2-(2-Methyl-1,3-propanediol)-4,4,5,5-tetramethyl-3-oxylimidazoline 1-Oxide − An Antiferromagnetically Coupled Nitronyl Nitroxide

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The synthesis, X-ray structure, and the magnetic properties of 2-(2-methyl-1,3-propanediol)-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide are described. The nitronyl nitroxide packs in stacks of dimers. Two CH_2O–H···O–N hydrogen bonds and one CH_2OH group of each nitronyl nitroxide link two molecules into a dimer. The additional CH_2OH group in each molecule forms CH_2O–H···O–N hydrogen bonds to a second dimer and so on, leading finally to columns of dimers. Each column is surrounded by six other columns. The magnetic behaviour of the crystal is strongly temperature dependent, evidence for intermolecular interactions between the molecules at room temperature. DFT calculations support an antiferromagnetic coupling of nitronyl nitroxide molecules in the dimer.

Introduction

Organic magnetic materials are currently of high interest[1−4] in the search for organic materials which are ferromagnetic not only at very low temperature but also at room, or even higher, temperatures. Magnetic properties, as bulk properties, are dependent on the relative three-dimensional alignment of the spin-carrying units and the distance between them.[2] Nitronyl nitroxides as a class of stable organic radicals are of special interest, especially since one of these radicals was the first purely organic radical to exhibit ferromagnetism, although only at very low temperature.[5,6] In order to influence the spatial position of radicals in a crystal lattice, hydrogen bonds were introduced as directing forces in the synthesis of hydroxyphenyl-substituted nitronyl nitroxides.[7−11] We recently studied *o*-, *m*-, and *p*-hydroxymethyl-substituted 2-phenylnitronyl nitroxide[12] in the context of our general interest in crystal engineering.[13] It was discovered that the magnetic properties of these radicals depend on the position of the substituent at the aromatic ring. The *meta* isomer displays antiferromagnetic coupling of the electron spins at low temperature while the other two isomers are characterized by temperature-independent paramagnetism, with an onset of a weak ferromagnetism at very low temperature. Here we describe the synthesis, X-ray structure, and the magnetic properties of a nitronyl nitroxide with a 2-methyl-1,3-propandiol unit in the 2-position of the heterocycle. The magnetic properties of this nitronyl nitroxide radical are evaluated by DFT calculations.

Results and Discussion

2-(2-Methyl-1,3-propanediol)-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**1**) was prepared in 55% overall yield by condensation of 3-hydroxy-2-hydroxymethyl-2-methylpropanal[14] and 2,3-diamino-*N*,*N'*-dihydroxy-2,3-dimethylbutane,[15] and oxidation of the 1,3-dihydroxy-imidazoline derivative in situ by lead dioxide. The compound was purified by sublimation.

The structure of nitronyl nitroxide **1**, as obtained by X-ray diffraction,[16] is shown in Figure 1. The nitronyl nitroxide unit is planar while the five-membered ring is slightly puckered (dihedral angle $N^1-C^2-C^3-N^2$ = 27°). The puckering relieves strain between the methyl groups at C^2 and C^3. One hydroxy group is involved in an intramolecular

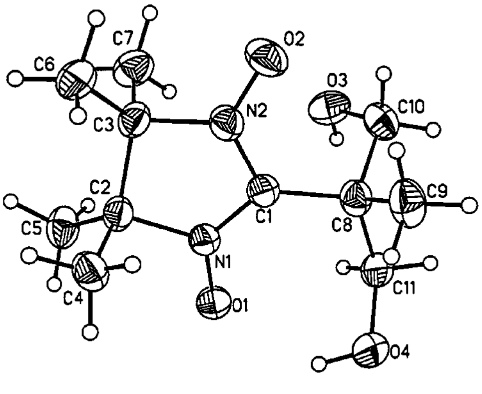

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Figure 1. X-ray structure of 2-(2-methyl-1,3-propanediol)-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**1**)

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O−H···O−N hydrogen bond (OH···O: 212 pm; O···O: 279 pm; O−H···O: 134°). The dihedral angles between N^1C^1 of the nitronyl nitroxide and the $C-CH_2OH$ bonds of the substituent are 175° and 302°, respectively. The OH group involved in the intramolecular hydrogen bond binds to the oxygen atom of an NO group of a second nitronyl nitroxide molecule (Figure 2) resulting in a dimer that is held together by two such strong O−H···O interactions (OH···O: 225 pm; O···O: 298 pm; O−H···O: 141°). The planes of the nitronyl nitroxide units in the dimer adopt an angle of 79°, and are thus almost orthogonal. The closest O···O distance between two oxygen atoms of NO groups of different molecules is 293 pm; the distance between an oxygen atom and the nearest C^1 of a nitronyl nitroxide is 464 pm.

