

Stabilization Mechanism of a Black Leuco-Developer System and Its Tinctorial Strength as Viewed from the Crystal Structure

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Abstract. Certain leuco dyestuffs are known to exhibit a brilliant color by reaction with a phenolic developer; 2-[(4-hydroxyphenyl)sulfonyl]-phenol (BPS) is a well-known developer for black leuco dyes such as 6'-(diethylamino)-3'-methyl-2'-(phenylamino)-spiro[isobenzofuran-1(3H), 9'-[9H]-xanthen]-3-one (ODB) in thermosensitive papers. Although BPS is a small molecule (molecular weight: about 250), it is thermally stable as characterized by a high melting point of about 184°C. Furthermore, the stability of BPS is also extended to the 1:1 “leuco/developer” system. In this connection, structure analysis of BPS has been carried out in order to elucidate the stability of BPS itself as well as its leuco/developer system. Then, we found that one BPS molecule is hydrogen bonded to four different neighboring ones, forming an OH···O two-dimensional hydrogen-bond network. This ensures a high thermal stability of BPS. On the other hand, in the ODB/BPS system, only one of the four hydrogen bonds in BPS is used for the formation of the 1:1 ODB/BPS colorant while the remaining three hydrogen bonds keep the network. As for the tinctorial strength in spin-coated ODB/BPS, the color intensity is found to be limited to about 70% of the maximum available value. This is because there is a fraction of ODB molecules, whose lactone ring is still closed owing to the steric hindrance. © 2010 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2010.54.2.020502]

INTRODUCTION

Colorless leuco dyestuffs are known to exhibit a brilliant color in the solid state when the lactone ring is opened by a phenolic developer.¹ This coloration is widely used in practice for facsimile as well as rewritable media. In practical systems, the color is generated by heating a mixture of dye and developer particles with a thermal head. The operational temperature is largely determined by the melting point (mp) of a developer, whose melting point is usually lower than that of the leuco dye. In addition, a higher melting point leads to an improved archiving-stability of the printed document.

2-[(4-hydroxyphenyl)sulfonyl]-phenol (BPS) (Figure 1) is a phenolic developer used especially for black-generating leuco dyes, for example, as shown in the left of Figure 2: 6'-(diethylamino)-3'-methyl-2'-(phenylamino)-spiro[isobenzofuran-1(3H), 9'-[9H]-xanthene]-3-one (ODB).²

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Here, the black appearance is achieved by two absorption bands of nearly equal color strength in the visible region that absorb complementary colors.³ The lactone ring is opened by BPS to form OH···O intermolecular hydrogen bonds between ODB and BPS. BPS is a small molecule (molecular weight: about 250). Nevertheless, it is thermally stable as characterized by a high melting point of 184°C, which is higher than that of ordinary phenolic developers, such as bisphenol A (mp: 158°C) and ethyl gallate (mp: 154°C). The stability as measured by the melting point is closely related to the cohesive forces of the component molecules in the solid state. Our initial motivation in the present investigation is to elucidate the high melting point of BPS on the basis of the crystal structure. On the other hand, BPS is also known to enhance the image permanence of the 1:1 ODB/BPS colorant. In this connection, structure analysis of BPS has been carried out in order to elucidate the stability of BPS itself as well as its “leuco/developer” system.

EXPERIMENTAL

Materials, Crystal Growth, and Spin-Coated Films

BPS and ODB were obtained from Mitsubishi Paper Mills, Ltd. Single crystals of BPS were grown by recrystallization from an ethanol solution. After 48 h, a number of colorless single crystals (size: 0.39 × 0.35 × 0.29 mm³) were obtained

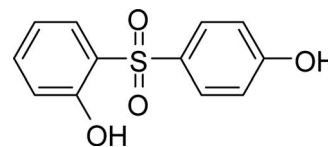


Figure 1. Molecular structure of BPS.

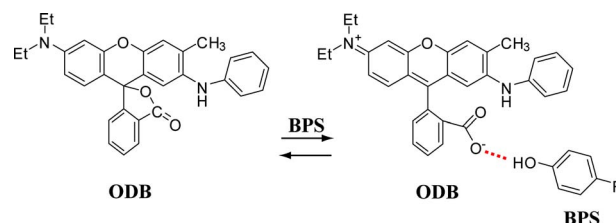


Figure 2. Color generation of ODB owing to BPS through intermolecular hydrogen bonding.

Table I. Crystallographic parameters for BPS.

