Crystal Structures and Magnetic Properties of a Nitronyl Nitroxide and of Its Imino Analogue. Crystal Packing and Spin Distribution Dependence of Ferromagnetic Intermolecular Interactions

Fabrice Lanfranc de Panthou, Dominique Luneau, Jean Laugier, and Paul Rey*

Contribution from the Commissariat à l'Energie Atomique, Département de Recherche Fondamentale sur la Matière Condensée, Laboratoire de Chimie de Coordination (URA, CNRS 1194), Service d'Etude des Systèmes et Architectures Moléculaires and Service de Physique des Matériaux et Microstructures, Centre d'Etudes Nucléaires de Grenoble, BP 85X, 38041 Grenoble Cedex, France

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Abstract: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-3-oxoimidazol-1-oxyl (**1**) and 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (**2**) have been prepared and structurally characterized by X-ray diffraction. While in the imino nitroxide **2** the molecules are arranged in pairs, in **1** the radicals are regularly stacked with the pyrimidyl planes being parallel. The magnetic behavior of the two compounds is strikingly different: in **2** intrapair antiferromagnetic interactions are fairly strong ($J = -54$ cm^{-1}, $H = -2JS_iS_j$), and in **1** a moderate intrastack ferromagnetic coupling (+18 cm^{-1}) is observed. This intrastack ferromagnetic behavior is rationalized in the frame of the McConnell mechanism, which involves short distances between atoms carrying spin densities of opposite sign. Relevant crystallographic parameters are as follows: **1**, tetragonal, space group $P4_2bc$, $a = 18.245(4)$ Å, $c = 7.427(2)$ Å, $Z = 8$; **2**, triclinic, space group $P\bar{1}$, $a = 6.888(2)$ Å, $b = 8.994(2)$ Å, $c = 9.469(3)$ Å, $\alpha = 91.56(1)°$, $\beta = 98.27(1)°$, $\gamma = 88.96(1)°$, $Z = 2$.

Considerable attention is being focused on molecular magnetic materials.[1] Approaches to their design include transition-metal ions linked by suitable ligands[2] or inorganic and organic spin carriers adequately arranged in a lattice.[3,4] Strategies aimed at synthesizing purely organic molecular materials have also been developed.[5,6] Using stable organic free radicals as building blocks, numerous molecules possessing a high-spin ground state have been described[6–8] but no three-dimensional polymeric materials which would exhibit bulk magnetic properties have been reported yet.

However, ferromagnetic three-dimensional order has been characterized in pure organic solids[9] which do not correspond to any predictive strategy. Uncontrolled crystal packing and uncharacterized intermolecular coupling pathways are responsible for the onset of bulk magnetic properties in these compounds. Among the three crystal phases of (*p*-nitrophenyl)nitronyl nitroxide, only the β phase exhibits a ferromagnetic behavior. This result points to the need of controlling crystal packing and intermolecular interactions for achieving bulk order in organic free radicals in the solid state.

Considering nitroxides, intermolecular nitroxyl–nitroxyl interactions have been reported[10,11] whose signs and magnitudes have been rationalized in the frame of crude theoretical methods.[11,12] While these calculations suggest that ferromagnetic interactions are possible, all the coupling pathways experimentally characterized so far document antiferromagnetic behaviors; the structural arrangement of the atoms of the NO groups at the corners of a parallelogram insures overlap of the magnetic orbitals and spin pairing. Therefore, this type of intermolecular contact is very efficient and hides any interaction of opposite sign which could result from another coupling mechanism.

We report, herein, the structural characterization and magnetic properties of two closely related nitroxide free radicals: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-3-oxoimidazol-1-oxyl (**1**) and 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (**2**). In the nitronyl nitroxide **1**, the molecules are arranged in stacks where the intermolecular coupling is ferromagnetic and fairly large. In the imino analogue **2**, the molecules are antiferromagnetically paired. In both compounds the magnetic properties are easily modeled and the structural features determining the magnetic behavior are fairly well understood. Compound **1** affords the first experimental evidence for a unidimensional structural arrangement of nitroxides in the