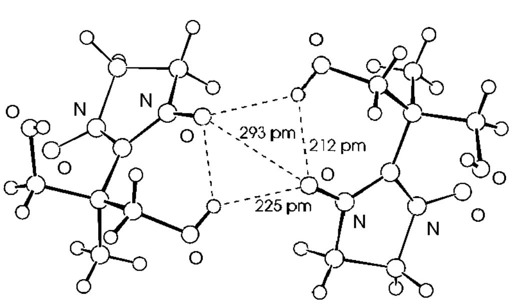

Figure 2. Dimer formation of **1** in the crystal showing the hydrogen bonds (methyl groups removed)

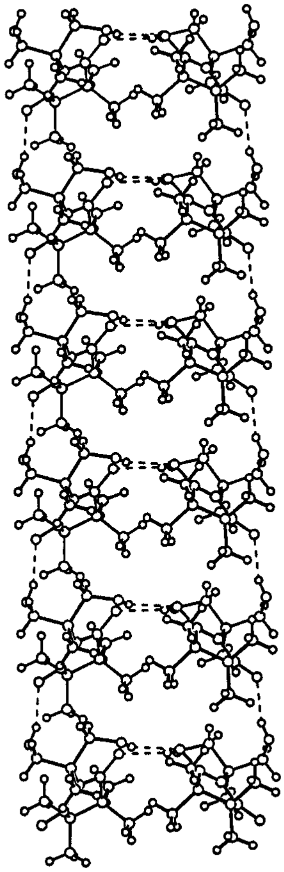

Figure 3. Stacks of dimers of **1** in the crystal lattice

The OH group of the hydroxymethyl group of each nitronyl nitroxide that is not involved in dimer formation points to the oxygen atom of a nitronyl nitroxide unit of a second dimer, thus connecting the two dimers by two hydrogen bonds (OH···O: 201 pm; O···O: 278 pm; O−H···O: 160°). This leads to a stack formation (Figure 3). Identical nitronyl nitroxide molecules in a stack are packed parallel to each other. The stacks are arranged in columns. An analysis of these columns and a top view (Figure 4) reveals that the only interactions between molecules in different columns are van der Waals interactions: there are no inter-column hydrogen bonds.

What is the influence of the crystal packing on the magnetic property of the bulk material? Figure 5 displays the result of the SQUID measurement as the product of the magnetic susceptibility and temperature versus the temperature. The value of the product χT at room temperature is, at 0.371 cm^{-1} K mol^{-1}, slightly lower than the theoretical value for non-coupled spins (0.375 cm^{-1} K mol^{-1}). On lowering the temperature the product χT decreases steadily reaching a value of 0.06 cm^{-1} K mol^{-1} at 2 K. In the $1/\chi$ presentation it is shown that the experimental data can be simulated using the Curie−Weiss law with a Weiss constant Θ of −24.2 K ($g = 2.063$) over almost the whole temperature range. Since the crystal packing of **1** clearly shows short intermolecular contacts between two adjacent radicals and a columnar structure of these radical pairs, several attempts were made to fit the susceptibility data using either a simple dimer model with the Heisenberg−Dirac−Van Vleck (HDVV) Hamiltonian $H = -2J{\cdot}S1{\cdot}S2$ or with a linear-chain model of antiferromagnetically coupled $S = 1/2$, using Equation (1) with $x = |J|/kT$.[17]

$$\chi = \frac{Ng^2\beta^2}{kT}\frac{0.25+0.074975x+0.075235x^2}{1+0.9931x+0.172135x^2+0.757825x^3} \tag{1}$$

The calculated susceptibilities, representing the best fit to the experimental data for both models, are shown in Figure 5 as dotted and dashed lines for the dimer model and for the chain model, respectively. The agreement for both curves to the experimental data is relatively poor.

A good fit, however, was obtained using the dimer model with an additional Theta−Weiss correction for intermolecular interactions between the dimers. In order to elucidate the supposed strong correlation between the parameters J and Θ an error surface was calculated. As shown in Figure 6 the correlation was found to be very strong, and only a broad local minimum was found. All pairs of parameters along the local minimum gave a satisfactory simulation of the experimental data. The best fitting parameters with the lowest Theta−Weiss constant were found to be $g = 2.00$ (fix), $J = -6.4(3)$ cm^{-1} and $\Theta = -14.9(5)$ K. The reliability of the fit is 3.9×10^{-7} if the correlation of the parameters J and Q is suppressed by holding one or the other value constant. These values are most reasonable with respect to the results of the crystal structure determination.