Formula	C ₁₂ H ₁₀ O ₄ S
Molecular weight	250.27
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
<i>a</i> (Å)	7.036
<i>b</i> (Å)	14.44
<i>c</i> (Å)	10.953
β (deg)	93.815
<i>V</i> (Å ³)	1110.35
Density (g/cm ³)	1.497
<i>R</i> 1 ^a	0.058

^a*R*1 is defined as the *R*-factor calculated for reflections of $F^2 > 2\sigma(F^2)$, where *F* and σ denote the intensity and standard deviation, respectively.

in the form of blocks. Spin-coated films of BPS alone or 1:1 ODB/BPS colorants were prepared from solution in methylethylketone without using any polymer binder at a rate of 3000 rpm for 30 s (film thickness: about 300–350 Å). These films were found to be amorphous according the x-ray diffraction diagrams. The former film was used for the color generation as caused by protonation with vapors of nitric acid while monitoring the change in absorption spectra; whereas the latter was employed for measurements of the optical absorption as well as for additional protonation with vapors of nitric acid.

Equipment

Reflection data were collected at -180°C on an *R*-axis RAPID-F diffractometer from Rigaku (Cu *K* α radiation: $\lambda = 1.5418$ Å). Absorption correction was made by the multiscan method. The structure was solved by direct methods (SIR2004⁴) and refinement was carried out by the full matrix least square method of F^2 (SHELXL-97⁵).

UV-visible absorption spectra were recorded on a UV-2400PC spectrophotometer (Shimadzu). Infrared (IR) spectra were measured a JASCO MET-2000.

RESULTS AND DISCUSSION

Structure of BPS

Table I details the crystallographic parameters for structure of BPS at -180°C .⁶ The crystal system is monoclinic and the space group is *P*2₁/*c*.

The ORTEP plot of BPS is shown in Figure 3. The two benzene rings with the 2-hydroxy or 4-hydroxy group are nearly perpendicular to each other [dihedral angle: $91.5(1)^\circ$]. The S atom forms a quasitetrahedral configuration, where O1, O2, C1, and C7 are the ligands.

Figure 4 is the projection of the crystal structure onto the (*b*, *c*) plane, showing the hydrogen-bond network of BPS. There are OH $\cdots$ O intermolecular hydrogen bonds between the OH group of one molecule and the sulfonyl O atom of the neighboring one along the *b* and *c* axes. One

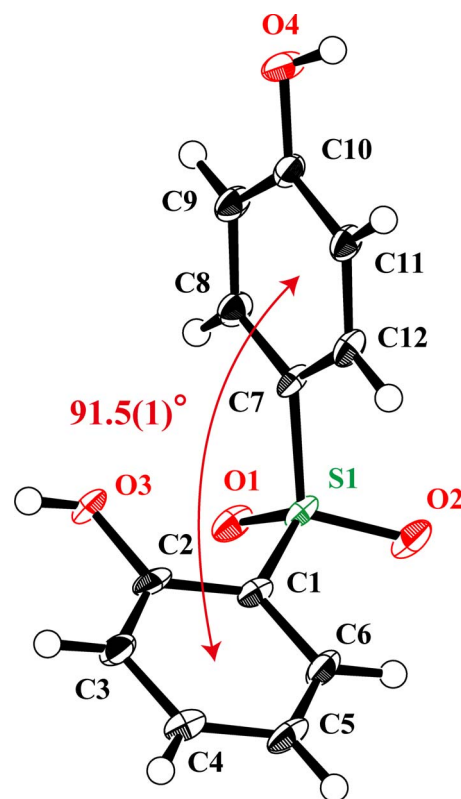


Figure 3. ORTEP plot of BPS. The two benzene rings with the 2-hydroxy or 4-hydroxy group are nearly perpendicular to each other.

