Two-dimensional Network of the Ferromagnetic Organic Radical, 2-(4-Nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-Oxide

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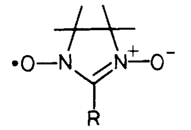
X-Ray crystal analysis and MO calculations have been carried out on the organic radical, 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide, revealing a 2-D ferromagnetic network linked by $N^{\delta+} \cdots O^{\delta-}$ Coulombic attraction.

The quest for molecular/organic ferromagnetism is a subject of contemporary interest. We have already reported[1,2] the magnetic properties of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide (**1**); this radical possesses a ferromagnetic (FM) intermolecular interaction comparable to the thermal energy of 1 K, while most organic radicals exhibit antiferromagnetic (AFM) interactions. The FM interaction in (**1**) is, further, proved to cover more than 4 radicals by magnetization curve measurements. We now describe the molecular and crystal structure of (**1**).† The magnetostructural correlation of (**1**) is discussed, based on the results of MO calculations.

The nitroxide (**1**) was prepared by the reported method[3] and was crystallized from benzene. The atom numbering scheme and the molecular conformation of (**1**) are given in Figure 1. The phenyl ring is almost coplanar with the nitro group, but forms an angle of 50.3° with the plane of the nitronyl nitroxide, O(1)–N(1)–C(1)–N(2)–O(2). In the phenyl analogue (**2**), the corresponding dihedral angle is about 30°.[4,5] The nitroxide (**1**) is more twisted than (**2**), in spite of the fact that (**1**) can resonate with the planar quinonoid-type structure. The molecular distortion in (**1**) may be ascribed to the effect of intermolecular interaction, as is shown later.

The projection of the crystal structure of (**1**) along the *b* axis is shown in Figure 2. Weak intermolecular contacts between the O atoms in the NO groups and the N atoms in the NO_2 groups are possible, and the radical (**1**) forms a 2-D network by these contacts. Figure 3 shows the intermolecular conformation in this network. N(3) of the NO_2 group is located almost at the mid point between O(1^{i}) and O(2^{ii}) in neighbouring radicals. O(1^{i}) ··· N(3) and N(3) ··· O(2^{ii})



(**1**)R = p-$O_2NC_6H_4$
(**2**)R = Ph

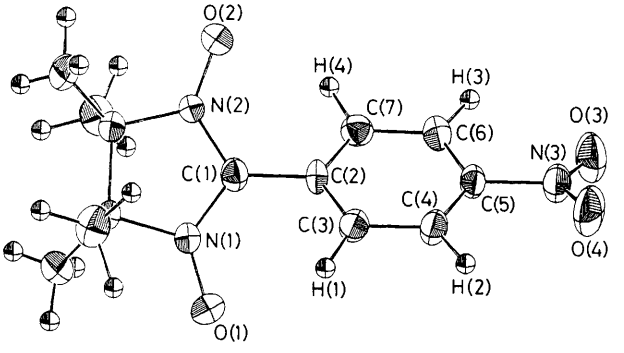


Figure 1. Atom numbering scheme and molecular conformation of (**1**). Selected interatomic distances (Å) and angles (°): O(1)–N(1) 1.276(6), N(1)–C(1) 1.357(10), N(2)–O(2) 1.267(9), N(2)–C(1) 1.351(7), C(1)–C(2) 1.470(6), C(2)–C(3) 1.385(6), C(3)–C(4) 1.397(7), C(4)–C(5) 1.382(8), C(5)–N(3) 1.473(6), N(3)–O(3) 1.224(7), N(3)–O(4) 1.216(6); O(1)–N(1)–C(1) 125.5(4), N(1)–C(1)–N(2) 108.7(4), C(3)–C(2)–C(7) 121.3(4), C(2)–C(3)–C(4) 119.6(5).

