymorphs that are determined by the intramolecular H-bond are very similar; the torsion angles are 36.6° and 38.2° in the two polymorphs, respectively, and the corresponding $O \cdots H$ distances are 1.59 and 1.73 Å.

In the compounds investigated, most bond lengths and angles at the radical site are practically equal, however some are significantly different. As a result of the intramolecular H-bond, the bond lengths involving the $O(1)-N(1)-C(1)-N(2)-O(2)$ moiety is significantly different in **4**. The $O(1)$ -atom is involved in a H-bond with the OH group and, therefore, the $N(1)-O(1)$ bond is longer than $N(2)-O(2)$ (1.312 and 1.292 Å, respectively), while the average of this bond in the other compounds is 1.280(5) Å. The $N(1)-C(1)$ bond shortens, and its double-bond character increases at the expense of $C(1)-N(2)$, whose double-bond character decreases (1.319 and 1.376 Å, respectively), while the average of this bond in the other compounds is 1.329(8) Å. The bond angles of the nitronyl nitroxide moiety in **3** and **4** are significantly different. The average of the $C(1)-N(1)-O(2)$ (equivalent to $C(1)-N(2)-O(2)$) bond angle is $125.8(3)^\circ$, while in **3** it is $126.2(2)^\circ$, and $124.6(4)^\circ$ in **4**. The average inner-ring bond angle at $N(1)$, $C(1)-N(1)-C(2)$ (and the equivalent $C(1)-N(2)-C(3)$) is $112.0(7)^\circ$, while it is $113.4(2)^\circ$ in **3** and $114.9(4)^\circ$ in **4**.

When **4** was heated to 100° , an exothermic process was observed by means of differential scanning calorimetry (DSC) (Fig. 6) ($\Delta H = 267.2$ kJ/mol). The major product (**5**) was isolated, crystallized, and its crystal structure was determined. As can be seen from Fig. 7, the two $N-O$ O-atoms are lost. The phenyl ring and the five-membered ring are almost coplanar ($N(1)-C(1)-C(8)-C(13)$ torsion angle of $9.5(5)^\circ$) due to the H-bond formed between $N(1)-H$ and $O(3)$ ($N(1)-H = 0.84(3)$ Å, $H \cdots O(3) = 1.976(7)$ Å, $N(1) \cdots O(3) = 2.600(4)$ Å, and $N(1)-H \cdots O(3)$ is $129.7(5)^\circ$). However the most-striking structural parameters are the bond lengths within the five-

membered ring of **5**. The geometry may be compared with the average values obtained from the similar compounds **6–10**. The C(8)–C(13) and C(13)–C(12) bonds (1.440(4) and 1.421(4) Å, respectively) are longer than typical C–C bonds in aromatic compounds, the average in **6–10** being 1.421(8) and 1.413(6) Å. The C(8)–C(9), C(9)–C(10), and C(10)–C(11) bonds are normal (1.387(4), 1.370(4), and 1.355(4) Å, respectively). Bonds N(1)–C(1) and N(2)–C(1) in the five-membered ring are too short for an N(sp³)–C(sp²) bond, and the average of the same bond in **6–10** is 1.298(16) Å. The O(3)–C(13) bond is longer (1.275(3) Å) than a classical carbonyl bond, the average in **6–10** is 1.307(10) Å. The H-bond between the charged O-atom and partially charged N-atom is strong, resulting in a short O...HN distance (1.98(3) Å relative to 1.52(15) Å in **6–10**).