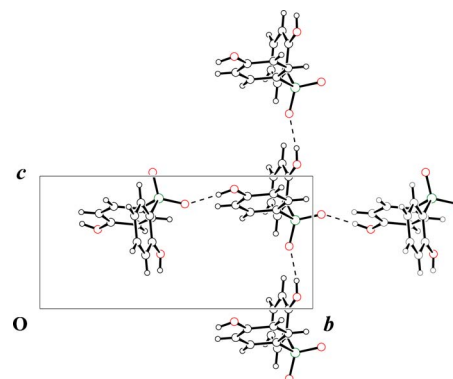


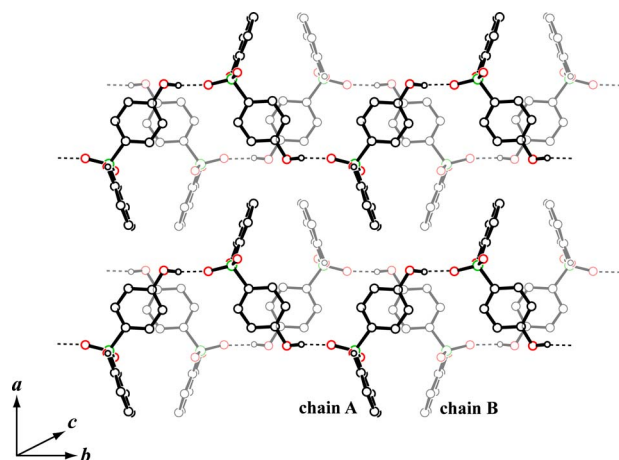
Figure 4. Projection of the crystal structure onto the (*b*, *c*) plane, showing the two-dimensional hydrogen-bond network of BPS.

molecule is hydrogen bonded to four different molecules, forming a two-dimensional hydrogen-bond network. The hydrogen-bonding geometry is given in Table II (for atom notation, see Fig. 2). The strong hydrogen bond is generally characterized by the short *D*–*A* distance less than 2.8 Å and the *D*–*H*⋯*A* is linear (to within about 10°).⁷ The hydrogen bonds in BPS satisfy these requirements.

Figure 5 shows the molecular arrangement of the molecules projected onto the (010) plane. There is a sheetlike hydrogen-bond network composed of the two kinds of chains A and B arranged alternately along the *c* axis. Chain A is depicted in bold lines, while chain B is designated by faint lines. The present two-dimensional sheet is stacked along the

Table II. Hydrogen-bonding geometry (Å and °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
03-H30 $\cdots$ 02 ^a	0.87(3)	1.90(3)	2.753(2)	168(3)
04-H40 $\cdots$ 01 ^b	0.88(4)	1.85(4)	2.733(2)	173(3)

^aSymmetry code: (i) x, y , and $1+z$;^b(ii) $1-x, -1/2+y$, and $3/2-z$.**Figure 5.** Molecular arrangement of BPS. Chains A and B are arranged alternately along the c -axis, forming a two-dimensional hydrogen-bond network. The present hydrogen-bond sheets are stacked along the a -axis.

a axis. The present hydrogen-bond network ensures a high thermal stability, yielding a melting point of 184°C.

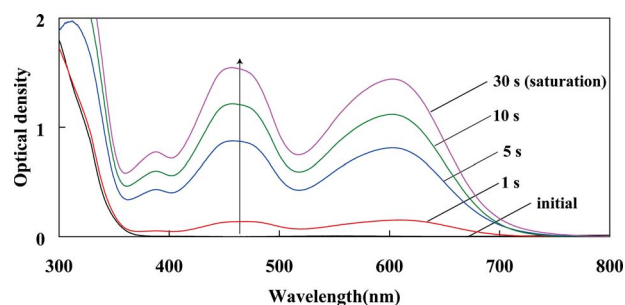
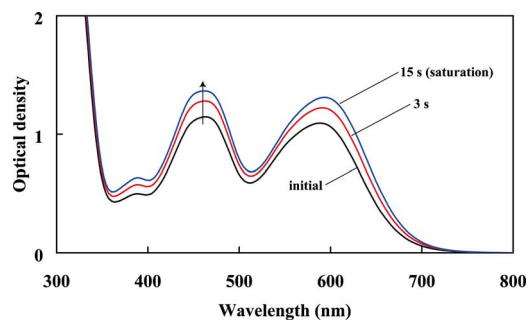
Correlation Between the Stability of BPS Alone and the Stability of the “ODB/BPS” System

The high stability of BPS itself is obvious from the hydrogen-bond network, as shown in Fig. 4. The stabilization of a compound owing to the formation of intermolecular hydrogen bonds is well known, as found in hydrogen-bonded pigments such as indigo,^{8,9} quinacridone,^{10,11} and pyrrolopyrrole.^{12,13}

Then, an important question arises how BPS stabilizes the 1:1 ODB/BPS system when the complex is formed through hydrogen bonding. This stabilization is attributed to the existence of four $OH\cdots O$ intermolecular hydrogen bonds in BPS. One of the four hydrogen bonds in BPS is used for the lactone-ring opening of ODB (Fig. 2), while the remaining three hydrogen bonds keep the hydrogen-bond network. This means that ODB is integrated into the hydrogen-bond network of BPS based on three $OH\cdots O$ hydrogen bonds per molecule, which explains the stabilization of the ODB/BPS system owing to BPS.

