Structure and Optical Properties of a Thermochromic Schiff Base. Thermally Induced Intramolecular Proton Transfer in the N,N'-Bis(salicylidene)-p-phenylenediamine Crystals

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A thermochromic derivative of salicylideneaniline, N,N'-bis(salicylidene)-p-phenylenediamine (BSP), has been prepared and subjected to structural and optical studies in the crystalline state. An X-ray crystallographic analysis has shown that the molecules are planar and are stacked in a parallel fashion to form one-dimensional columns. The interplanar spacing has been found to be quite short, suggesting the existence of an intermolecular charge-transfer interaction. The molecule contains fairly short O-H ⋯ N hydrogen bonds, the strength of which is manifested in an OH stretching absorption band in the infrared region, showing considerable broadening and a low-frequency shift. The BSP crystals are remarkably thermochromic, and visible absorption and emission spectral changes with temperature have been interpreted in terms of an intramolecular proton transfer from the hydroxyl oxygen to imine nitrogen through the O-H ⋯ N hydrogen bond. The emission spectra have also been examined under high pressures.

N-Salicylideneaniline and its derivatives have long been known to show photochromism in the solid state,[1] and a number of studies have revealed that the chromism is produced by intramolecular proton transfer associated with a change in the π-electron configuration and, subsequently, in a molecular conformation (Scheme 1; the nonplanar molecule undergoes the geometric isomerization, i.e., cis–trans isomerization, following the proton transfer reaction[2]). On the other hand, crystals of some other salicylideneaniline derivatives are thermochromic.[3] This chromism is also due to a change in the π-electron configuration induced by a proton transfer (Scheme 2). In this case, the proton transfer can occur in the ground state. On the basis of comparative structural studies on photochromic and thermochromic salicylideneaniline derivatives, Bregman et al. have concluded that the significant difference lies in the

manner of molecular packing in the lattice.[4,5] Namely, photochromic salicylideneanilines are packed rather loosely in the crystal, in which nonplanar molecules may undergo some conformational changes, while thermochromic salicylideneanilines are planar and packed tightly to form one-dimensional columns. It should be noted that this planar structure makes it possible for the proton to transfer through the hydrogen bond in the ground state with a small energy requirement. The title compound is also one of the thermochromic derivatives of salicylideneaniline.

The thermochromic salicylideneanilines, which have attracted less attention, have proved to be interesting to us in that they may be a candidate to construct a novel type of conductive organic material in which the proton motion is essentially correlated to the electron conduction. Particularly favorable features are (1) the proton transfer inevitably involves a π-electron con-
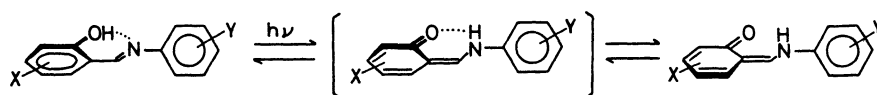
Scheme 1.
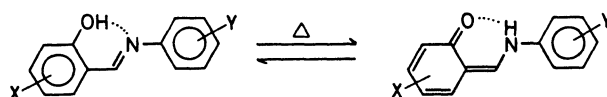
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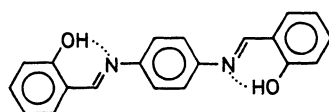
N,N'-bis(salicylidene)-p-phenylenediamine
(BSP)

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figrational change, (2) two interconvertible molecules which have different energy levels are thermally distributed, (3) the planar conjugated systems are stacked one-dimensionally, and (4) the π-electron system can be easily extended by chemical modification. When conduction electrons are introduced into these systems, which seems possible because of the one-dimensional stacking nature and the ease of extension of the conjugated system, one would expect that the proton motion would couple to the conduction electron motion. Consequently the proton transfer could operate as a kind of "phonon." Apparently this "phonon" is quite different from the normal variety since the mass of proton is extremely light compared with the whole mass of the molecule. The possibility of this type of "electron–phonon coupling" has never been examined experimentally.

Bearing in mind a subsequent extension to systems furnished with conduction electrons, this study has been initiated by investigating the basic nature of proton transfer of the title compound. Little has been reported on the thermochromism, even for such a simple derivative of salicylideneaniline. In this paper are described the crystal and molecular structures and the single crystal optical properties of the N,N'-bis(salicylidene)-p-phenylenediamine (BSP). Especially noted is that in the infrared region the OH stretching absorption band was clearly observed for the first time for salicylideneaniline analogues by using a single crystal.