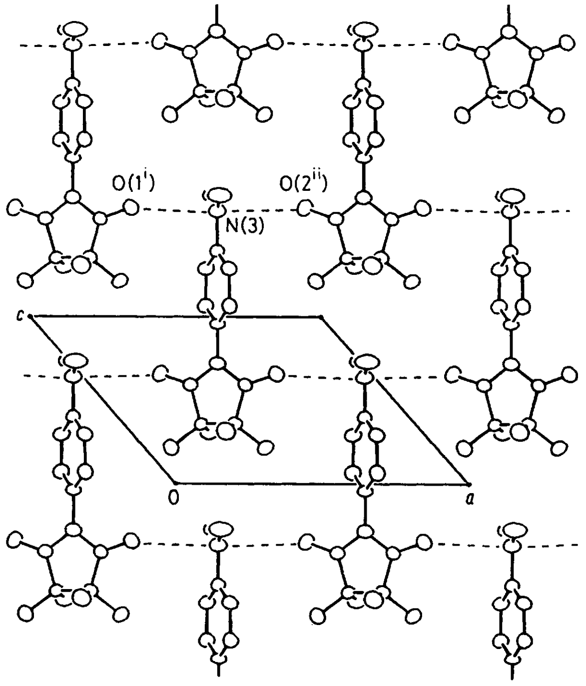


Figure 2. Projection of the structure of (**1**) along the *b* axis. Symmetry operations: (i) *x*, *y*, *z* + 1; (ii) *x* + 1, *y*, *z* + 1.

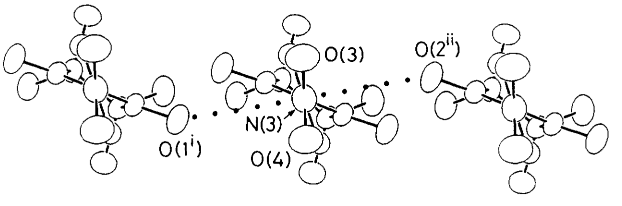


Figure 3. Molecular arrangement of (**1**) in the 2-D network projected on the *ab* plane.

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† *Crystal data:* $C_{13}H_{16}N_3O_4$, green–black, $M = 278.29$, monoclinic, space group *Cc*, $a = 10.960(3)$, $b = 19.350(3)$, $c = 8.257(3)$ Å, $\beta = 131.61(1)°$ at room temp., $U = 1309.2(7)$ Å^3, $Z = 4$. Data with $2 < 2\theta < 60°$ were collected on a RIGAKU AFC-5 four-circle diffractometer with monochromatic Mo-K_α radiation. $R(F) = 0.0412$ for 902 independent reflections with $|F_o| > 3\sigma(F_o)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. The calculated atomic charges of (**1**).

O(1)	−0.3370	C(3)	−0.0267
O(2)	−0.3370	C(4)	0.0039
O(3)	−0.3386	C(5)	−0.0700
O(4)	−0.3386	C(6)	0.0039
N(1)	0.0960	C(7)	−0.0267
N(2)	0.0960	H(1)	0.0891
N(3)	0.4853	H(2)	0.0976
C(1)	−0.0290	H(3)	0.0976
C(2)	0.0334	H(4)	0.0891

distances are 3.359(8) and 3.372(8) Å, respectively, and the angle O(1^{i}) · · · N(3) · · · O(2^{ii}) is 175.9°. The nitrophenyl plane is almost perpendicular to the O(1^{i}) · · · N(3) · · · O(2^{ii}) vector.

MO calculations have been carried out using an MNDO RHF-doublet method. The atomic charges obtained are in Table 1. Large positive and negative charges appear on N(3) and O atoms, respectively. The calculation implies that the 2-D network arises mainly because of Coulombic attraction between the negative charges on O(1^{i}) and O(2^{ii}), and the positive one on N(3). These intermolecular contacts probably result in the twisted molecular structure of (**1**). The results of the MO calculation also indicate that the unpaired electron occupying the SOMO is localized on the side of the nitronyl nitroxide and has little population in the nitrophenyl ring, whereas NHOMO and NLUMO (the highest doubly occupied and the lowest unoccupied MO) are distributed mainly in the nitrophenyl ring. At the contact points in the 2-D network, therefore, the intermolecular overlap between SOMOs could be much smaller than those between SOMO–NHOMO and/or between SOMO–NLUMO. This feature resembles that in the FM organic radical, galvinoxyl.[6–8] Thus, the FM interaction of (**1**) originates mainly in the SOMO–NHOMO and/or SOMO–NLUMO interactions, and the same applies to the FM coupling of galvinoxyl. This mechanism is given in detail in ref. 8. The FM interaction in (**1**) is considered to operate in this 2-D sheet *via* N · · · O contacts, consistent with the magnetization curve measurements.[1,2]

α-Nitronyl nitroxides are known to form complexes with various transition metals, and FM interactions between nitroxides and metal ions have been reported in some metal complexes.[9] The intermolecular contacts of (**1**) in the 2-D sheet, N(1^{i})–O(1^{i}) · · · N(3) · · · O(2^{ii})–N(2^{ii}), are similar to the co-ordination bonding mode between nitroxides and transition metals, N–O · · · M^{n+} · · · O–N, N(3) with a positively polarized-charge playing the role of the metal ion.

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