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

Physical Properties Derived from Protondynamics in Hydrogen-Bonded Organic Molecular Crystals

Tadashi Sugawara [a], Tomoyuki Mochida [a] & Akira Izuoka [a]

[a] Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Tadashi Sugawara , Tomoyuki Mochida & Akira Izuoka (1992): Physical Properties Derived from Protondynamics in Hydrogen-Bonded Organic Molecular Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 291-296

To link to this article: http://dx.doi.org/10.1080/10587259208047056

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 291–296
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

PHYSICAL PROPERTIES DERIVED FROM PROTON-DYNAMICS IN HYDROGEN-BONDED ORGANIC MOLECULAR CRYSTALS

TADASHI SUGAWARA, TOMOYUKI MOCHIDA, and AKIRA IZUOKA
Department of Pure and Applied Sciences, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153 Japan

Abstract Physical properties derived from proton-dynamics in hydrogen-bonded molecular crystals are discussed from two aspects. First, the effect of a static or dynamic modulation is discussed on conduction property of Ni(dmit)2 caused by a hydrogen-bonded counter cation system. An anomaly was observed in conduction property of $Ni(dmit)_2 \cdot Li_n(H_2O)_m$ salt which is presumably due to a change in the hydration scheme. Second, physical properties of hydrogen-bonded tautomeric molecules are examined in the case of 3-hydroxy-phenalenone (1) and its derivative (2). No dynamic processes were detected in the crystals of 1, although the crystal is polar and exhibits second harmonic generation. On the other hand the crystal of 2-carboxy derivative 2 behaves as paraelectrics at room temperature at ambient pressure with a phase transition to an antiferroelectric phase at 40 K. This remarkable property is ascribed to the rapid tautomerization mediated by 2-carboxyl substituent coupling with proton-transfer in intermolecular bifurcated hydrogen bonds.

INTRODUCTION

In biological systems, fixation of a substrate into a favorable conformation in the active site of an enzyme is ingeneously performed by formation and breaking of intermolecular hydrogen bonds. Recently a conformational change of ATP (adenosine-5'-triphosphate) coupled with a change in the hydration scheme was successively monitored by X-ray crystallographic analysis[1]. Moreover, phonon modes of the crystal was found to be regulated by humidity-control. The phenomenon is more prominent in the crystals of guanosine hydrate[2]. The crystal structure of these nucleosides or nucleotides are characterized by the stacking of purine rings and hydration schemes in intra- and/or intercolumnar regions. The reason for the modulation on the phonon modes may be ascribable to variation of the

stacking structure caused by the change in hydration schemes. In addition, purine bases, which have both proton-donor sites and -acceptor ones, undergo prototropic tautomerization. If intermolecular proton-transfer takes place in crystals coupling with tautomerizm, one can expect novel dynamic properties. With these intelligent biological systems in mind, the authors will discuss some physical properties derived from proton-dynamics in hydrogen-bonded systems constructed by well-designed organic molecules.

MODULATION ON PHYSICAL PROPERTIES BY STRUCTURAL CHANGE OF HYDRATION SCHEME

In order to examine the effect of a change in hydration schemes on electrical conductivity, Miyazaki et al. prepared Ni(dmit)$_2$ salts with a hydrogen-bonded cationic system as a counter ion. In a Ni(dmit)$_2$ salt with morpholinium cation, a remarkable structural modulation was observed on the hydrogen-bonded dmit ligands in the conduction column. The salt behaves as a semiconductor (σ_{rt}=0.07Scm^{-1},Ea=0.1eV) and no unusual behavior of conductivity was observed down to 100K.

On the other hand temperature dependence of conductivity of Ni(dmit)$_2$ salt with hydrated lithium ion shows a hysteresis around 230 K. This might be ascribed

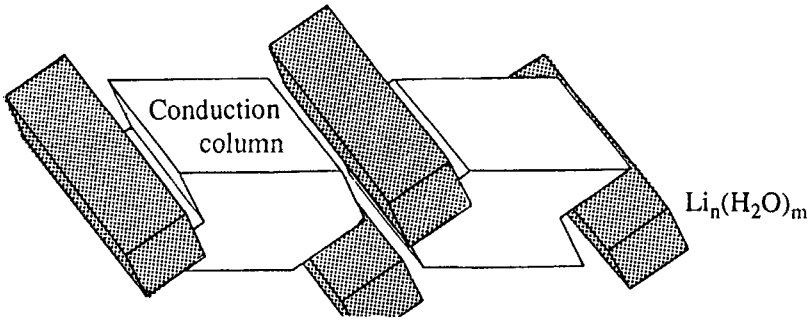


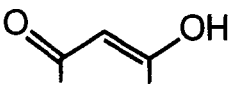
FIGURE 1 Schematic structure of Ni(dmit)$_2$•$Li_n(H_2O)_m$.