Experimental

Materials. A conventional synthetic method for Schiff base compounds was applied for the preparation of BSP. A methanolic solution containing p-phenylenediamine and salicylaldehyde at $1:2$ molar ratio was refluxed for a couple of hours. Orange microcrystals formed upon cooling, which were then recrystallized from benzene. Slow evaporation of the solvent resulted in the formation of orange platelets of $1\times1.5\times0.03$ mm^3 size. The preparation of the deuterated analogue, BSP-d_2, was carried out by refluxing 40 mg of the above product in a mixture of 10 ml of methanol-d_1 and 10 ml of benzene-d_6 for 25 hours. Slow evaporation of the solvent under an argon flow over a period of one week yielded orange platelets typically of $1\times1\times0.02$ mm^3 size. Mass spectral analysis confirmed completion ($>90\%$) of the deuteration reaction.

Optical Measurements. Single-crystal infrared absorption spectra were measured using an assembled optical system that consisted of a JASCO infrared radiation source, a JASCO CT-25C monochromator, an SBRC HgCdTe detector, and a PAR Model 124A lock-in amplifier. Visible absorption spectra were obtained with a similar system comprising a halogen-gas-filled tungsten incandescent lamp, an ISA Jobin Yvon Type HR1000 monochromator, and a HAMAMATSU R376 photomultiplier. Emission spectra were recorded using the same optical components, except that the light source was replaced by a sample crystal which was irradiated with an argon laser (457.9 nm, 50 mW). The Air-Products HELI-TRAN cryostat was used for variable-

temperature measurements. The flat (100) face of the crystals was irradiated with incident light throughout the optical measurements. Emission spectra under high pressures were obtained using a diamond anvil cell with an 0.50-mm aperture. Pressures were monitored by the shift of the ruby R_1 fluorescence line using the linear pressure scale ($+0.365$ Å kbar^{-1}).

X-Ray Measurements. An automated RIGAKU AFC-5R diffractometer with graphite monochromatized Mo $K\alpha$ radiation was used for data collection. Twenty-five reflections with $20°{<}2\theta{<}30°$ were used to determine the lattice parameters. Crystal data; monoclinic, space group $P2_1/c$, $a=$ 14.643(3), $b=4.573(1)$, $c=12.224(3)$ Å, $\beta=112.04(1)°$, $V=758.8$ (3) Å^3, $Z=2$, and $D_c=1.385$ g cm^{-3}. The intensity data was collected in the region of $2\theta{<}60°$ in θ-2θ mode at scan rate of $6°$ min^{-1}; three standard reflections, -1 -1 5, 6 1 -2, and 2 -1 4, were monitored every 100 reflections. Then, 1428 independent reflections with $|F_o|{>}3\sigma(F_o)$ were used for structure analysis. The structure solution was obtained by a direct method with MULTAN-71 in the UNICS III[6] computer program system at IMS. An anisotropic block-diagonal least-squares refinement for non-hydrogen atoms and isotropic refinement for hydrogen atoms gave the final R value (weighting scheme, $1/w=\sigma^2+(0.015 |F_o|)^2$), $R=0.059$, for the 1428 reflections.

Results and Discussion

Molecular and Crystal Structures. The atomic parameters obtained by the X-ray structure analysis are listed in Table 1,[6] and the molecular geometry is illustrated in Fig. 1. The molecule is located on the center of inversion so that half of molecule is crystallographically independent. Attention was focused first on the equilibrium position of the proton. As revealed by the optical measurements (vide infra), the proton-transferred state of BSP is populated to some extent at

