# An Organic Ferromagnet: α-Phase Crystal of 2-(2′,5′-Dihydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide (α-HQNN)

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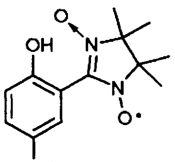
The α-phase crystal of 2-(2′,5′-dihydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide (α-HQNN), which consists of one-dimensional arrays formed by intra- and inter-molecular hydrogen bonds, showed a ferromagnetic phase transition at 0.5 K.

The intermolecular hydrogen bond enables the construction of organized molecular assemblies.[1] Introduction of hydrogen-bonding sites into stable organic radicals may, therefore, systematize open-shell molecules into a molecular assembly of prominent magnetic properties.[2] We have designed a nitronyl nitroxide derivative (HQNN) carrying a hydroquinone (HQ) moiety at the C(1′)-position. Since the nitronyl nitroxide group (NN) is a hydrogen bond acceptor, both hydroxy and nitroxide nitromide groups may participate in intra- and inter-molecular hydrogen bonding.

The nitronyl nitroxide derivative, HQNN, was prepared by oxidizing the corresponding bishydroxylamine using lead dioxide in THF. Crystallization of HQNN from diethyl ether afforded two crystal phases: an α-phase crystallized above 4 °C, bluish-purple blocks, mp 109 °C (decomp.),† and a β-phase crystallized below 0 °C, blue needles, mp 108 °C (decomp.).‡ Both crystals can be obtained selectively by using a seed crystal at room temperature.

The crystal structure of α-HQNN was determined by X-ray crystallography. The phenolic hydroxy group [O(1′)H] forms a strong intramolecular hydrogen bond [O(1′)···O(1) 2.507(2) Å] with the NN group [N(1)–O(1)]. This hydrogen bond causes a bond alternation of the NN group: the bond lengths of N(1)–O(1) and C(1)–N(1) bonds at the hydrogen-bonded site are 1.303(2) and 1.332(2) Å, respectively, whereas those of N(2)–O(2) and C(1)–N(2) at the opposite side are 1.272(2) and 1.367(2) Å, respectively, as shown in Fig. 1(*a*). The hydroxy group O(1′)H also participates in an intermolecular hydrogen bond with the O(2′)H group of the translated molecule along the *c* axis, resulting in a one-dimensional hydrogen-bonded array along this direction. A similar one-dimensional array runs parallel with inversion symmetry between the two facing molecules. Two NN groups related by inversion symmetry are located in proximity with the NO···ON distance ($d_2$) of 3.159(2) Å as shown by the dashed line in Fig. 1(*b*), presumably due to the presence of a bifurcated hydrogen bond between the two phenolic hydroxy groups.[3] These two arrays form a herringbone type structure.

The magnetic susceptibility of the polycrystalline sample of α-HQNN was measured by a Faraday-type magnetic balance (main field 5 kOe, gradient 200 Oe $cm^{-1}$). A Curie constant of 0.383 emu K $mol^{-1}$ at ambient temperature assures the purity of the sample. The $\chi T$ value increases at temperatures lower than 20 K. The plot was well reproduced by the Curie–Weiss equation with a Weiss temperature of +0.8 K.



HQNN

The ac susceptibility of the sample, $\chi_{ac}$, was measured down to 40 mK in a $^3$He–$^4$He dilution refrigerator at an ac magnetic field of about 10 nT (127 Hz). The ac susceptibility increases rapidly around 0.5 K, suggesting that a phase transition to the ferromagnetic state takes place at this temperature (Fig. 2). In order to clarify the nature of the low temperature phase, we

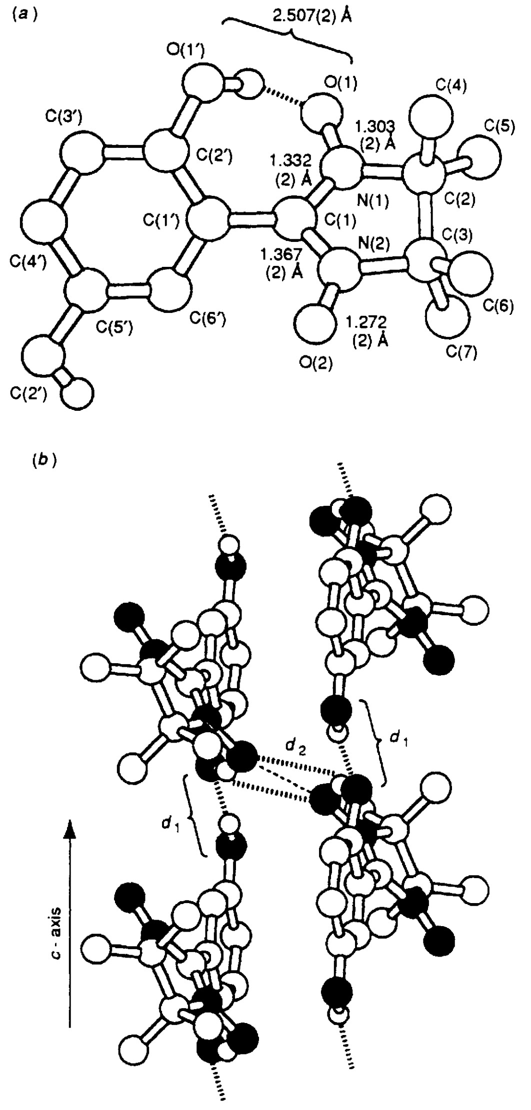


Fig. 1 Crystal structure of α-HQNN: (*a*) bond alternation caused by the intramolecular hydrogen bond; (*b*) parallel one-dimensional hydrogen-bonded arrays formed by the intermolecular hydrogen bonds [$d_1$(O···O): 2.752(2) Å] within an array and by the bifurcated hydrogen bonds between two arrays. Hydrogen bonds are depicted by dotted lines (||||).