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Table I. Crystal Data and Experimental Parameters

compd	**1**	**2**
chem formula	$C_{11}H_{15}N_4O_2$	$C_{11}H_{15}N_4O$
space group	$P4_2bc$	$P\bar{1}$
a, Å	18.245(4)	6.888(2)
b, Å		8.994(2)
c, Å	7.427(2)	9.469(3)
α, deg		91.56(1)
β, deg		98.27(1)
γ, deg		88.96(1)
V, Å^3	2472.3	580.2
Z	8	2
T, °C	20	20
ρ, g cm^{-3}	1.264	1.255
μ, cm^{-1}	0.8	0.50
R	0.046	0.054
R_w[a]	0.039	0.060

[a] Weight = $1/[\sigma(F)^2+0.0001(F^2)]$.

solid state leading to a sizeable ferromagnetic intermolecular interaction corresponding to the McConnell mechanism.[13]

Experimental Section

Syntheses. Pyrimidine-5-carboxaldehyde[14] and 2,3-(dihydroxylamino)-2,3-dimethylbutane[15] were prepared by following reported procedures. The two free radicals were obtained as described by Ullman for the phenyl-substituted analogues[16] (**1**, 51%, mp = 138 °C; **2**, 23% from **1**, mp = 67 °C). Both compounds analyzed satisfactorily for the proposed formulas and exhibited expected solution EPR spectra. Crystals suitable for X-ray diffraction studies were grown by slow evaporation in the dark of concentrated solutions of **1** in benzene and **2** in hexane.

X-ray Data Collection and Structure Determination. Preliminary Weissenberg photographs showed the tetragonal and triclinic systems for **1** and **2**, respectively. Crystals of approximate dimensions 0.2 × 0.2 × 0.2 mm^3 were mounted on an Enraf-Nonius four-circle CAD-4 diffractometer equipped with graphite-monochromatized Mo Kα radiation. The unit cell parameters were obtained by a least-squares fit of the automatically centered settings from 25 reflections; they are reported in Table I with pertinent details regarding the determination of both structures. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

Concerning **1**, systematic absences were consistent with the $P4_2bc$ and $P4_2/mbc$ space groups. Density measurements ascertained the presence of $Z = 8$ molecules in the cell. Since the molecule might posses a C_2 axis, the second possibility ($P4_2/mbc$) could not be disgarded. Therefore, both possibilities were tested and the $P4_2bc$ space group was fully confirmed by all subsequent developments during the structure determination. For **2**, the same problem was solved, similarly taking as an initial choice the centrosymmetric space group $P\bar{1}$. In both cases, using direct methods included in the SHELX86 package,[17] the positions of most of the non-hydrogen atoms were obtained. Difference Fourier maps revealed electron densities appropriately located for the remaining heavy atoms. These were refined anisotropically; in the last refinement model, hydrogen atoms were included in fixed and calculated positions with isotropic thermal parameters equal to those of the connected carbon atom. Selected bond lengths and angles are reported in Table II. Summaries of crystal data and experimental parameters (Table SI), atomic positional parameters (Tables SII and SIII), bond lengths (Tables SIV and SV) and angles (Tables SVI and SVII), and anisotropic thermal parameters (Tables SVIII and SIX) are deposited as supplementary material.

Magnetic Measurements. Magnetic data were collected by use of a Quantum Design MPMS Superconducting SQUID susceptometer working at a 0.5-T field strength in the 2-300 K temperature range. The SQUID outputs were corrected for the contribution of the sample holder, and the magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms by use of Pascal constants.

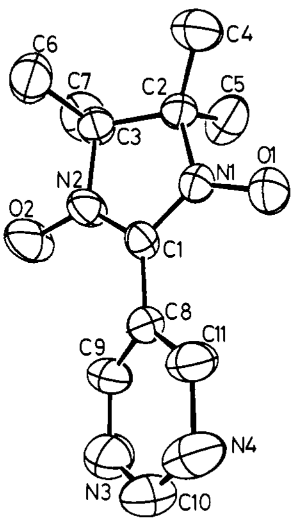

Figure 1. View of the molecular structure of **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