Table 1. Atomic Parameters for BSP

Atom	x	y	z	B_{eq}[a]
O	0.7933(1)	−0.2668(4)	0.1408(1)	4.2
N	0.8640(1)	−0.5744(3)	0.0111(1)	2.4
C1	0.7344(1)	−0.2258(4)	−0.0700(2)	2.4
C2	0.7305(1)	−0.1485(4)	0.0393(2)	2.8
C3	0.6605(1)	0.0535(5)	0.0439(2)	3.8
C4	0.5963(2)	0.1790(5)	−0.0583(2)	3.9
C5	0.6002(1)	0.1099(5)	−0.1669(2)	3.6
C6	0.6691(1)	−0.0895(4)	−0.1720(2)	3.0
C7	0.8043(1)	−0.4388(4)	−0.0795(2)	2.4
C8	0.9311(1)	−0.7866(4)	0.0008(1)	2.2
C9	0.9957(1)	−0.9095(4)	0.1053(2)	2.6
C10	1.0639(1)	−1.1186(4)	0.1052(2)	2.7
H3	0.661(2)	0.093(5)	0.121(2)	4.7
H4	0.547(1)	0.319(5)	−0.051(2)	5.1
H5	0.558(1)	0.201(5)	−0.237(2)	4.5
H6	0.675(1)	−0.142(5)	−0.249(2)	4.8
H7	0.802(1)	−0.484(4)	−0.159(2)	4.3
H9	0.991(1)	−0.840(4)	0.181(1)	3.2
H10	1.109(1)	−1.187(4)	0.177(2)	3.4
H11	0.833(2)	−0.396(6)	0.113(2)	6.6

a) Thermal parameters of the non-hydrogen atoms are given by the equivalent isotropic temperature factors (Å^2).

Fig. 1.　Bond lengths (Å) and bond angles (degree, standard diviations are 1° for the angles including bond with hydrogen and 0.2° for the other angles).

room temperature. The bond length between O and H11 atoms is still normal as an ordinary hydroxyl group, although the H11 atom has a relatively large thermal parameter (see Table 1).[7] The distance between O and N atoms, which are intramolecularly hydrogen bonded, is 2.607(2) Å and is comparable to those observed for the thermochromic N-5-chloro-salicylideneaniline (2.584 Å)[4,8] and the photochromic 2-chloro-N-salicylideneaniline (2.609 Å).[8] It is notable that the C3–C4 and C5–C6 bond lengths are considerably shortened. This is a characteristic feature observed among most of the thermochromic salicyl-ideneanilines.[4,8,9] As shown schematically in Scheme 2, the phenol moiety is converted into the o-quinoid structure upon proton transfer and the shortening of C3–C4 and C5–C6 bonds should reflect the resonance contribution from the quinoid structure. Such a quinoid contribution is not observed in 2-chloro-N-salicylideneaniline, which is photochromic.[8] A reduction in the bond length was also observed for the C2–O bond (1.349 Å), compared with 2-chloro-N-salicyl-ideneaniline (1.365 Å); this is due to a contribution from the C2=O quinoid structure.

The dihedral angle between the central and terminal benzene rings is only 2.9° and the molecule is practically planar; the deviation from the mean plane, consisting of three benzene rings, is less than 0.06 Å for nonhydrogen atoms. The crystal structure is shown in Fig. 2. The planar molecules are stacked one-dimensionally along the b-axis with an interplanar distance of 3.29 Å. This value appears to be small compared with aromatic hydrocarbons and also with other thermochromic salicylideneanilines, e.g. 3.4 Å for N-5-chlorosalicylideneaniline,[8] 3.50 Å for N-salicylidene-2-aminopyridine and 3-methyl-N-(3-me-thoxysalicylidene)-2-aminopyridine,[9] 3.42 Å for N-(5-bromosalicylidene)-2-aminopyridine,[9] and 3.43 Å for 5-chloro-N-(5-methoxysalicylidene)-2-aminopyri-dine.[9] There must be some intermolecular interaction in BSP; the most probable is that due to charge transfer. It should be recalled that the molecular structure after the proton transfer consists of the o-benzoquinone and the aromatic amine moieties. The

(a)

(b)

(c)

Fig. 2.　Crystal structure of BSP (a), (b), and molecular overlap (c).