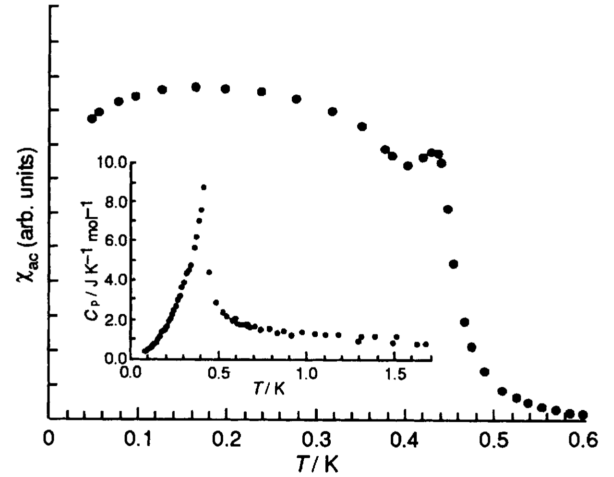


**Fig. 2** Temperature dependences of the ac susceptibility $\chi_{ac}$ and of the heat capacity $C_P$ (insert)

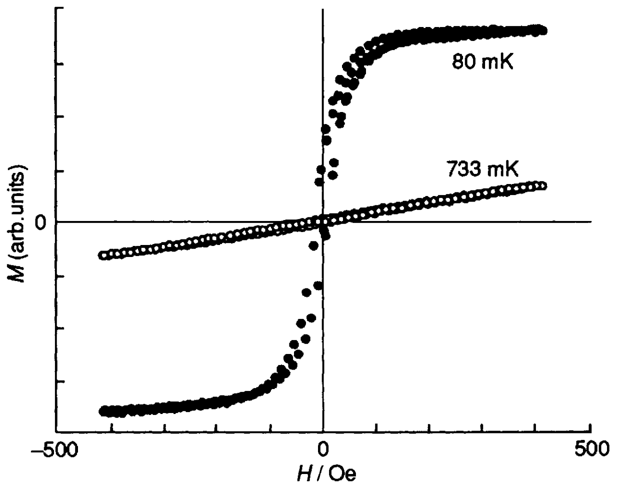


**Fig. 3** Magnetization curves measured at 773 and 80 mK

measured M–H hysteresis curves by integration, as described elsewhere.[4] The magnetization curves above and below $T_c$ (0.5 K) are shown in Fig. 3. The magnetization curve at 80 mK exhibits a rapid saturation at 100 Oe. Since the estimated saturation value of magnetization was very close to the theoretical one (1 $\mu_B$ mol$^{-1}$) for the measured sample, the phase transition can be regarded as a bulk-transition. It also shows a hysteretic behaviour, although the coercive field is very small (less than 20 Oe). This is in agreement with the tendency found in β-NPNN which is the first purely organic ferromagnet.[4,5,6]

Temperature dependence of the heat capacity, $C_p$, of the α-HQNN was measured in the range 0.09–1.67 K. The heat capacity exhibits a λ-shaped anomaly with a peak at 0.43 ± 0.01 K (Fig. 2 insert). The associated entropy change is evaluated to be 5.29 J K$^{-1}$ mol$^{-1}$, which is in accord with a theoretical value of Rln2 = 5.765 J K$^{-1}$ mol$^{-1}$ within experimental error. This result is independent evidence for the bulk nature of the phase transition.

The temperature dependence of the magnetic susceptibility for the polycrystalline sample of β-HQNN was well reproduced by a S–T model ($J/k_B = +3.2$ K). The result can be rationalized by applying McConnell theory (Type I),[7] as HQNN molecules in the β-phase crystal are stacked in a dimerized manner, connected with intermolecular hydrogen-bonding between the hydroxy and the NN groups.

In order to rationalize the spin ordering of α-HQNN at lower temperatures, a couple of possible mechanisms may be considered. First, spin polarization may operate *via* a hydrogen bond[8] provided that the electron spin density is distributed over the hydroxy group of O(2′)H to some extent. Second, through space dipole–dipole interaction may play an essential role between two NN groups located closely by the bifurcated hydrogen bond.[9] Since the degree of intermolecular magnetic interaction is very weak, it is difficult to specify the decisive mechanism.

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## Footnotes

† Elemental analysis (α-HQNN): Calcd. for $C_{13}H_{17}N_2O_4$: C 58.85; H 6.46; N 10.56(%). Found: C 58.89; H 6.47; N 10.54(%).

*Crystal data* for (α-HQNN): $C_{13}N_{17}N_2O_4$, $M$ = 265.29, monoclinic, space group $P2_1/n$, $a$ = 15.142(3), $b$ = 12.320(1), $c$ = 7.196(1) Å, β = 99.18(2)°, $V$ = 1325.3(4) Å$^3$, $Z$ = 4, $D_c$ = 1.331 g cm$^{-3}$; Mo-Kα radiation (graphite monochromator, λ = 0.71073 Å), final conventional $R$ factor 4.7% for 2204 independent reflections [$|F_o| \geqslant 3\sigma(|F_o|)$] and 241 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Elemental analysis (β-HQNN): Calcd. for $C_{13}N_{17}N_2O_4$: C 58.85; H 6.46; N 10.56(%). Found: C 58.78; H 6.46; N 10.53(%).

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