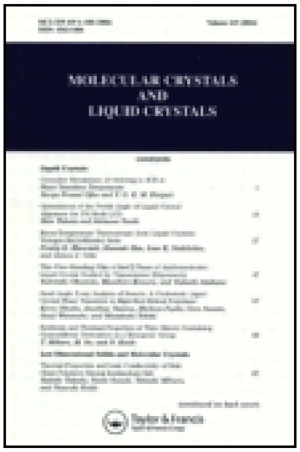

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Magnetic Property of Stable Organic Radicals Bearing Imidazole Ring

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Version of record first published: 04 Oct 2006

To cite this article: Naoki Yoshioka, Munetoshi Irisawa, Yuichiro Mochizuki, Takashi Aoki & Hidenari Inoue (1997): Synthesis and Magnetic Property of Stable Organic Radicals Bearing Imidazole Ring, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 403-408

To link to this article: http://dx.doi.org/10.1080/10587259708044594

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 403–408
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SYNTHESIS AND MAGNETIC PROPERTY OF STABLE ORGANIC RADICALS BEARING IMIDAZOLE RING

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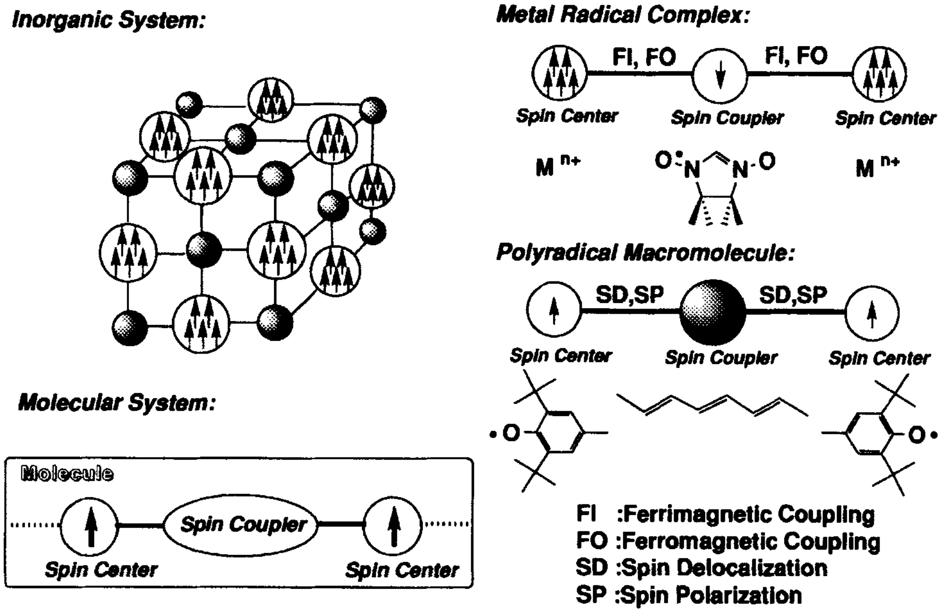
Abstract Three imidazole derivatives with stable radical groups at 2-position were prepared and their magnetic property were characterized. The effect of NH hydrogen bonding site was also discussed.

INTRODUCTION

Recently, there have been increasing research interest in the study of molecular-based magnetism. The syntheses of organic radicals, polyradical macromolecules, and coordination polymers have been in progress based on individual strategies.[1] In the design of molecular based magnetic materials, the first condition is constituent molecules or ions should be paramagnetic, second, these paramagnetic centers should be assembled to realize long-range magnetic interaction. These requirements are fulfilled for the transition metal elements which constitute ferromagnets of natural origin. In contrast to inorganic system, molecular system can be characterized by discrete covalently bonded molecule with relatively weak intermolecular interaction. A promising approach using organic radicals as a spin coupler is to build up coordination polymers in which the ferro- or ferri-magnetic chain is composed of metal ions and bridging radical ligands.[2] Another approach is to design polyradical macromolecules with a large ground spin multiplicity based on the intrachain spin delocalization and/or polarization mechanism.[3] The methodology involves the application of theoretical models[4] of magnetic coupling to conjugated polymers bearing paramagnetic centers (SCHEME 1). However, expected through-bond ferromagnetic coupling based on theoretical model was not observed in polyacetylene based polyradicals.[3] A non zero spin density distribution over the conjugated backbone structure is indispensable for strong through-bond interaction.[5] The spin density at the polyacetylene chain was not large enough to cause ferromagnetic coupling or to overcome through-space antiferromagnetic interactions between side-chain radical substituents.[6] Amorphousness of polyacetylene based polyradicals prevented the control of interchain spin coupling which is essential for bulk magnetism.