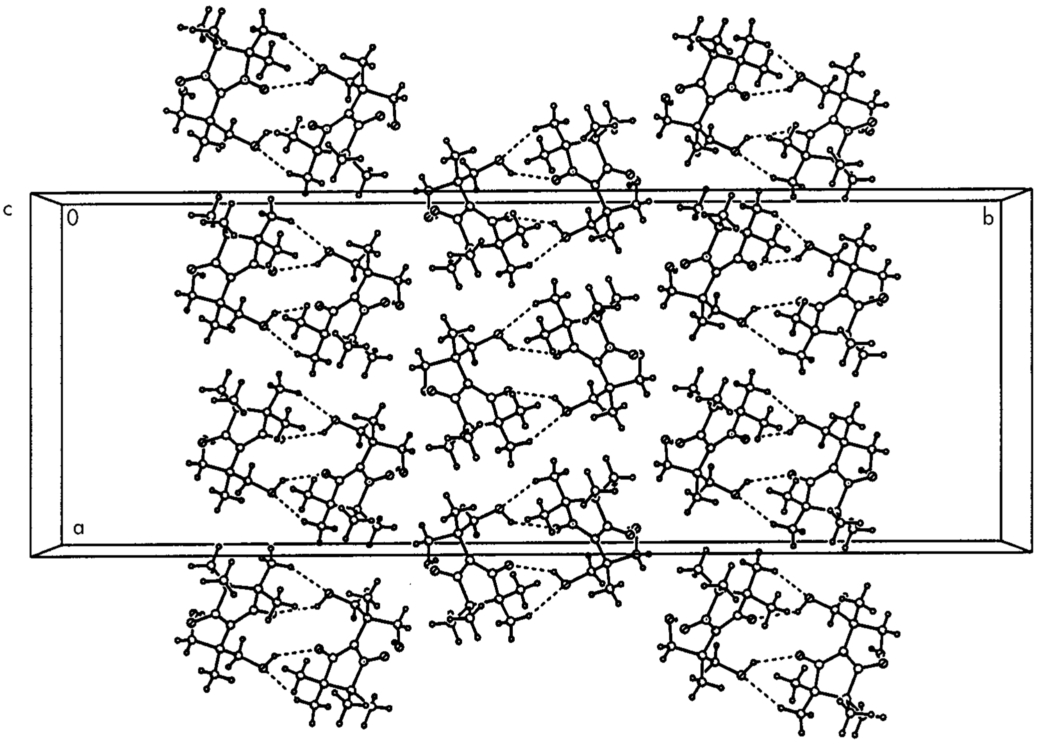

Figure 4. View on the top layer of individual stacks of **1** along [001]

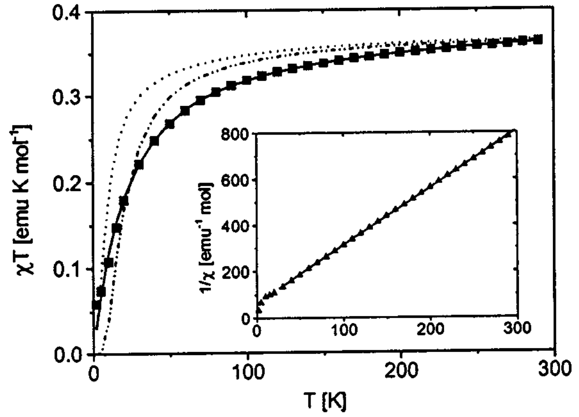

Figure 5. Experimental (■) and calculated temperature dependence of the χT product for radical **1**; the dotted line represents the calculated curve for the linear chain model (with $|J| = 8.18$ cm^{-1}), the dashed line represents the best fit using a strictly dimeric model (with $2J = -12.33$ cm^{-1}), and the solid line represents the best fit using a dimeric model with an additional correction for intermolecular interactions [$2J = -6.4(3)$ cm^{-1}, $\Theta = -14.9(5)$ K]; the inset shows the temperature dependence for $1/\chi$ (▲) together with the Curie–Weiss curve for $g = 2.063$ and $\Theta = -24.2$ K