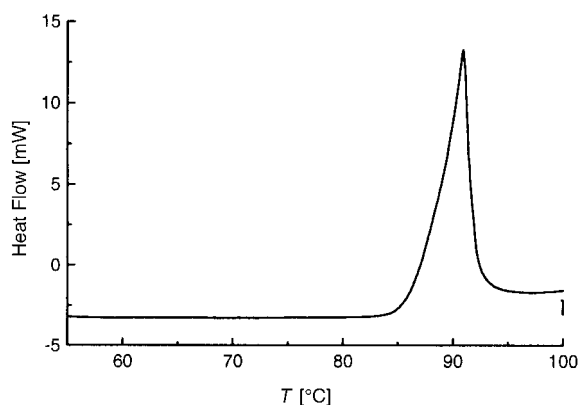
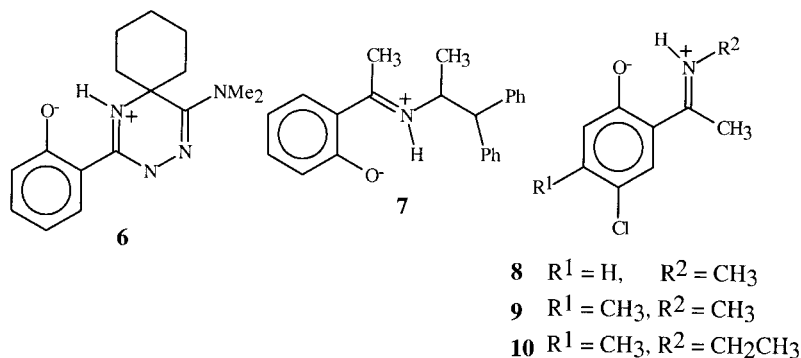
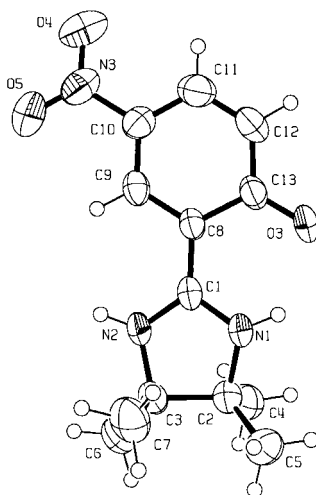


Fig. 6. DSC Thermograph of **4** at a heating rate of 3°/min

Magnetic Properties. The magnetic measurements have been performed on a *SQUID* magnetometer between 1.8 and 300 K using an externally applied magnetic field of 500 Oe. The value of the effective magnetic moment (μ_{eff}) of the β polymorph of **1** at room temperature, plotted per dimer (Fig. 8), is in reasonable agreement with the theoretical value of $1.73 \times \mu_{\text{B}}$ for an unpaired spin ($S=1/2$). However, $\mu_{\text{eff}}(T)$ decreases with decreasing temperature, with $\mu_{\text{eff}}=0.4 \times \mu_{\text{B}}$ at 1.8 K. This suggests a

Fig. 7. Molecular structure of **5**

dimer with a singlet ground-state and triplet excited state. The best fitting with the experimental data ($J = -15.0$ K) was obtained using *Bleany–Bower’s* singlet-triplet model [18] (Eqn. 1) with the effective *Dirac–Van Vleck–Heisenberg* Spin Hamiltonian ($H = -2\sum_{i,j} J_{i,j} S_i S_j$ [19]).

$$\chi = \frac{Ng^2 \mu_B^2}{3k_B T (3 + e^{-2J/k_B T})} \quad (1)$$

χ is the molar paramagnetic susceptibility, N is *Avogadro’s* number, g is the *Zeeman* g factor, μ_B is the electronic *Bohr* magneton, k_B is *Boltzmann’s* constant, T is the temperature, and J is the isotropic magnetic exchange coupling constant. The J value and μ_{eff} of the α polymorph have been previously reported to be -11.2 K and $2.0 \times \mu_B$, respectively [13]. We failed to reproduce the synthesis of the α polymorph to refine the magnetic measurements. The larger J value for the β phase of **1** in comparison with the α phase may be rationalized by the shorter H-bonds.

The dependence of the magnetic susceptibility on temperature for compounds **3** and **4** is shown in Fig. 9. The χT value for **3** and **4** (0.36 and 0.35 emu K/mol, respectively) in the high-temperature region corresponds to the theoretical value of 0.375 emu K/mol for unpaired spin ($S = 1/2$). Compounds **3** and **4** show no evidence of spin coupling ($\theta = 0$), in accord with the absence of short intermolecular contacts.