former is a particularly well-known electron acceptor. Thus, the molecule contains both acceptor and donor portions and the proton transferred species can be an intramolecular charge-transfer compound. The optical studies by Cohen et al.[10] revealed that the thermochromic electronic transition is polarized along the long axis in the molecular plane. Since the intermolecular charge-transfer interaction in their system is not so strong, it is likely that the intramolecular

charge-transfer absorption mainly occurs. In the case of BSP one donor portion carries two acceptor portions. By considering the packing arrangement, a more effective donor–acceptor overlap is seen in BSP (Fig. 2(c)). It should also be noted that the effective overlap between the azomethine groups and the benzene rings may produce intermolecular charge-transfer interactions in the stack of enol form molecules. The contribution from these charge-transfer interactions may lead to a contraction of the interplanar spacing. In order to generate a conduction electron system, the existence of intermolecular interactions in solids is essential. Attempts have been made to extend the system to those which have a stronger charge-transfer interaction; the results will be published elsewhere.[11]

Vibrational Spectra of BSP. The short $O \cdots N$ distance indicated by the crystal structure should be advantageous for the intramolecular proton transfer and an optical study in the infrared spectral region was made in order to obtain information on the vibrational states. Although a few infrared spectroscopic studies of salicylideneanilines to investigate the proton transferring behavior have so far been reported,[12-14] none of the reports has mentioned the OH stretching mode. The infrared measurements with solution,[12] polycrystalline thin film,[14] or KBr disc[12,13] specimens are apparently not adequate for detecting this particular mode. Preliminary experiments using a conventional Nujol mull also faced the same difficulty. However, in this study the OH stretching band was clearly observed for the first time when the spectra were taken using a single crystal specimen. The spectra, thus obtained, are shown in Fig. 3. A broad absorption centered at 2620 cm^{-1} (half width, $\nu_{1/2}$, ca. 550 cm^{-1}) with some subband structure is assigned to the OH stretching mode. A deuteration experiment clearly confirmed this assignment; the absorption

band shifts to 2050 cm^{-1} on deuteration, as shown in Fig. 3, with the isotopic frequency ratio ν_{OH}/ν_{OD} of 1.28. The band observed at around 3040 cm^{-1}, which does not shift by deuteration, is assignable to the ν_{CH} band. Changes are also observed in the range below 1600 cm^{-1} upon deuteration. Another pronounced change on deuteration is the disappearance of the band at 1200 cm^{-1}, which is reasonably assigned to the OH in-plane bending mode. The band at 1370 cm^{-1}, which is not influenced by deuteration, can be assigned to the C–O stretching mode. A bunch of bands between 1500 and 1650 cm^{-1} which are slightly affected by deuteration, are assigned to the overlapping bands of the aromatic ring vibration and the C=N stretching. Further assignments have not been attempted.

The broadening and low-frequency shift of this OH stretching absorption band, compared with the free OH group, are characteristic of fairly strongly hydrogen-bonded hydroxyl groups. Novak established a relationship between ν_{OH} frequency and $O \cdots O$ distances for a number of systems involving linear $O–H \cdots O$ hydrogen bonds.[15] Decreasing the $O \cdots O$ distance results in decreasing ν_{OH} and the dependence of the $O \cdots O$ distance on ν_{OH} varies with the hydrogen-bond strength. On the other hand, Wood et al. conducted an IR spectroscopic study on β-diketones and found that the prediction of $O \cdots O$ distances (2.6—2.7 Å) from ν_{OH}, γ_{OH}, and their isotopic frequency ratios based on the Novak's relationship did not coincide with the observed distances (2.42—2.55 Å).[16] These authors suggested that the discrepancy comes from a bent configuration of the $O–H \cdots O$ bond in β-diketones. In the case of BSP, the $O–H \cdots N$ bond is indeed non-linear ($O–H \cdots N$ angle, ca. 155°). However, the observed frequency, 2620 cm^{-1}, predicts the $O \cdots N$ distance as 2.6—2.7 Å on the basis of Novak's relationship (taking into account the larger van der