Table II. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

		compd **1**			
O1–N1	1.284(7)	O2–N2	1.283(5)	C1–N1	1.338(5)
C1–N2	1.336(5)	C1–C8	1.452(5)	C2–N1	1.492(5)
C3–N2	1.497(5)	C2–C3	1.551(7)		
C1–N1–O1	125.6(4)	C2–N1–O1	120.3(4)	C1–N1–C2	113.4(4)
C1–N2–O2	125.7(4)	C3–N2–O2	120.7(4)	C1–N2–C3	113.3(4)
		compd **2**			
O1–N1	1.268(4)	C1–N1	1.394(4)	C1–N2	1.280(4)
C2–N1	1.492(4)	C3–N2	1.504(3)	C1–C8	1.477(3)
C1–N1–O1	127.3(3)	C2–O1–N1	123.9(3)	C1–N1–C2	108.5(3)
C1–N2–C3	107.7(3)				

Results

Structural Studies. In compound **1**, the asymmetric unit comprises one molecule of the free radical. This molecule, represented in Figure 1, is unexceptional in exhibiting all the structural features already reported for numerous nitronyl nitroxides.[4,8,9] Of interest, however, is the angle between the five-membered ring and the aromatic pyrimidine ring, which amounts to 28.7(4)°.

By contrast, the intermolecular arrangement needs some comments. The unit cell comprises eight molecules of the free radicals which are arranged in pairs. Molecules within a pair are related by a $(-^1/_2 + x, ^1/_2 + y, ^1/_2 + z)$ symmetry which includes a translation of $\vec{c}/2$. Since the pyrimidyl rings are almost perpendicular to *c*, at the crystal level, one observes stacks of regularly spaced radicals parallel to the *c* axis. Close intrastack contacts are observed between adjacent pyrimidyl rings which are rigorously parallel, their main axis (C8–C10) making an angle of 57° so that the shortest distance (3.6(1) Å) is observed between nitrogen atoms of one ring and carbon atoms of the next ring. Such a short distance is possible because this arrangement brings the two five-membered fragments carrying the NO groups sufficiently far apart to avoid steric complications. However, short intermolecular distances involving NO groups are observed. As shown in Figure 2, one NO group of each molecule is directed inside the stack and the other directed outside the stack. Within a stack the groups are fairly close (N1–O′1 = 3.24 Å), and despite the complicated geometry, the four atoms (N1, O1, N′1, and O′1) are in the same plane at the vertexes of a trapezium. Along a stack one observes a distorted ladder whose steps are the NO

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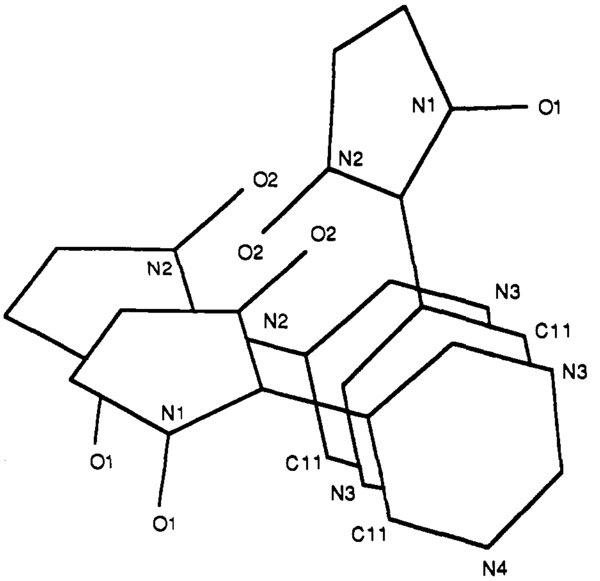

Figure 2. View of a triad of molecules stacked along the *c* axis in **1**. The methyl groups have been omitted.

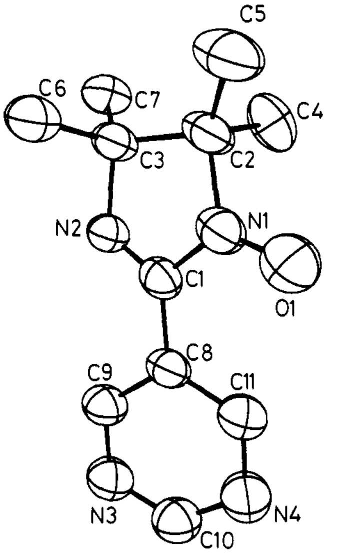

Figure 3. View of the molecular structure of **2** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