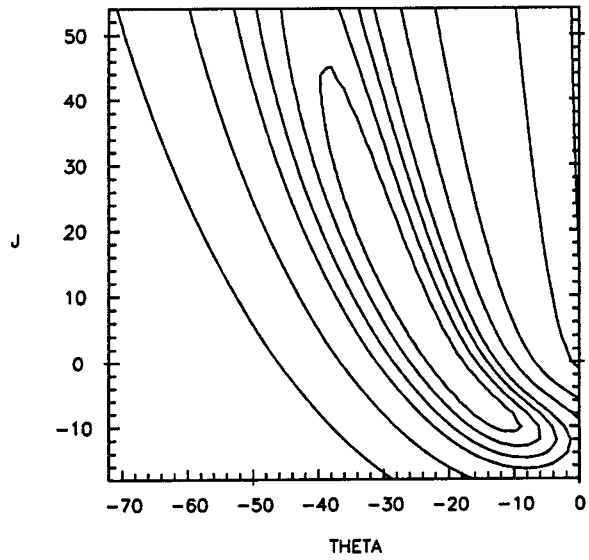

Figure 6. Error surface for the parameters J and Θ

Strong magnetic interactions are expected when spin-carrying units come close to each other. This system fulfils this requirement, as the nearest O···O distance of two NO groups of different molecules is 293 pm. However, a requirement for the stabilization of a high-spin state is that the SOMOs of different radicals do not overlap: they should be orthogonal. One of these conditions, a small separation, is fulfilled, whereas the other one, the orthogonality of the SOMOs, is not realized satisfactorily, which, as a consequence, leads to an antiferromagnetic coupling of the unpaired electron spins.

Theoretical Considerations

The first theoretical treatment of ferromagnetism in solid organic radicals was given by McConnell as early as 1963,[18] and extended later in 1967.[19] The role of orbital interactions in the context of ferromagnetic interactions has been discussed more recently by Yoshizawa and Hoffmann.[20] A comprehensive treatment of molecular

Table 1. Energy differences ($\Delta_{S-T;}$ kcal mol^{-1}) between singlet and triplet states of dimers of 2-(2-methyl-1,3-propanediol)-4,4,5,5,-tetramethyl-3-oxylimidazoline 1-oxide according to the arrangement in the crystal

Entry	Method	E_S (au)	E_T (au)	Δ_{S-T} (cm^{-1})
1	UB3LYP/6−31G*[a]	−1683.614834	−1683.614605	−49.0
2	UB3LYP/6−31G*[b]	−1369.311576	−1369.311370	−45.5
3	UB3LYP/6−31G*[c]	−754.237710	−754.237480	−52.5
4	UB3LYP/6−311G**[b]	−1369.732871	−1369.732687	−42.0
5	UBLYP/6−31G*[b]	−1368.849891	−1368.849428	−101.6
6	UBP86/6−31G*[b]	−1369.314749	−1369.314223	−115.6
7	USVWN/6−31G*[b]	−1362.250433	−1362.249667	−168.1

[a] Original dimer with all substituents. − [b] Dimer with methyl groups at C-4 and C-5 replaced by hydrogen atoms. − [c] All substituents removed and replaced by hydrogen atoms.

magnetism is given by Khan.[2] The spatial arrangement of the spin-carrying molecules will finally determine the overall magnetism. Model ab initio MO calculations demonstrated how the spin-carrying molecular orbitals have to be placed in order to obtain ferromagnetism.[21,22] The importance of through-bond and through-space effects has been studied by Barone et al.,[23] and the role of hydrogen bonds in transmitting magnetic interactions has been discussed by Veciana et al.[24]

Among the numerous theoretical calculations, agreement seems to exist that, on the basis of ab initio MO theory, including electron correlation, reliable results can be obtained for exchange interactions.[25−32] Density functional theory (DFT) has been applied successfully several times. Although magnetism is a bulk property, and therefore calculations should be carried out on large three-dimensional arrays, a limitation in size is imposed by the feasibility of such calculations. Thus, in most cases where attempts have been made to obtain theoretical support for observed magnetic properties, the calculations were restricted to pairs of molecules or to small molecular clusters.

Nitronyl nitroxide **1** displays a pronounced antiferromagnetic coupling, and the relative arrangement in the crystal is governed by hydrogen bonds. We therefore decided to study the magnetic properties of dimers of **1** in the arrangement of the crystal lattice by DFT methods. The systems were gradually simplified in order to emphasize the importance of the presence of certain structural features. The results of the DFT calculations[33] on the singlet and triplet states of the dimer of 2-(2-methyl-1,3-propanediol)-4,4,5,5-tetramethyl-3-oxylimidazoline 1-oxide (**1**) in the geometry established by X-ray diffraction are reported in Table 1.