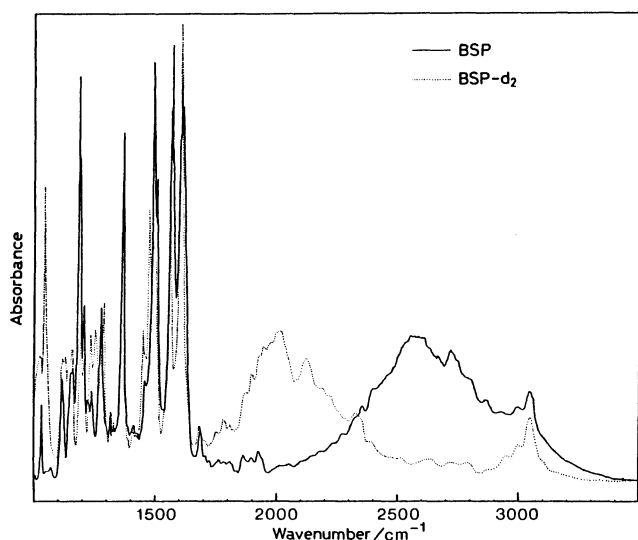
Fig. 3. Single-crystal infrared spectra for BSP and BSP-d_2 recorded at room temperature.
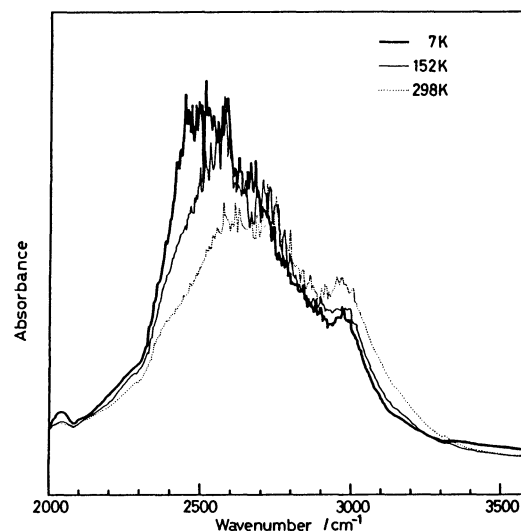

Fig. 4. Single-crystal infrared spectral change of the ν_{OH} band with temperature. The hump near 3000 cm^{-1} is the ν_{CH} band.

Waals radius of nitrogen), which is in good agreement with the observed distance, 2.607 Å. The structural situation of the present system lies between the above two cases of linear and bent hydrogen bond configurations. However, it is found that the small deviation from the linear hydrogen bond configuration does not influence the ν_{OH} frequency.

As shown in the following section, the BSP crystal exhibits an electronic absorption spectral change with a temperature in accord with the π-electron structural change induced by a proton transfer from the hydroxyl oxygen to the imine nitrogen. This self-isomerization process is believed to have some effect on the OH stretching band. In order to investigate this effect, the temperature dependence of the infrared spectra has been measured (Fig. 4). At low temperatures the population of proton-transferred species can be ignored and the crystal is regarded to contain only a single component with all protons bound to the oxygen atoms. At the lowest temperature, the band is still broad ($\nu_{1/2}$ 460 cm^{-1}) and asymmetric. Factors affecting the ν_{OH} band profile may include anharmonic coupling between the ν_{OH} and ν_{OH-N} modes, Fermi resonances between ν_{OH} and combinations or overtones involving δ_{OH} and γ_{OH} modes, and an anharmonicity in the ν_{OH} mode itself. Other factors specific to the solid state, such as Davidov coupling and structural disorder, cannot be ignored.[17] In the case of BSP the primary factor which causes the band to be broad seems to be the anharmonic coupling between the ν_{OH} and ν_{OH-N} modes. Far-infrared spectra[18] have also been measured in order to search for the ν_{OH-N} frequency and, indeed, the spectrum observed at 8 K has exhibited a single peak at 240 cm^{-1}, which can be assigned to the ν_{OH-N} mode. Other peaks in the spectrum are located below 100 cm^{-1}. Then the broad ν_{OH} band observed at 7 K can be fitted to the progression of several bands separated

Fig. 5. Simulated infrared band profile as a progression of Gaussian bands equally separated by 240 cm^{-1} (solid line) and the observed OH stretching band at 7 K (dotted line).

by 240 cm^{-1} (Fig. 5). It can be seen that each of the bands is still broad, suggesting the additional anharmonic coupling with lower-energy phonon modes and/or anharmonicity in the ν_{OH} mode itself.

