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LETTERS

Synthesis, Structural, EPR and Magnetic Analysis of Nitronyl-nitroxide labelled Isophthalic acid

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Abstract: The high yield synthesis of an isophthalic acid derivative bearing a nitronyl-nitroxide moiety at the 5-position was achieved. The structural analysis in the crystalline phase by X-ray diffraction on single crystals revealed the formation of a 3-D network through strong H-bonds between the acid groups and the nitronyl-nitroxide moieties. The spin label obtained was also analysed by EPR spectroscopy which showed a five line pattern with a_N=7.51 G and a g-factor of 2.0066. Magnetic measurements revealed that at low temperature, the systeme showed a Curie-Weiss like behaviour with weak ferromagnetic intermolecular interactions. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Macroscopic properties such as magnetism, electronic or optical conductivity result from the tridimensional organisation of atoms or molecules. Crystalline molecular materials are defined by the nature of molecules composing the solid and by the interactions between them in the condensed phase.[1] So far, our efforts were mainly directed towards the understanding of structural factors governing the formation of molecular networks in the solid state. The ultimate goal of our approach is to extend the structural features to functional aspects. Since the discovery of nitronyl-nitroxide as stable free radical[2], and the report on the first purely organic molecular magnet based on organic stable radicals[3,4], substantial effort has been devoted to the design and synthesis of substituted nitronyl-nitroxide[5-8]. On the other hand, the role of H-bonding on magnetic response of a variety of nitronyl-nitroxide derivatives bearing phenol moieties has been recently investigated[9]. Having in mind our own investigations on the formation of H-bonded 1- and 2-D molecular networks[10] using cyclic bis-amidinium dications and dicarboxylates such as isophthalate, we thought we could design magnetic molecular networks by using a stable isophthalic acid derivative bearing an unpaired electron such as compound **1**.

In the present communication we report the first synthesis of the compound **1** composed of the isophthalic core bearing at the 5-position the 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-N-oxide moiety as well as its structural (X-ray), spectroscopic (EPR) as well as magnetic investigations .

The synthetic route used for the preparation of compound **1** is shown on the following scheme. The strategy followed is based on the elegant work of Ulmann consisting in the coupling of an aldehyde with a dihydroxylamine derivative[2]. The starting material used was the commercially available trimesic acid **2**. The latter was first transformed into the triester[11] **3** and then partially saponified to the mono acid **4**[12]. The acid was first

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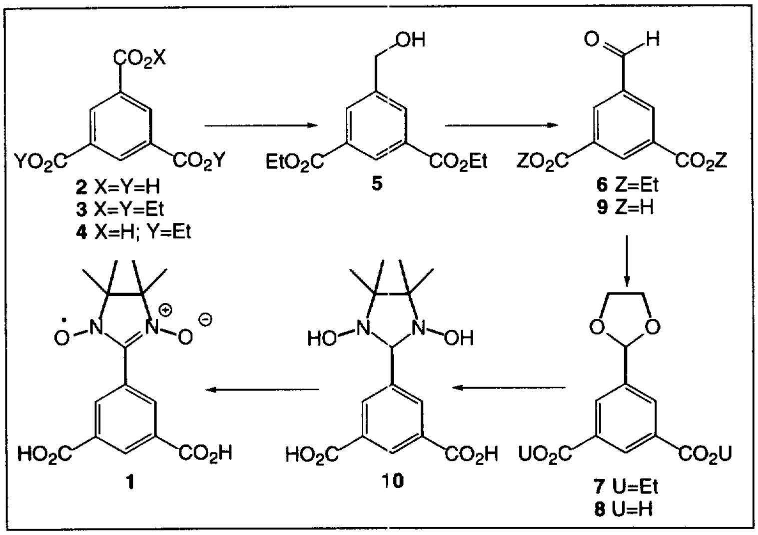
reduced in 86 % yield using Me_2S-BH_3 complex in THF[12] and the resulting alcohol **5** was oxidised in 85 % yield to the aldehyde **6** using MnO_2 in CH_2Cl_2[13]. After protection of the aldehyde (86 % yield) using glycol and *para*-toluenesulfonic acid in toluene, the compound **7** thus obtained was saponified (NaOH, H_2O, EtOH) to the diacid **8** in 86 % yield. The quantitative deprotection of the latter by 2M HCl in acetone afforded the aldehyde **9** which was condensed with 2,3-dimethyl-2,3-butanediylbis-(dihydroxyl ammonium) sulfate leading thus to the bis-N-hydroxyl amine derivative **10** in 67 % yield. The oxidation of the latter by $NaIO_4$ in H_2O give the desired stable nitronyl-nitroxide **1** in 77 % yield as a violet solid.



The solid structure of compound **1** was investigated by X-ray crystallography on single crystals obtained from THF/hexane mixture[14]. The following features were observed. Compound **1** crystallised in the tetragonal space group (Figure 1).