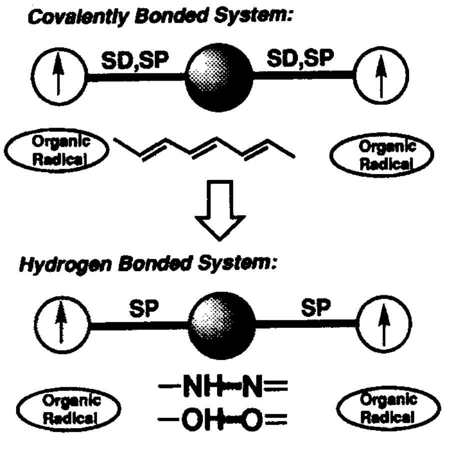


SCHEME 1

MOLECULAR DESIGN

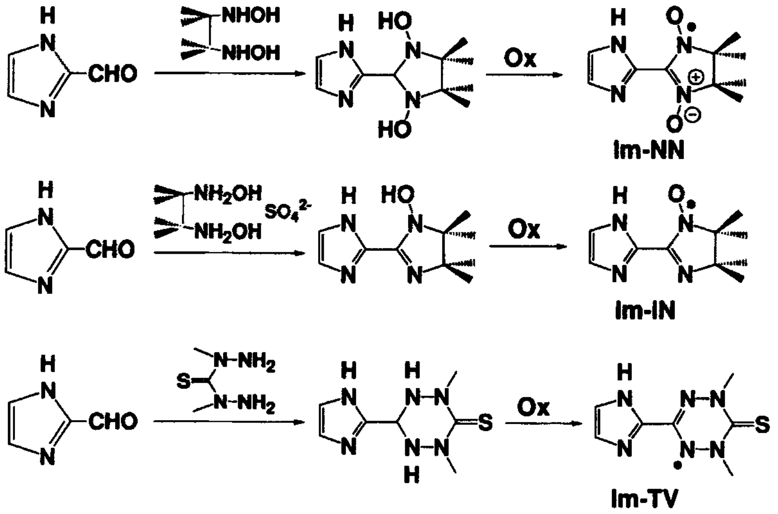
As an alternative way of covalently bonded system, we have been interested in hydrogen bonded network to assemble paramagnetic center (SCHEME 2). Among various intermolecular interactions, hydrogen bonds are strong in energy and whose directional properties are better understood than many other types of non-bonded interactions. Introduction of hydrogen bonding sites into organic radicals is useful way of controlling molecular arrangement in the crystal. So far various type of organic radicals with OH site have been reported and structurally characterized.[7]

We have been interested in the electronic structure of imidazole derivatives which have both proton donor site (NH) and proton acceptor site (=N). Imidazole is an important constituent of histamine and of the histidine residues of proteins. Proton migrations involving histidine have been implicated in the enzyme mechanism. While the hydrogen bonding between imidazoles and nitroxide in the solution has been reported,[8] few study on the effect of NH site on the physicochemical properties of organic radicals have been carried out. As a model system of hydrogen-bonded radical chain, we have designed and synthesized imidazole derivatives with stable radical at 2-position such as 2-imidazole-nitronylnitroxide and -iminonitroxide[9] in order to control the molecular arrangement of paramagnetic species.



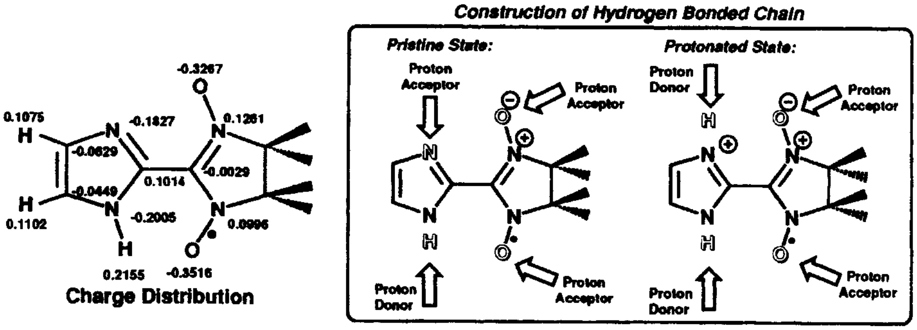
SCHEME 2

Im-NN (mp. 142-143°), Im-IN (mp. 140-142°), and Im-TV (mp. 129-132°) were prepared by coupling of 2-imidazolecarboxaldehyde[10] and 2,3-dimethyl-2,3-bis(*N*-hydroxyamino)butane,[11] its sulfate salt,[11] and 2,4-dimethylthiocarbohydrazide,[12] respectively, followed by chemical oxidation according to the method described in the literature (SCHEME 3).[13] Im-IN could also be isolated as a byproduct of Im-NN during column chromatography. IR spectra of these radicals indicated the presence of hydrogen-bonded N-H stretching around 2800 cm^{-1} - 3200 cm^{-1} similar to that of parent imidazole.[14] Im-TV was obtained in low yield and less stable than Im-NN and Im-IN.