With increasing temperature the intensity of the low-energy side of the band decreases, while the high-energy side changes slightly in the opposite way. Below 80 K the ν_{OH} band shows almost no change (for clarity the band observed at 72 K is not presented in Fig. 4). These changes parallel the visible spectral changes (vide infra). The ν_{OH} band profile at 298 K is not satisfactorily explained merely by the progression of bands due to the coupling with the ν_{OH-N} mode, which is observed at 230 cm^{-1} at 323 K in the far-infrared spectra. This must be a consequence, at least partly, of the proton transfer. In the simplest case the two tautomers are distributed statistically as observed in NQR measurements of salicylideneanilines.[19] In the ^{14}N NQR spectra of thermochromic salicylideneanilines, growth of a pair of new absorption peaks which corresponds to the thermally induced species has been observed by increasing temperature, as the original pair of peaks diminishes. Thus, the two chemical species are separable on an NQR time scale. However, the time scale is several orders greater in the infrared experiment. If the dynamic or resonance effect is to be considered, the band profile should not be thought of as a simple superimposition of two components. Furthermore, if the chemical species are interacting with each other in the crystal, which is very likely, the situation becomes more complicated. In any case the band profile cannot be considered as being due to a simple local mode and more information on dynamic and microscopic aspects is required to understand the situation completely.

Electronic Absorption and Emission Spectra of BSP. Crystals of BSP are an orange color at room temperature and turn yellow upon cooling in liquid nitrogen. This thermochromic change was followed spectrophotometrically over a wide temperature range (4—293 K); the results are given in Fig. 6. At the lowest temperature an absorption edge is observed rising sharply around 2.8 eV and tailing down to 2.4 eV; the former is assigned to the π-π^* transition in the enol form. The latter tail has some structure; the slope changes in two regions, 2.42—2.61 and 2.61—2.80 eV. The width of both ranges is 0.19 eV. We feel that this tailing is due to the non-Franck-Condon type absorption and that the appearance of two different slopes is due to the coupling with the CN or CO stretching mode. Up to 80 K practically no temperature effect on the spectra was observed, which agrees well with the observation of the temperature dependence of the ν_{OH} band profile as mentioned in the previous section.

As the temperature rises above 80 K, the absorption band at 2.4 eV grows in and at room temperature this band shows its edge at 2.26 eV. With this band assigned to the keto isomer, the energy difference
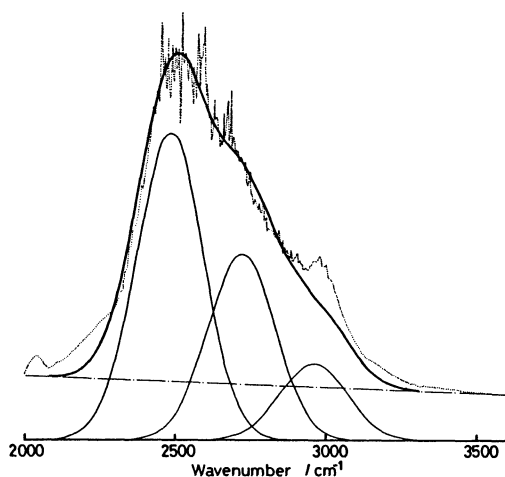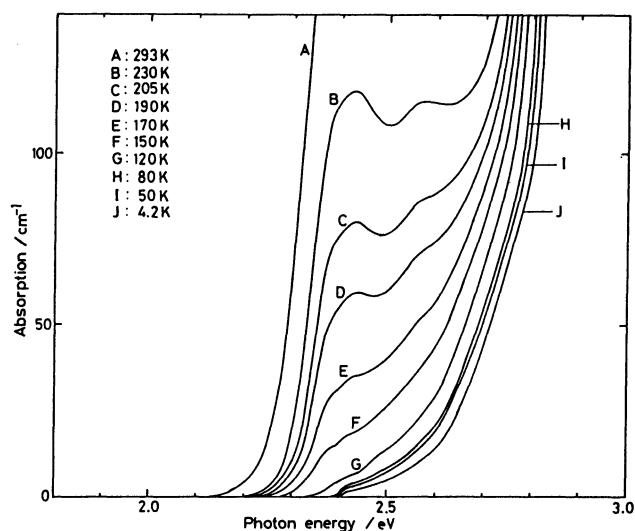
Fig. 6. Single crystal absorption spectral changes with temperature for BSP.
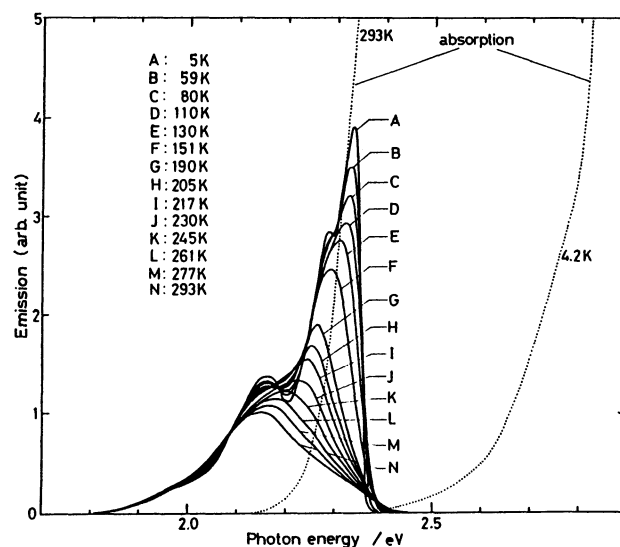