bonds. In addition, each of these inner NO groups experiences another interaction with an external group of the adjacent molecule at similar distances (3.37 Å). The closest intermolecular contact (2.92(1) Å), however, is observed between the oxygen atom of one molecule and the bridging sp^2 carbon (C1) of the next molecule. No contact shorter than 6.2 Å is observed between the NO groups which have their oxygen atoms directed toward the outside of the stack and those of the four neighboring parallel stacks. Since, in a molecule, the five- and the six-membered rings are not coplanar (28.5°), within a stack, the conjugated fragments of two adjacent molecules (O1–N1–C1–N2–O2 and O′1–N′1–C′1–N′2–O′2) make an angle of 48.5(6)°.

The structure of compound **2** is shown in Figure 3. Other structural information about imino nitroxides is available from coordinated species[18] or from the α-dinitroxide[19] whose structure is partly disordered. Therefore, the present report is probably the more reliable concerning the structural properties of this class of nitroxides. Compared to the nitronyl nitroxide **1**, the conjugated imino–nitroxyl fragment (O1–N1–C1–N2) is also planar but no longer symmetrical, the imino nitrogen atom being short–bonded to the adjacent carbon atom. Significantly shorter also is the NO bond length (1.268(4) vs 1.283(5) Å). Finally, in **2**, the two ring fragments make an angle of 19.1(4)°.

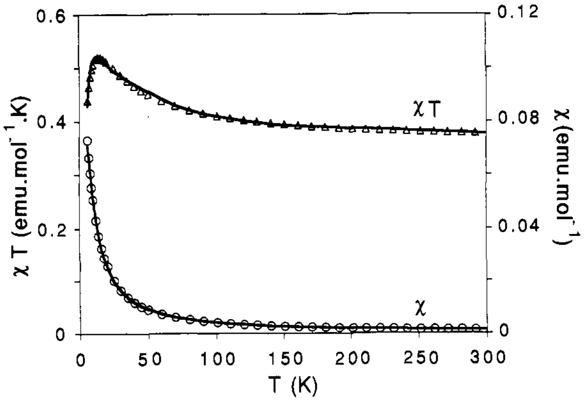

Figure 4. Temperature dependence of X (○) and XT (△) for compound **1**. The solid lines are calculated with the parameters reported in the text.

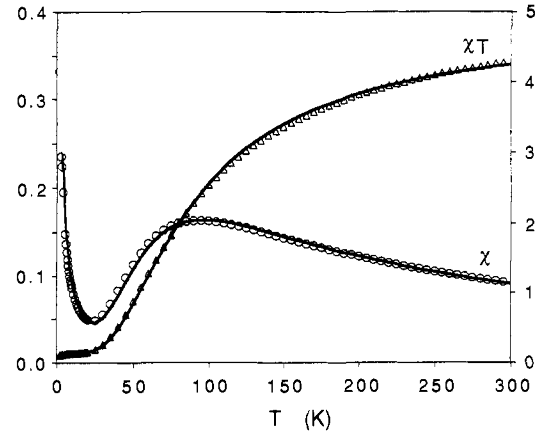

Figure 5. Temperature dependence of X (○) and XT (△) for compound **2**. The solid lines are calculated with the parameters reported in the text.

In the crystal, the unit cell contains a pair of centrosymmetrically related molecules of the imino nitroxide where the head-to-head arrangement brings the nitroxyl groups far apart. However, close internitroxyl contacts (3.14(8) Å) are observed within pairs of molecules related by the center of inversion and an $\vec{a} + \vec{b}$ translation. Therefore, from the magnetic point of view, the two compounds are strikingly different. While in **1** identical intermolecular contacts between NO groups are observed within a stack, in **2** contacts are limited to pairs. It is worth noting that interpair distances between atoms carrying spin density are larger than 8.9(2) Å.

Magnetic Studies. The magnetic behavior of the compounds is depicted in Figures 4 and 5 in the form of the temperature dependence of the magnetic susceptibility and of the product of the magnetic susceptibility with the temperature for **1** and **2**, respectively. For both compounds the room temperature value of XT (0.378 and 0.376) emu K mol^{-1}) is identical to that expected for uncorrelated spins (0.375 emu K mol^{-1}, 1.73 μ_B). On lowering the temperature, in **1** XT increases and exhibits a maximum at 14 K (XT = 0.52 emu K mol^{-1}, 2.00 μ_B) and then decreases, while in **2** a constant decrease of XT from 0.376 to 0.03 emu K mol^{-1} is observed. These qualitative features suggest that in **2** the free radicals are antiferromagnetically coupled, while in **1** some ferromagnetic interaction is predominant at intermediate temperatures and then weaker antiferromagnetic couplings are involved at lower temperatures.

