Crystal structure of two new developers for high-performance thermo-sensitive paper

- Hydrogen-bond network in urea-urethane derivatives -

Shinya Matsumoto*, Sakiko Takeshima, Sori Satoh and Kazuo Kabashima[1,2]

Department of Environmental Sciences, Faculty of Education and Human Sciences,

Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[1] *Fine Ace Corporation, 1-44-10, Higashi-ikebukuro, Toshima-ku, Tokyo 170-0013, Japan*

[2]*Chemipro Kasei Kaisha, Ltd., 83 Kyomachi, Chuo-ku, Kobe 650-0034, Japan*

*Corresponding author: Phone: +81-45-339-3366, Fax: +81-45-339-3345, E-mail: smatsu@edhs.ynu.ac.jp (S. Matsumoto)

Abstract

A crystal structure analysis was carried out on two new developers for high-performance thermo-sensitive paper, the urea-urethane derivatives. The urea-urethane derivatives are known to improve the fastness of coloured images and reduce the environmental loads, as compared to the conventional phenolic developers. Two UU derivatives were found to form a multiple hydrogen-bond network in crystals between their urea and urethane moieties. This hydrogen-bonding ability should be considered to stabilize the coloured state of the fluoran dyes to achieve a very high fastness of the printed images.

Keywords: Thermo-sensitive paper, Developer, Urea-urethane derivative, Crystal structure, Hydrogen-bond network, Fluoran dye

Introduction

Direct thermal-printing technology is now widely used in facsimiles, receipts and many kinds of tickets, for simple, small and maintenance-free printing devices as well as its printing ability for manifold objects [1]. Its application fields have expanded with the development of information technologies and therefore its market will be expected to increase. Thermo-sensitive paper is a key technology of this printing system. The paper consists of a paper substrate and a recording layer which includes a lueco dye and its developer. Fluoran dyes are typically used as a leuco dye. Its spiro lactone ring is cleaved by an acidic developer to produce the coloured state. In order to obtain a black colour from one dye component, dichroic fluoran dyes were developed on the basis of molecular orbital calculations [2]. The black-coloured dye has two absorption maxima with almost the same molar absorption coefficient. These two absorption maxima were adjusted to be complementary to give a "pure" black colour in one component. This colouring process is the most important characteristic of this printing system.

Many kinds of acidic compounds were examined as the developer which produces ring cleavage of the sipro lactone ring of the fluoran dyes. Acidic phenol derivatives are generally used, but recently, questions have been raised about their effect on the environment [3,4]. In addition, the low stability of the coloured state poses a problem in the preservation of printed images over prolonged durations. Urea-urethane (UU) derivatives were developed as a new developer for high-performance thermo-sensitive paper without a phenolic hydroxyl group [5,6]. The UU derivatives have no acidic protons, but they can promote the ring cleavage of the fluoran dyes. They exhibit a high stability of the coloured state of the thermo-sensitive paper as compared to the conventional developers having phenolic hydroxyl groups. They are also characterized by a low-environmental loading. These derivatives are already on the market, but the mechanism of their colour development are still uncertain.

During the course of our study on the colour development mechanism of the UU

derivatives, we carried out a crystal structure analysis to investigate the hydrogen-bonding ability of these compounds in the solid state, because one of the reasons for the excellent fastness of the coloured state using the UU derivatives could be connected to their hydrogen bonds in the solid state. In this paper, the result of the crystal structure analysis for two UU derivatives is reported from the standpoint of its hydrogen-bonding ability.