SCHEME 3

Atomic charge of Im-NN obtained by semiempirical MO calculation are summarized in SCHEME 4. Large negative charges appear on nitroxide oxygen and two imidazole nitrogen atoms, and large positive one is observed at NH site. The preliminary calculation implies that hydrogen bond occurs between the positive charge on hydrogen at HN site and the negative charge on oxygen at NO group or imino nitrogen of imidazole ring. In the protonated state if two equivalent NH site locate on imidazolium ring, two set of proton donor - acceptor site will be formed. The protonation experiment was carried out by the flowing of dry HCl or HBr gas into the dry benzene solution of Im-NN. Im-NN-HCl and Im-NN-HBr were obtained as a brown powder and a green one, respectively.



SCHEME 4

STRUCTURE AND MAGNETIC PROPERTIES

Among these radicals Im-NN gave a suitable crystal for X-ray analysis. Im-NN crystallizes in the centrosymmetric space group $P\,2_1/a$. In the crystal N-H...N hydrogen

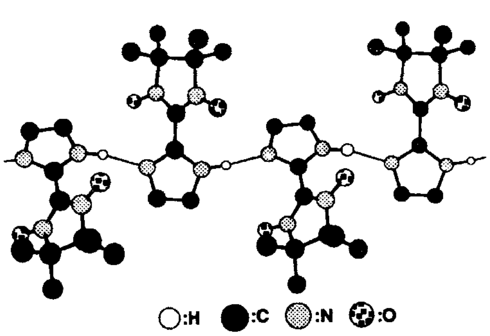


FIGURE 1 Schematic representation of hydrogen bonded chain in **Im-NN**.

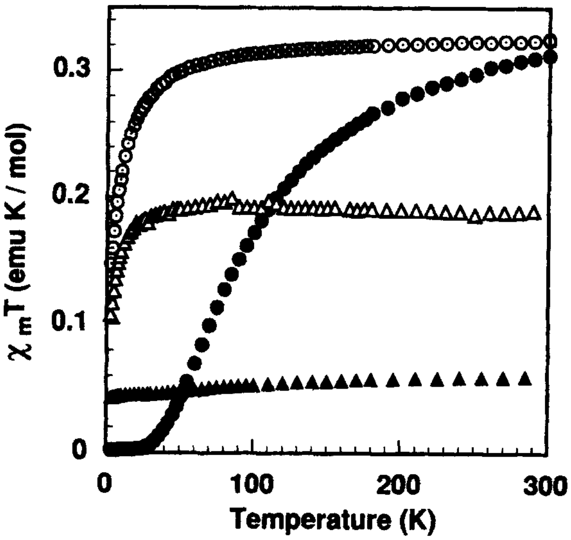


FIGURE 2 Temperature dependence of χ_mT for **Im-NN** (●), **Im-IN** (○), **Im-NN-HCl** (△) and **Im-NN-HBr** (▲).

bonded chain with N...N distance of 2.811(6)Å is found as shown in FIGURE 1. Intermolecular shortest distances are found between NH...N' which corresponds to the hydrogen bond along *b* axis whose length is a little longer than that of imidazole (2.811(6)Å). Dihedral angle between the plane of O-N-C-N-O and imidazole ring equal to 48.4 deg which is larger than those reported for phenyl[15] or pyridyl[16] derivative whose corresponding angle are ca. 30 deg. Between the hydrogen bonded chains Im-NN formed spin pair within nitroxide oxygen atoms (3.483(5) Å).

Magnetic susceptibility of Im-NN showed maximum at 110 K and minimum at 20 K. The magnetic data were fit to a Bleaney-Bowers expression of the magnetic susceptibility for a dimer (FIGURE 2). Non-linear curve fitting afforded singlet-triplet gaps, $2J = -122.8$ cm^{-1}. The magnetic data can be interpreted by direct overlap between the magnetic orbitals of the two nitronylnitroxide at the paired site. The magnetic behavior was similar to that reported for 1,5-dimethyl-nortropinone nitroxide[17]. Magnetic interaction through hydrogen bonded chain could not be observed in Im-NN because spin density distribution localized over nitronylnitroxide moiety. IR measurement at LN_2 indicated the presence of free NH group (3320 cm^{-1}) in Im-IN and its magnetic susceptibility follows Curie-Weiss law. These data suggest the relation between hydrogen-bonded structure and spin pairing at NN site. Magnetic susceptibility of Im-NN-HCl and Im-NN-HBr shows paramagnetic behavior, and the reduced Curie constants imply the degradation of NO group during the protonation process. Protonation under milder conditions are now underway.

Synthesis of new radicals with extended spin delocalization over imidazole ring is in progress.

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