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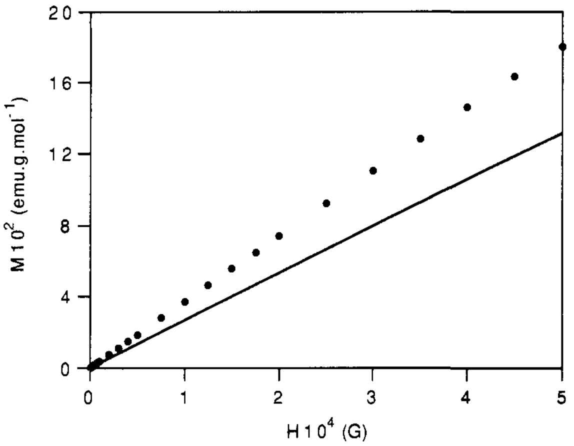

Figure 6. Field dependence of the magnetization for compound **1** at 14 K. Experimental data (●) and the Brillouin function for $S = {}^1/_2$ (—).

The structural results suggest models for interpreting the magnetic data. In **1**, intra- and interchain interactions of opposite sign must be included in the model. Both antiferro- and ferromagnetic intrachain interactions were considered and interchain couplings were modeled in the frame of the mean molecular field approximation. Assuming isotropic Heisenberg interactions, published expressions of the magnetic susceptibility for antiferro-[20] and ferromagnetically[21] coupled linear arrays of ${}^1/_2$ spins are respectively

$$X_{\mathrm{ch1}} = ((Ng^2\mu_B{}^2)/kT)(A + Bx + Cx^2)/(1 + Dx + Ex^2 + Fx^3)$$

where $x = J/kT$, $A = 0.25$, $B = 0.149\,95$, $C = 0.300\,94$, $D = 1.9862$, $E = 0.688\,54$, and $F = 6.0626$, and

$$X_{\mathrm{ch2}} = [(1.0 + 5.797\,991K + 16.902\,653K^2 + 29.376\,885K^3 + 29.832\,959K^4 + 14.036\,918K^5)/(1.0 + 2.797\,991\,6K + 7.008\,678K^2 + 8.653\,864\,4K^3 + 4.574\,311\,4K^4)]^{2/3}$$

where $K = J/2kT$.

In both cases, the total magnetic susceptibility is[22]

$$X_{\mathrm{i}} = X_{\mathrm{chi}}/[1 - 2zJ'X_{\mathrm{chi}}/(Ng^2\mu_B{}^2)]$$

where J' is the interchain interaction and $z = 4$ is the number of neighboring chains.

Fitting the data to the first expression gave very poor results, while a very good agreement was obtained using the second expression. This finding agrees with the fact that the stronger interaction which shows up at intermediate temperatures is ferromagnetic and corresponds to the behavior of the chain where intermolecular contacts are short. The best fit values are as follows: $J = +18.2(3)$ cm^{-1}, $J' = -0.77(2)$ cm^{-1}, $R = \sum(X_{\mathrm{obsd}} - X_{\mathrm{calcd}})^2/\sum(X_{\mathrm{obsd}})^2 = 3.4 \times 10^{-5}$.

Since the XT value at 14 K (0.52 emu K mol^{-1}) exceeds that expected for independent spins, the field dependence of the magnetization at this temperature was examined. This dependence is shown in Figure 6 and compared to the Brillouin function calculated for independent $S = {}^1/_2$ spins. The data clearly show that there is a ferromagnetic correlation between the $S = {}^1/_2$ units at 14 K. The field dependence of the magnetization was also examined at the lowest temperature (2 K) and up to the highest field (5.5 T) we could reach. This experiment was suggested by a reviewer and designed in order to check if the compound could behave as a metamagnet. No evidence for such a behavior was observed; very low temperature measurements will be performed using the SNCI facilities in Grenoble.