2-Chlorophenyl nitronyl nitroxide radicals exhibit a weak antiferromagnetic coupling with $J = -0.95$ K [20], and the α and β phase of 2,5-dihydroxyphenyl nitronyl nitroxide radicals exhibit a ferromagnetic coupling with $J = 0.95$ and 5.0 K, respectively (α phase ordered ferromagnetically below 0.5 K) [10].

Although the radicals **1**, **3**, and **4** form different types of H-bonds and *Van der Waals* interactions, only **1** exhibits spin coupling due to the strong intermolecular H-bonds. The weak *Van der Waals* forces in **3** and **4** do not transmit a similar magnetic coupling observed for 2-chlorophenyl nitronyl nitroxide radicals [20]. The H-bonds of **1** are

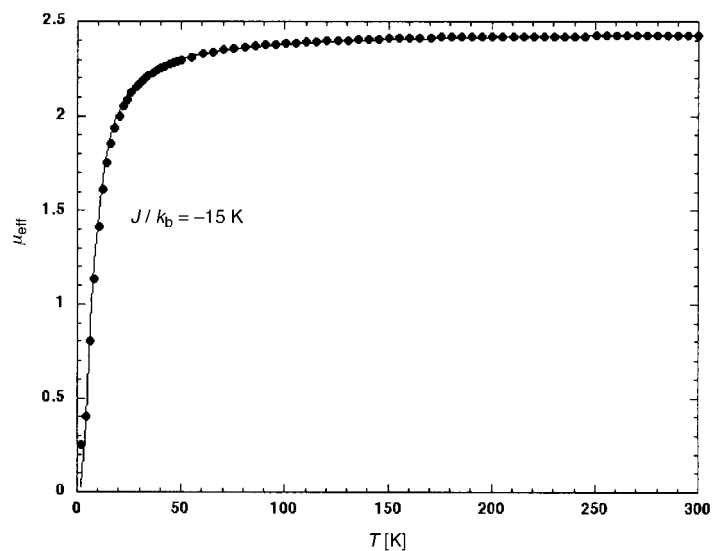


Fig. 8. Effective magnetic moment of **1** (β phase) as a function of temperature

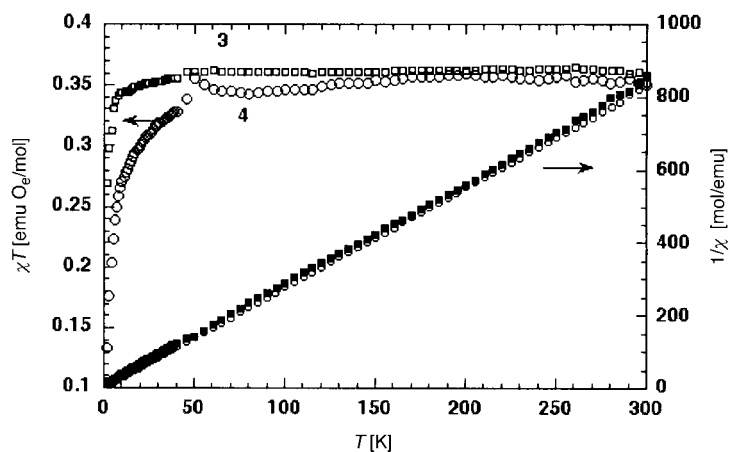


Fig. 9. Temperature dependence of χT and χ^{-1} for **3** and **4**

stronger than those of the 2,5-dihydroxy nitronyl nitroxide radical, but due to the lack of H-bonding networks, it does not exhibit any ferromagnetic coupling.