(Figure 1)

Experimental

These UU derivatives were prepared by a previously reported procedure [5,6]. Single crystals of compounds **1** and **2** were grown by the diffusion method using the combination of good (1,4-dioxane for **1**, ethylacetate for **2**) and poor (*n*-hexane for **1**, benzene for **2**) solvents. Colourless platelet crystals were obtained for both compounds. The diffraction data were collected using a Rigaku R-AXIS Rapid imaging plate area detector with graphite-monochromated Cu-$K\alpha$ radiation (50 kV, 40 mA). Both structures were solved by the direct method [7] and refined by least-squares calculations using the Crystal Structure 3.10 program package [8]. All non-hydrogen atoms were anisotropically refined except for the disordered benzene molecules in the solvate crystals of **2**. The benzene molecule was refined on the assumption that they are disordered into two conformations with a 50 % occupancy sharing of one C-C bond. All hydrogen atoms were located on the calculated positions and refined by the riding model. The crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained upon request, free of charge, by quoting the publication citation and the deposition number (**1**: CCDC294123 and **2**: CCDC294124). Crystal data for **1**: $C_{16}H_{17}N_3O_3$, *Mw* = 299.33, monoclinic, $P2_1$, $Z = 4$, $a = 12.583$ (7), $b = 7.715$ (3), $c = 16.152$ (8) Å, $\beta = 99.43$ (2) °, $D_{calc} = 1.285$ g/cm^3, 13009 reflections were collected, 2845 unique ($R_{int} = 0.044$), 431 parameters, R_1

= 0.053, wR_2 = 0.081, GOF = 1.00, refinement on F. **2**: $C_{27}H_{25}N_3O_3$, Mw = 439.52, monoclinic, $C2/c$, Z = 8, a = 26.295 (5), b = 12.359 (3), c = 16.587 (4) Å, β = 118.07 (2) °, D_{calc} = 1.211 g/cm^3, 21598 reflections were collected, 3932 unique (R_{int} = 0.048), 303 parameters, R_1 = 0.074, wR_2 = 0.097, GOF = 0.98, refinement on F.

Results and Discussion

As shown in Figure 2, two unsymmetrical molecules were found in the crystal of compound **1**. They have different molecular conformations. In molecule A, two phenyl groups and the urea moiety are aligned in an almost planar manner. However, the urethane moiety is turned about its N-C bond to the central phenyl ring through an angle of about 97 °. On the other hand, in molecule B, the central phenyl ring is twisted by about 47 ° against the almost planar arrangement of the terminal phenyl ring and the urea moiety. A further 48 ° torsion angle was recognized between the central phenyl ring and the urethane moiety. These two unsymmetrical molecules are located along the c-axis to form a complementary hydrogen bond between the carbonyl group of the urea moiety and the amino group of the urethane moiety (see Figure 3). A hydrogen-bond network was also found along the b-axis. This is caused by a bifurcated (three-centered) hydrogen bond between the carbonyl group of the urethane moiety and two amino groups of the urea moiety. This network is built between molecules associated with a 2-fold screw axis along the b-axis. The geometry of these hydrogen bonds is summarized in Table 1. These results indicate that compound **1** has the ability to form strong hydrogen bonds [9]. Compound **1** can be thus regarded as a multiple hydrogen-bond module. The colouration reaction based on the ring cleavage in fluoran dyes is an equilibrium reaction. The coloured form of the fluoran dyes has several donors and acceptors for hydrogen bonds [10]. If a hydrogen-bond network will form between the coloured fluoran dyes and the UU developers, this equilibrium should be displaced for production of the coloured state. The present hydrogen-bonding ability is therefore considered

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to be an important parameter affecting the fastness of the coloured images of the thermo-sensitive paper using **1**.

The strong hydrogen-bonding ability of **1** in the solid state can be explained by the bond lengths of the urea and urethane moieties from the viewpoint of its electrostatic nature. The bond lengths of C=O and C-N in the urea moiety for both unsymmetrical molecules are slightly short (1.21 - 1.22 Å) and long (1.36 – 1.37 Å), respectively, as compared to those of the unsubstituted urea and aliphatic urea derivatives [11]. This result also shows that the two amino-protons of the urea moiety can be expected to exhibit a slightly higher acidity as compared to that of the other urea derivatives. The bond lengths of the C=O in the urethane moiety for both unsymmetrical molecules are also found to be slightly shorter than that of the other urethane derivatives (1.21 Å) [11]. These relatively polarized carbonyl groups are considered to result in the formation of a strong hydrogen bond. Comparatively short aromatic C-C bonds were also observed in the terminal phenyl ring attached to the urea moiety This can be ascribed to a ring-puckering motion.