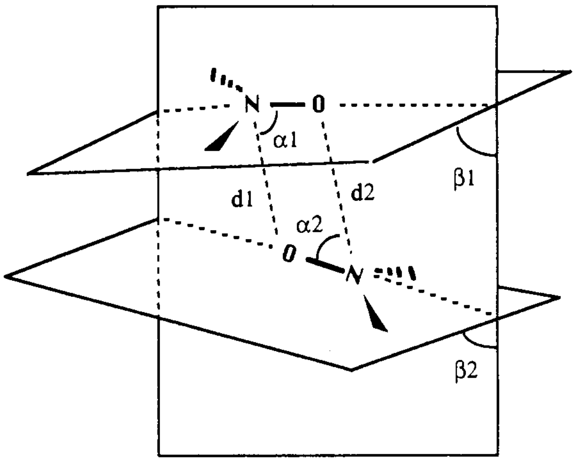

Figure 7. Definition of the parameters used in the discussion of nitroxyl–nitroxyl interactions.

Finally, the presence of magnetic interactions in **1** is further supported by EPR spectra which show an exchange-narrowed single line with a Lorentzian line shape.[23]

For compound **2**, according to the structural results, the magnetic data were fitted to a Bleaney–Bowers expression[24] of the magnetic susceptibility for a pair:

$$X = (Ng^2\beta^2/kT)/(3 + \exp(-2J/kT))$$

where $2J$ is the singlet–triplet gap and the other symbols have their usual meaning. Since the data concern organic radicals, calculations did not include a contribution from the temperature-independent paramagnetism.

Although Figure 5 shows that antiferromagnetic interactions are predominant in **2**, the rising tail observed at low temperatures for the temperature dependence of the magnetic susceptibility is the signature for the presence of a small amount of an uncoupled paramagnetic impurity. The Bleaney–Bowers formula was modified accordingly, and fitting of the data leads to the following parameters: $g = 2.007$, $J = -54(1)$ cm^{-1}, P(impurity) = 0.7%, $R = 7 \times 10^{-5}$.

Despite their related chemical structures, in the solid state, different structural arrangements result in predominant magnetic interactions of opposite sign in **1** and **2**.

Discussion

Intermolecular ferromagnetic interactions[7] have been observed in nitroxides and even three-dimensional long-range order[9] has been characterized in a few compounds. The magnitude of these interactions, however, is usually so weak that precise exchange pathways have not been ascertained. In contrast, numerous antiferromagnetic intermolecular interactions have been characterized for piperidinyl and pyrrolidinyl nitroxides. They are spread over a large energy range. Actually, some nitroxides are so strongly coupled in the solid state that they are diamagnetic at room temperature,[25,26] while others exhibit uncorrelated spins down to 2 K.[27] Complete or partial radical spin pairing may be described considering the structural parameters defined in Figure 7, which depicts the most commonly observed planar arrangement of the NO groups at the corners of a trapezium. Large interactions

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Table III. Geometrical Parameters Describing Nitroxyl–Nitroxyl Interactions in **1** and **2**

compd	**1**[a]		**2**	$CuCl_2(NITPh)_2$	$[Ni(hfac)_2NITEt]_2$	$[CuCl_2(NIT_pPy)_2]$[a]	
d_1, Å	3.24	3.27	3.88	3.53	3.53	3.73	3.67
d_2, Å	4.41	4.89	3.88	3.53	3.53	3.73	3.67
α_1, deg	50.6	21.2	46.3	97.9	65.3	76.8	72.3
α_2, deg	101.3	100.5	133.7	82.1	114.7	103.2	107.7
β_1, deg	59	61	95	84	66	56	79
β_2, deg	32	63	95	84			
J, cm^{-1}			–55	–67.5	–36	–3.7	

[a] There are two coupling pathways.

occur when the nitroxyl groups are oriented in a head-to-tail fashion at distances $d \approx 3$ Å and when the α and β angles are such that σ overlap between the individual π^* orbitals is maximum ($\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 90°$). Worth noting, ferromagnetic couplings are accounted for by this scheme when $\beta_1 = 90°$ and $\beta_2 = 0°$, a geometry resulting in orthogonal magnetic orbitals. Intermediate situations lead to weaker positive or negative couplings. Available examples of interacting nitronyl nitroxides[28] are not so numerous, but correlation between geometry and exchange coupling follows the same trends.[11]