to the change in the hydrogen-bonded network incorporated among the conduction columns (Figure1). The crystal structure and the conduction property of the complex will be described in detail elsewhere[3]. Thus proton-dynamics in hydrogen-bonded

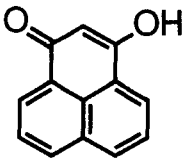
systems not only causes the conformational alternation or the regulation of phonon modes but may also provide a novel method for modulating conduction property.

OPTICAL NON-LINEARITY OF HYDROGEN-BONDED POLAR π-CONJUGATED MOLECULES

Hydrogen bond is powerful in constructing molecular assemblies as seen in purine bases, since the direction of a hydrogen bond is predictable when appropriate proton-donor and/or -acceptor sites are introduced to constituent molecules. We are interested in 3-hydroxyenones as simple but well-equipped functional molecules. This family is known to form strong intermolecular hydrogen bonds and affords various crystal structures depending on the relative orientation of OH and C=O•••H moieties. Among them, 3-hydroxyphenalenone (1) seems to be in favor of strong intermolecular hydrogen bonds, because both protonated and deprotonated species



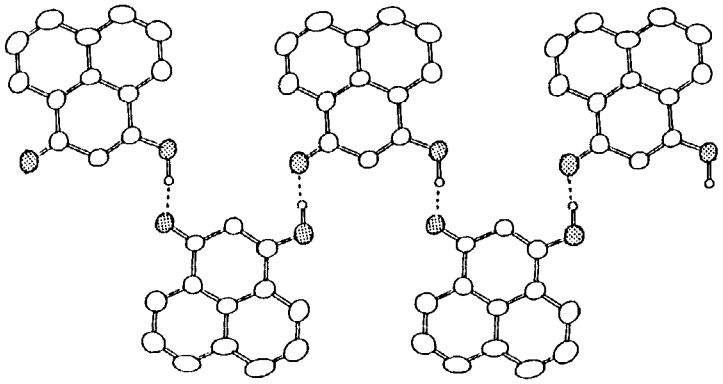
3-hydroxyenone



1

of 1 are expected to be adequately stable due to the resulting phenalenyl structure[4]. The characteristics of the crystal structure of 1 is as follows[5] (Figure 2). There are four independent molecules (A, B, C, D), constituting two kinds of one dimensional in-plane chains (A-B-A-B- ; C-D-C-D-). The geometry of the hydrogen bonds is in a syn-syn configuration with short intermolecular O-O distances (Av. 2.58 Å). The crystal turns out to be SHG active, the magnitude being 0.2 relative to that of urea. The result is in agreement with the polar crystal packing(space group Pc), where the O=C-C=C-OH moieties are all directed to the same direction along the *a* axis.

Since 3-hydroxyphenalenone 1 is a tautomeric molecule, it may interconvert between two symmetric enol forms coupling with intermolecular proton-transfer. Thus the crystal may have a chance to show ferroelectric property. However, dielectric response of the crystal was not observed in the temperature range between



Crystal data : monoclinic, Pc, Z=8, a=9.089(2)
b=17.737(2), c=14.265(2)A, β =125.65(2)

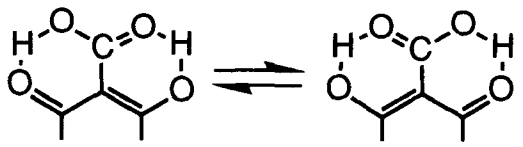
FIGURE 2 Crystal structure of 3-hydroxyphenalenone (1).

300 K and 450 K under 10 kHz modulation. Neither dynamic processes nor phase transitions were observed in the solid state ^{13}C NMR (CP/MAS) measurement even when the temperature was raised up to 393 K. Therefore we may conclude that the hydroxyl protons are tightly fixed at a particular site in the hydrogen bond even at high temperatures.