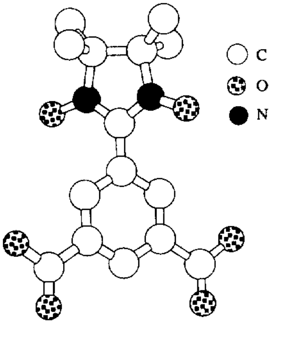


Figure 1 : solid-state structure of the molecular unit (for bond distances and angles see text). For sake of clarity H atoms are not represented.

Compound **1** was indeed in the acidic form with average C=O and C-OH bond distances of 1.194 Å and 1.313 Å. This was further confirmed by IR (KBr) which showed the presence of a band at 1726 cm^{-1}. Whereas both carboxylic moieties were almost in the plane containing the phenyl ring with an average deviation of 3°, the nitronyl-nitroxide group on the other hand was tilted by 46.4°. The N2-O3 and N5-O6 bond distances of 1.282 Å and 1.290 Å respectively indicated, as expected, the delocalisation of the unpaired electron. Interestingly, all units were found to be interconnected through strong OH···ON hydrogen bonds with a distance of 2.627 Å between carboxylic acids and nitronyl-nitroxide fragments (Figure 2). Thus, the overall structure may be described as a 3-D network (Figure 3). The formation of H-bonded network was previously reported for benzoic acid bearing at the 4 position the nitronyl-nitroxide unit.[15]

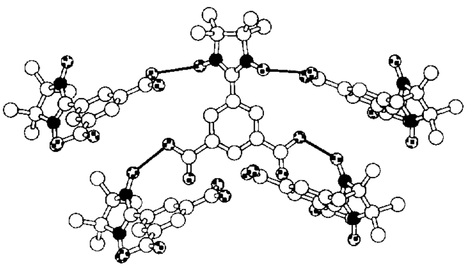


Figure 2 : Surroundings of molecular units in the lattice. All units are interconnected through strong OH···ON hydrogen bonds with a distance of 2.627 Å between carboxylic acids and nitroxide fragments. For the sake of clarity, H atoms are not represented.

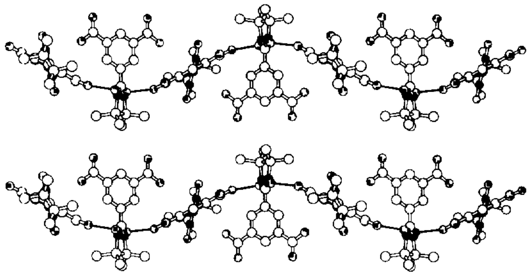


Figure 3 : A portion of the crystal structure showing the interconnection through strong OH···ON hydrogen bonds of molecular units in the solid state. The overall structure may be described as a 3-D network. For the sake of clarity, H atoms are not represented.

The EPR solution signal of the compound **1** was recorded at room temperature in THF ($8x10^{-4}$ mol/l). As expected, a five lines pattern due to two equivalent ^{14}N nuclei with a_N=7.51 G and a *g*-factor of 2.0066 was observed. These values are in agreement with the reported values for nitronyl nitroxide radical derivatives[2]. The complete oxidation of the radical precursor **10** was confirmed upon estimating the doublet spin concentration ($N_{S=1/2}$) which was found to be 1.0 ± 0.1 spin/molecule. The UV-Visible spectrum in MeOH at rt. showed absorption bands at 257, 363 and 584 nm.

For compound **1**, the temperature dependence of the product of the static molar susceptibility by the temperature (χT) was measured using a SQUID susceptometer(0.5 T). The room temperature value of the χT product for **1** was close to the expected value for an isolated single radical (χT 0.38 emu.K.mol^{-1}). A Curie-Weiss like behaviour was observed for **1** with a small upturn at low temperature. It revealed weak ($\theta<0.5$ K) but ferromagnetic intermolecular interactions throughout the H-bond network in the lattice.

In summary, the synthesis of isophthalic acid functionalised with the 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-N-oxide unit at the 5-position was achieved in high yield and its solid state structure was elucidated by X-ray analysis which revealed the formation of a 3-D network based on H-bonding between the acidic OH protons and oxygen atoms of the nitronyl-nitroxide groups. Magnetic measurements revealed that at low temperature, the systeme showed a Curie-Weiss like behaviour with weak ferromagnetic intermolecular interactions. The use of the above mentioned compound in the formation of molecular networks in the presence of amidinium type building blocks as well as the study of their magnetic properties are under current investigation.

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14. *X-ray data for* **1** : $C_{15}H_{17}N_2O_6$, M = 321.31, tetragonal, a = 8.0500(1), c = 23.5145(5) Å, U = 1523.80(7) Å^3, space group P 4_1 2_1 2, Z = 4, Dc = 1.40 gcm^{-3}, μ(Mo-Kα) = 0.110 mm^{-1}, crystal dimensions 0.20x0.15x0.15 mm. Data were measured at 294K on a Kappa CCD. R = 0.053, Rw = 0.074 for 875 independent observed reflections $[|F_o| > 3\sigma(|F_o|]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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