This scheme corresponds to the structural arrangement of the interacting NO groups within a pair in **2** with parameters $d = 3.88$ Å, $\alpha_1 = 46.3°$, $\alpha_2 = 133.7°$, and $\beta_1 = \beta_2 = 95°$. One notices that the short distance and the β angles close to 90° favor orbital overlap, which is reduced by values of α angles far from 90°. Examples of geometries leading to intermolecular interaction in nitronyl nitroxides[11,28] are reported in Table III, for comparison. It can be seen that a value of $J = -54$ cm^{-1} for **2** is quantitatively in agreement with the parameters describing the geometry of the interacting NO groups in this compound.

Relevant geometrical parameters describing the interactions between NO groups in **1** are also reported in Table III. As described before (Figure 3), two types of nitroxyl–nitroxyl intrastack interactions are observed. Considering a molecule, the NO group directed inside the stack experiences two equivalent interactions with the corresponding nitroxyl groups of the two nearest neighbor molecules and a third interaction with the NO group directed outside of the stack of one of the neighbors. Despite this complicated network, examination of the parameters reported in Table III leads to the following qualitative results. Ferromagnetic coupling through direct interaction of the NO groups can be excluded because both types of geometries are far from that which would bring the magnetic orbitals orthogonal. Considering antiferromagnetic interactions, one notes inter-nitroxyl distances slightly larger than 3 Å and angles within the trapeziums far from 90°. The resulting overlap is reduced because the O1–N1–C1–N2–O2 planes of two adjacent molecules are not parallel (48.5°). Thus, considering only inter-nitroxyl interactions, one expects moderate antiferromagnetic coupling within a stack in **1**.

Since the magnetic data bring unambiguous evidence for an intrastack ferromagnetic interaction, one must consider other possible mechanisms for exchange coupling between the individual nitroxide molecules in **1**. Rationalization of ferromagnetic behavior in conjugated π radicals is very often rationalized on the basis of an intermolecular coupling mechanism suggested by McConnell,[13] which involves spin polarization leading to alternating positive and negative spin densities on the carbon backbone of these molecules. The theoretical background of this mechanism has been recently settled down by Kollmar and Kahn,[29,30] who also demonstrated its implication in unidimensional coordination compounds.[31]

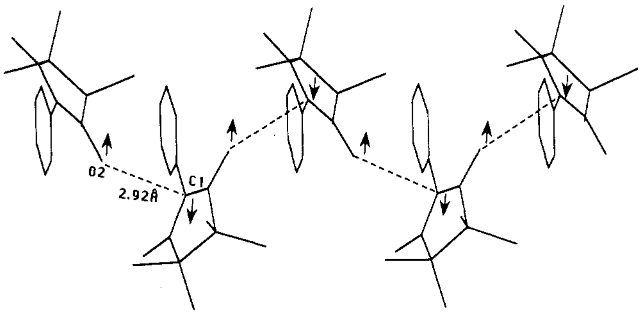

Figure 8. Sketch of a stack in **1** showing the alternating spin densities responsible for the ferromagnetic coupling.

Distribution of the spin density in nitronyl nitroxides substituted by aromatic groups is experimentally documented by a recent polarized neutron diffraction study of the phenyl-substituted radical.[32] Most of the contribution to the magnetization comes from the NO groups which carry equal positive spin densities. However, a large negative spin density on the sp^2 carbon atom bridging the two NO groups and weak alternating contributions on the phenyl ring are observed. These features were qualitatively known from theoretical calculations[33] which, in addition, suggested that in pairs of interacting nitronyl nitroxides close contact of a NO group carrying a positive spin density with the sp^2 carbon atom belonging to the other molecule would result in strong ferromagnetic coupling. Accordingly, it is now accepted that such a spin distribution arising from polarization in these conjugated π radicals may play an important role regarding the nature of intermolecular interactions in the solid state.