Entry 1 describes the results for the unmodified dimer, and shows a small preference for a singlet ground state. This preference is maintained when the methyl groups are replaced by hydrogen atoms and different basis sets are applied (entries 2 and 4). The Δ_{S-T} values increase somewhat, from −101.6 to −168.1 cm^{-1}, when applying pure density functionals.[24]

The transmittance of spin polarization by hydrogen bonds has been discussed previously,[24,34] and was postulated to be of importance in alkyne-substituted nitronyl nitroxide radicals.[35] Thus it could be that the two strong, intermolecular hydrogen bonds influence the stability of the spin states. This has been tested in a calculation in which all substituents in the dimer were replaced by hydrogen atoms, thus making the transmittance of spin polarization by the hydrogen bonds impossible. Again, no change in the preferred spin multiplicity (entry 3) is observed.

The small energy separation between the two states, and the preference of the singlet as the ground state, seem to be in agreement with the experimental findings. The calculation corresponds to zero Kelvin, and is therefore in line with the predominance of antiferromagnetic interactions in the low temperature range. The S−T separation is so small that thermal energy should lead to a statistical spin distribution, i.e. to paramagnetic material at higher temperatures.

Conclusion

Radical **1** is one of the smallest substituted nitronyl nitroxides in which O−H···O hydrogen bonds determine the crystal structure. This leads to relatively small distances between nearest neighbours in the lattice and favours large exchange interactions. The structure imposed by the hydrogen bonds generates a large antiferromagnetic coupling. This is confirmed by DFT calculations on segments of the crystal lattice.

Experimental Section

General: IR: BIO-RAD FT-IR 135. − ^{1}H NMR and ^{13}C NMR Spectra: Bruker DRX 500. − Mass spectra: VG ProSpec 3000; − ESR: Bruker ESP 300 E. − Carlo Erba elemental analyzer. − Quantum Design MPMS SQUID magnetometer. − melting points (uncorrected) Büchi 510.

3-Hydroxy-2-hydroxymethyl-2-methylpropanal: This compound was prepared according to ref.[14] starting from diethyl (diethoxymethyl)methylmalonate. The final step, the hydrolysis of the diethylacetal of 3-hydroxy-2-hydroxymethyl-2-methylpropanal, was modified: 10.3 g (53.0 mmol) of the acetal was added to 125 mL of 0.05 M sulfuric acid and stirred for 2 h at room temperature. The solution was then neutralized with saturated barium hydroxide solution. After filtration this solution was immediately introduced, without isolation of the aldehyde, into the condensation reaction with 2,3-bis(hydroxylamino)-2,3-dimethylbutane.

4,4,5,5-Tetramethyl-2-(2′-methyl-1′,3′-propanediol)-1-oxide-3-oxyl-imidazoline: 3-Hydroxy-2-(hydroxymethyl)-2-methylpropanal (6.22 g, 53.0 mmol) was added to a solution of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (7.83 g, 53.0 mmol) in 125 mL water (assuming a 100% yield in the previous step, product not isolated).[15] The mixture was stirred and kept under Ar overnight. Lead dioxide (50.7 g, 0.21 mol) was then added to this solution. After stirring for two hours the solution turned deep red. The solution obtained after removing the lead salts was extracted repeatedly with trichloromethane until the aqueous solution remained only slightly yellow. The trichloromethane was then removed under vacuum after drying over magnesium sulfate. The solid, deep-red coloured residue was dissolved in the minimum amount of ethyl acetate at room temperature. The crystals which formed after several days at 0 °C after keeping the vessel in the dark under an atmosphere of nitrogen were collected. Yield: 7.21 g (55%), m.p. 119 °C. For elemental analysis the nitronyl nitroxide was purified by sublimation under reduced pressure. $C_{11}H_{21}N_2O_4$ (245.3): calcd. C 53.86, H 8.63, N 11.42; found C 53.92, H 8.65, N 11.53. − ESR ($CHCl_3$): quintet 1:2:3:2:1, $a_N = 0.76$ mT.

X-ray Crystallographic Data

Crystal Structure of 1: $C_{11}H_{21}N_2O_4$, red crystals, dimensions 0.29 × 0.18 × 0.13 mm^3, measured with a Siemens SMART 1K CCD detector system at 193 K; $a = 17.168(10)$, $b = 47.18(3)$, $c = 6.193(3)$ Å, $V = 5016(5)$ Å^3, $Z = 16$, $\rho = 1.299$ g cm^{-3}, space group $Fdd2$, 5741 intensities measured ($\theta_{max} = 28.45°$), 1670 independent ($R_{int} = 0.0279$), 1576 observed [$F_o > 4\sigma(F)$], structure solution by direct methods and refinement of 154 parameters on F^2 with the Siemens-Bruker software package SHELXTL Vers. 5.03, $R1 = 0.0447$, $wR2$ (all data) = 0.1134, Gof = 1.150, max electron density 0.326 eÅ^{-3}.

Acknowledgments

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