(Figures 2 and 3)

(Table 1)

Figures 4 and 5 show the molecular and crystal structures of the inclusion crystals of **2** with benzene. Our group also found that compound **2** easily form similar inclusion crystals with solvent molecules such as THF and acetone. The included benzene molecules were found to be disordered in the two conformations sharing one aromatic C-C bond. These disordered benzene molecules are placed in such a way that the benzene molecules occupied the voids between the hydrogen-bond network of **2**. The molecules of **2** have a non-planar conformation. The urea moiety and the attached terminal phenyl ring are arranged in almost planar fashion, but this unit is twisted against the central phenyl ring by about 53 °. The

urethane moiety is also twisted against the central phenyl ring by about 41 °.   The dihedral angle between the urethane moiety and the attached terminal phenyl ring is almost perpendicular. A hydrogen-bond network was also found in compound **2** along the *c*-axis as shown in Figure 5. The network can be divided into two complementary hydrogen-bonded molecular pairs. In the first pair, two molecules form a complementary bifurcated hydrogen bond between the two amino groups of the urea moiety of one molecule and the carbonyl group of the urethane moiety of the molecule designated by the (-x, -y, -z+1) symmetry operation. Another complementary hydrogen bond is constructed in the second molecular pair in which the amino group of the urethane moiety of one molecule is bonded with the carbonyl group of the urea moiety of the molecule given by the (-x, -y, -z+1.5) symmetry operation to the first one. The geometry of these hydrogen bonds summarized in Table 2 indicates that compound **2** has the ability to form strong hydrogen bonds. Compound **2** is thus presumed to have the same property which affects the fastness of the thermo-sensitive papers like compound **1**.

The bond characteristics of the urea and urethane moieties in **2** were found to be almost similar to those of **1**. The bond lengths of C=O and C-N in the urea moiety are slightly short (1.21 Å) and long (1.36 Å), respectively, as compared to those of the other urea derivatives [11]. The C=O bond of the urethane moiety was also found to be relatively short (1.205 Å) as compared to those of the other urethane derivatives [11]. Comparatively short aromatic C-C bonds were also observed in the terminal phenyl ring attached to the urethane moiety. This can be a result from the ring-puckering motion the same as those of **1**.

(Figures 4 and 5)

(Table 2)

Conclusions

A crystal structure analysis was carried out on two new developers, the urea-urethane derivatives, for high-performance thermo-sensitive paper. These derivatives form a multiple hydrogen-bond network in crystals between their urea and urethane moieties. This hydrogen-bonding ability should be considered to stabilize the coloured state of the fluoran dyes in thermo-sensitive paper to achieve very high fastness of the printed images. A study of the colouration mechanism of these UU derivatives is also in progress and the result will be reported elsewhere.

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Figure Captions

Figure 1 Chemical structure of a common fluoran dye and UU derivatives.

Figure 2 Molecular structure of **1**. Two unsymmetrical units are depicted. A complementary hydrogen bond is indicated by the dotted line.

Figure 3 Hydrogen-bond network of **1**. The hydrogen bonds are indicated by the dotted line. The molecules are given by the following symmetry operation; A_1: -x, y+0.5, -z, A_2: -x, y-0.5, -z, A_3: x, y-1, z, B_1: -x, y+0.5, -z+1, B_2: -x, y-0.5, -z+1, B_3: x, y-1, z,

Figure 4 Molecular structure of **2** with the disordered benzene.

Figure 5 Hydrogen-bond network of **2**. The disordered benzene molecules are omitted for clarity. The hydrogen bonds are indicated by the dotted line.

Table 1 Geometry of hydrogen bonds in **1**.

Table 2 Geometry of hydrogen bonds in **2**.