(ANTI)FERROELECTRICITY OF HYDROGEN-BONDED TAUTOMERIC MOLECULE COUPLING WITH PROTON-TRANSFER

If a direction of the dipole moment of organic molecules in crystals inverts through a dynamic process, the crystal may exhibit a paraelectric property[6]. In order to realize paraelectricity under a moderate condition, we have designed a novel tautomeric molecule, 2-carboxy-3-hydroxyphenalenone(2), in which tautomerization is extremely facilitated by the mediation of the carboxyl group at the 2-position[4]. An X-ray crystallographic analysis reveals that 2 forms a dimeric pair by bifurcated intermolecular hydrogen bonds and each pair is stacked in columns.

The dielectric response of a single crystal of 2 was measured with an alternating electric field (50 V/cm) of 10 kHz under an ambient pressure. It shows a paraelectric behavior (Figure 3) at room temperature [7]. With lowering



temperature, the dielectric constant decreases rapidly at ca. 40 K, indicating the phase transition into an antiferroelectric phase. The inversion of the gross dipole moment between polar dimeric pairs should be responsible for the dielectric response under

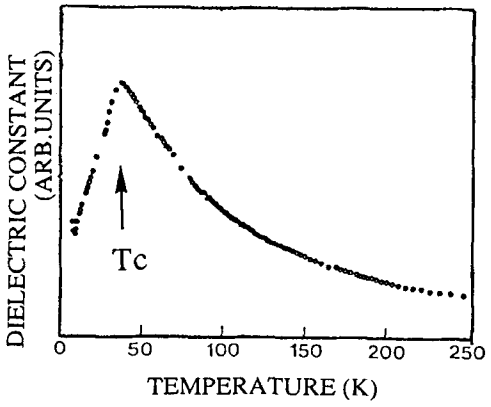


FIGURE 3 Temperature dependence of dielectric constant of 2

the electric field (Figure 4). At temperatures lower than Tc, the dipoles within the dimer start to order antiferroelectrically due to the dipole-dipole interaction, which corresponds to the fixation of the conjugated π-electronic system into a nonpolar form. The tautomerization of 2 seems to be accelerated in terms of the highly mobile

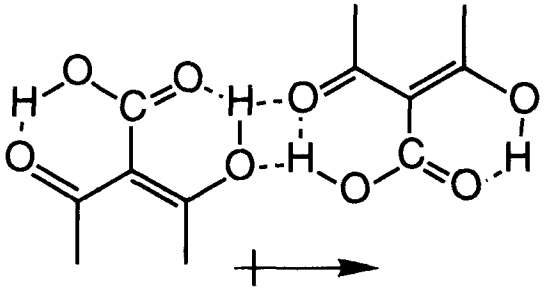


FIGURE 4 Schematic structure of the polar dimeric pair of 2

proton participating in the bifurcated hydrogen bond. Proton-transfer in bifurcated hydrogen bonds can also play a role of transmitting the phase of tautomerization to the adjacent molecule. Thus if hydrogen bonds extend in wider range, one can observe enhanced dielectric and/or solitonic phenomena in a tautomeric molecular assembly.

CONCLUSION

Some hydrogen-bonded systems which show interesting physical properties are described. Significance of proton-dynamics in controlling physical properties should increase in developing novel materials.

ACKNOWLEDGMENTS

The authors wish to thank Prof. Y. Tokura, Mr. Y. Moritomo of Dept. of Physics, The Univ. of Tokyo for the measurement of dielectric constants. They are also indebted to Prof. N. Sato for stimulating discussions. This study was partially supported by Grant-in-aid 02554016 from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Y. Sugawara, N. Kamiya, H. Iwasaki, T. Ito, Y. Satow, J. Am. Chem. Soc., 113, 5440 (1991).
2. H. Urabe, Y. Sugawara, M. Tsukakoshi, T. Kasuya, J. Chem. Phys., in press.
3. A. Miyazaki, A. Izuoka, T. Sugawara, Mol. Cryst. Liq. Cryst., this volume, 0000 (1991).
4. S. Matsumiya, A. Izuoka, T. Sugawara, N. Nakamura, J. Phys. Org. Chem., 3, 485 (1990).
5. T. Mochida, S. Matsumiya, A. Izuoka, N. Sato, T. Sugawara, Y. Sugawara, Acta Cryst.,C47, in press.
6. (a) G. A. Samara, D. Semmingsen, J. Chem. Phys., 71, 1401 (1979).
   (b) Y. Moritomo, S. Koshihara, Y. Tokura, J. Chem. Phys., 93, 5429 (1990).
7. T. Sugawara, T. Mochida, A. Miyazaki, A. Izuoka, N. Sato, Y. Sugawara, K. Deguchi, Y. Moritomo, Y. Tokura , to be published elsewhere.