Experimental Part

Syntheses. Compounds **1** and **2** have been prepared according to literature procedures [21]. Compounds **3** and **4** were synthesized by the following procedure: a soln. of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (1 mmol, 148 mg) and 1.1 equiv. of the corresponding aldehyde in MeOH (25 ml) was stirred at r.t. for 24 h. Then, the imidazolidine was oxidized to nitronyl nitroxide with PbO_2 (15 mmol, 3.59 g) for 2–3 h. The residue was separated and washed with MeOH. The solvent was removed *in vacuo*, and the residue was chromato-

Table 3. Crystallographic Data and Parameters for 1–5

	α -1	β -1	2	3	4	5
Formula	C ₇ H ₁₃ N ₂ O ₂	C ₇ H ₁₃ N ₂ O ₂	C ₈ H ₁₅ N ₂ O ₂	C ₁₃ H ₁₆ ClN ₂ O ₂	C ₁₃ H ₁₆ N ₃ O ₅	C ₁₃ H ₁₇ N ₃ O ₃
M_r	157.19	157.19	171.22	267.73	338.34	263.30
Crystal color, habit	light yellow, prism	red, plate	dark red, plate	dark blue prism	blue, needle	Colorless, crube
Crystal dimensions	0.60 × 0.20 × 0.15	0.60 × 0.30 × 0.05	0.90 × 0.60 × 0.105	0.60 × 0.30 × 0.15	0.39 × 0.13 × 0.10	0.30 × 0.30 × 0.25
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/c$	$Pna2_1$	$P2_1/n$
a [Å]	11.741(4)	12.065(2)	16.897(4)	8.166(2)	7.169(2)	12.057(2)
b [Å]	11.502(4)	14.033(3)	10.242(4)	18.841(4)	15.101(3)	10.381(3)
c [Å]	6.251(3)	19.785(4)	11.283(4)	8.866(3)	14.999(3)	12.197(4)
α [°]	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	104.18(3)	93.02(2)	90.00	105.81(9)	90.00	117.22(3)
γ [°]	90.00	90.00	90.00	90.00	90.00	90.00
V [Å ³]	818.4(6)	3345.0(2)	1952.6(11)	1312.45(6)	1623.8(6)	1257.6(7)
Z	4	16	8	4	4	4
D_{calc} [g cm ⁻³]	1.276	1.249	1.165	1.355	1.384	1.288
μ (MoK α) [cm ⁻¹]	0.094	0.092	0.084	0.287	0.108	0.093
$F(000)$	340	1360	744	565	716	560
$2\theta_{\text{max}}$ [°]	50.06	50.10	46.00	50.210	50.06	50.0
Reflections collected	1583	6317	2129	3032	4450	2657
Independent reflections	1449	5910	1458	2339	2578	2392
Observed reflections	1178	3361	1357	1999	1466	1505
Largest difference peak [eÅ ⁻³]	0.212	0.569	0.232	0.451	0.295	0.184
Largest difference hole [eÅ ⁻³]	–0.270	–0.369	–0.214	–0.358	–0.243	–0.188
No. of parameters	109	430	114	183	218	184
R^a)	0.0618	0.0588	0.0696	0.045	0.0603	0.0631
wR^a)	0.1455	0.1460	0.1815	0.107	0.1443	0.1276
GOF ^b)	1.275	1.026	1.042	1.031	1.031	1.062

^a) $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. ^b) Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

graphed (SiO_2 ; CHCl_3). Some of the compounds (especially β -**1**) are unstable, and their crystals do not diffract well, which affects the refinement.

X-Ray Crystallography. Crystals suitable for X-ray-diffraction studies were obtained by slow evaporation of the reaction solvent. The diffraction-intensity measurements for α -**1**, **3**, and **5** were carried out on a *Philips PW-1100* four-circle diffractometer, and a *Nonius KappaCCD* diffractometer was used for compounds β -**1**, **2**, and **4**, with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit-cell parameters were determined from 20 to 25 well-centered, intense reflections (*Philips*), or from all the data (*Nonius*). Structure solutions and full-matrix least-squares refinements were accomplished with the *SHELXS-97* PC package [22]. All non-H-atoms were refined anisotropically, except for the disordered solvent present in **4**. All methyl H-atom positions were calculated geometrically, fixed at a C–H distance of 0.96 \AA (not refined). Other H-atoms were isotropically refined. Crystal data and further data-collection parameters for the compounds studied are summarized in *Table 3*.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-201084 (**3**), CCDC-201181 (**4**), CCDC-201182 (**5**), CCDC-201183 (**2**), CCDC-201184 (β -**1**), and CCDC-201185 (α -**1**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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