Color Generation of ODB with Proton or BPS through Intermolecular Hydrogen Bonding

Figure 6 shows the change in the absorption spectrum of spin-coated ODB (thickness: about 300 Å) alone by protonation (i.e., ring opening) with vapors of nitric acid. The color generation with protons is assumed to proceed quite rapidly, resulting in the maximum available tinctorial strength of ODB, since the proton is by far smaller than BPS

**Figure 6.** Absorption spectrum of spin-coated ODB alone and its spectral changes by protonation with vapors of nitric acid.**Figure 7.** Changes in absorption spectra of spin-coated ODB/BPS (=1:1) by protonation with vapors of nitric acid.

and thus can freely diffuse throughout the spin-coated films of ODB. In experiments, the spin-coated film was exposed to the vapor and the resulting spectral changes were recorded as a function of exposure time. No optical absorption is observed before protonation in the visible region. Then, the two absorption bands appear around 463 and 590 nm, and subsequently grow rapidly with the increase of exposure time, leading to the saturation of the optical density in 30 s. The spin-coated protonated ODB is now colored greenish black since there is an absorption dip around 514 nm.

Figure 7 shows the absorption spectra of spin-coated ODB/BPS (=1:1; thickness: about 350 Å) without and with additional vapor treatment with nitric acid. It should be noted that the vapor treatment with nitric acid remarkably enhances the tinctorial strength, indicating that there is a fraction of ODB molecules whose lactone ring is still closed in spin-coated ODB. On the basis of the enhanced optical density, the percentage of the lactone ring opening is estimated to be about 70%. This signifies that the complete opening of the lactone-ring is rather difficult in spin-coated films, presumably because of the steric hindrance exerted by each component molecule. Similar or even greater steric hindrance can occur in practical systems composed of a mixture of leuco/developer particles.

Figure 8 shows the IR spectra of spin-coated films of colorless ODB alone and black ODB/BPS. The colorless ODB shows the characteristic band of the lactone ring around 1750 cm^{-1} . On the other hand, the black ODB/BPS is characterized by the appearance of the OH stretching band around 3400 cm^{-1} as well as those of the carboxylate

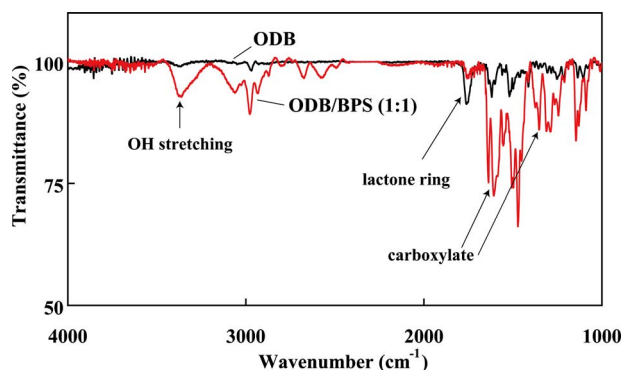


Figure 8. Infrared spectra of spin-coated ODB alone and ODB/BPS (=1:1).

($-\text{COO}^-$) around 1610 and 1350 cm^{-1} . These facts support the opening of the lactone ring as caused by the formation of $\text{OH}\cdots\text{O}$ intermolecular hydrogen bonds between ODB and BPS.

CONCLUSIONS

Structure analysis of BPS has been carried out in order to study the thermal stability of BPS alone and the stability mechanism of the ODB/BPS system. BPS is found to crystallize in a space group $P2_1/c$. One molecule is hydrogen bonded to four neighboring molecules through four $\text{OH}\cdots\text{O}$ hydrogen bonds, which constitutes a two-dimensional hydrogen-bond network, responsible for the high melting point of BPS. On the other hand, in the ODB/BPS system, only one of the four hydrogen bonds in BPS is used for the formation of the 1:1 leuco/developer colorant while the remaining three hydrogen bonds maintain the network. This means that the leuco dye molecules are integrated in the hydrogen-bond network of BPS, leading to the high thermal stability of the 1:1 “leuco/developer” system.

As for the tinctorial strength in spin-coated ODB/BPS, the color intensity is found to be limited to about 70% of the maximum available value, which we attribute to a fraction of ODB molecules, whose lactone ring is still closed owing to the steric hindrance.

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