As mentioned in the Results, in **1** the shortest intermolecular distance (2.92 Å) between adjacent nitronyl nitroxides within a stack involves the oxygen atom of one of the NO groups of a molecule and the sp^2 carbon atom of the neighboring molecule. Since these two atoms carry significant spin densities of opposite sign which alternate along the stack, the requirements of the McConnell mechanism are fulfilled. A schematic representation of the alternating spin densities is given in Figure 8, which also describes the geometrical features relevant to the interaction between the sites carrying the spin density. It can be seen that the O1(nitroxyl)–C1(sp^2) direction is perpendicular to the carbon containing a conjugated fragment of the free radical and that the interatomic distance (2.92 Å) is equal to the sum of the van der Waals radii of the two atoms. Since the spin densities are located in p orbitals perpendicular to the nitroxide mean planes, for a given angle between these planes, (48.5°) this geometry ensures the maximum interaction between the spin-carrying sites.

In addition to the nitroxyl–nitroxyl contacts, another significant short intermolecular distance is found between the regularly spaced parallel pyrimidyl fragments. Assuming on these rings an alternating spin distribution identical to that observed in the phenyl analogue,[32] the staggered arrangement of the neighboring

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rings along a stack in **1** affords another coupling pathway involving atoms carrying spin densities of opposite sign, which matches the McConnell's criteria. Such a situation is identical to that observed in bis(phenylmethylenyl)[2.2]paracyclophanes,[34] where a similar structural arrangement leads to a triplet ground state.

The magnitude of the interaction resulting from these two exchange pathways ($+18$ cm^{-1}) is weaker than expected. Actually, it is only twice as large as that reported for 2-(3-*R*-pyridinium)-nitronyl nitroxides,[7] in which the molecules are arranged into pairs where a ferromagnetic interaction develops through close contact (≈ 3 Å) between a nitroxyl oxygen and a remote atom of the pyridinium substituent. Since in **1** both the nitroxyl oxygen and the sp^2 carbon atoms carry spin densities that are 1 order of magnitude larger than those expected on an aromatic substituent,[32] a much larger coupling constant might have been anticipated. It is therefore likely that the antiferromagnetic contribution to the exchange coupling due to direct nitroxyl–nitroxyl interaction cancels a large part of the ferromagnetic contribution resulting from the McConnell mechanism.

Although compound **1** was designed for obtaining close stacking of pyrimidyl fragments, the remarkable arrangement of the other part of the molecule was not anticipated. Moreover, the crystal structure of compound **2** shows that the crystal structure depends on other intermolecular interactions which, in this case, are more efficient than stacking of the aromatic fragments. Among these, nitroxyl–nitroxyl interactions and spin pairing are probably important and seem to result in another structural arrangement. Concerning compound **1**, weaker nitroxyl–nitroxyl interactions are present but both exchange pathways involving opposite spin densities which also result in spin pairing probably contribute to minimize the lattice energy. In **2** the spin distribution is not known and, probably, such a contribution is not possible or weaker.

Nitronyl nitroxides are unique in exhibiting a negative spin density on the sp^2 carbon atom bridging the two NO groups, which is one third that carried by the adjacent nitrogen atoms.[32] Even in metal complexes where the spin distribution is strongly modified, such a large negative contribution to the magnetization has been observed.[35] This property has initiated much work aimed at understanding the properties of the few nitroxides which order at low temperatures. In (*p*-nitrophenyl)nitronyl nitroxide the onset of the ferromagnetic phase occurs at 0.65 K.[9] The low value of the Curie temperature points to very weak intermolecular interactions. In this case, the McConnell mechanism is probably also implicated through a weak negative spin density carried by a remote atom of the *p*-nitrophenyl group. Polarized neutron diffraction experiments currently under way in our laboratories will shed light on coupling mechanisms in this compound.

In summary, compound **1** is the first example of unidimensional material built from organic free radicals and exhibiting a fairly large intermolecular ferromagnetic interaction through a well-characterized exchange pathway involving contacts between atoms carrying spin densities of opposite sign. The unidimensional structure of the compound is promising for the design of species of higher dimensionality which would order ferromagnetically in the bulk.

Supplementary Material Available: Tables of crystal data and experimental parameters (Table SI), atomic fractional coordinates (Tables SII and SIII), bond lengths (Tables SIV and SV) and angles (Tables SVI and SVII), and anisotropic thermal parameters (Tables SVIII and SIX) (9 pages). Ordering information is given on any current masthead page.

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