Fig. 7. Single crystal emission spectral changes with temperature for BSP.

between the two tautomers in Scheme 2 is evaluated to be ca. 0.1 eV, which is comparable to that observed for N-5-chlorosalicylideneaniline (0.08 eV).[3] The electronic absorption spectral change with temperature indicates that a substantial amount of the proton-transferred species is present at room temperature. The relative population of the enol and keto species has been estimated to be about 50:1 at room temperature by assuming that the system is followed by the Boltzmann-type distribution. It is noticed that the absorption band of the keto isomer shows some vibrational structure with an energy difference of ca. 0.14 eV and a shoulder near the absorption edge.

An observation of emission spectra, shown in Fig. 7, gives support for the above explanation of the thermochromism as caused by the proton transfer. It should be noted that the emission spectrum A at 2.33 eV recorded at 5 K shows a large Stokes shift (ca. 0.4 eV) from the corresponding absorption. This is one of the characteristic features of the proton-transfer reactions in salicylideneaniline derivatives.[2] It can be seen that the emission band has some fine structure; humps appear at around 2.33, 2.29, 2.15, 1.97 eV. The separation between the first and the second peaks is small, and this detailed structure could be assigned to the ν_{OH-N} vibrational fine structure. The energy differences between the first and the third and between the third and the fourth are equally 0.18 eV. This energy may correspond to the CN or CO stretching mode. It may be noticed that this fine structure well corresponds to the structure observed in the thermochromic band. The energy of 0.14 eV, which is the energy difference between the second and the third peaks of emission at 5 K, is exactly the energy difference between the two peaks observed in the thermochromic band. The small energy difference between the first and the second peaks of the emission may correspond

to that between the shoulder and the first peak of the thermochromic band. Consequently, the emission band can be regarded as a mirror image of the thermochromic band. Cohen and Flavian studied the emission and absorption spectra of several thermochromic salicylideneanilines including BSP in the solid state,[20] and they concluded that the emission is due to deactivation from the same excited state to the same ground state as those involved in the thermochromic absorption. Our results are clearly consistent with their interpretation. Especially, low-temperature emission experiments have confirmed the origin of the largely shifted emission band. The emission gradually diminishes at elevated temperatures, the fine structure becoming less noticeable. At room temperature a broadened emission centered around 2.15 eV remains (spectrum N). The temperature dependence of the emission spectra is better explained by reabsorption by the thermally induced species as discussed in Ref. 19, since the emission intensity changes only at the high energy side where the absorption grows with increasing temperature. The reabsorption effect on the emission band is also reflected in spectral difference between the emissions from different crystal faces; when the (100) face is irradiated, a shoulder-like band observed at 2.25 eV on the higher-energy side in the emission from the flat (100) face is absent in the emission from the lateral (001) face, which reflects the longer penetration depth of this emitted light in this direction.

Since our interest lies in the extent of intermolecular interaction, we examined the pressure effect on the optical properties. Drickamer et al. extensively used high pressures to investigate intra- and intermolecular interactions in molecular crystals.[21] They also examined the pressure effect on the electronic spectra of several thermochromic derivatives of salicylideneani-

line both in the crystalline state[22] and in solid dispersions.[23] According to these authors, thermochromic crystals of N-5-bromosalicylideneaniline, for instance, exhibit piezochromic absorption in the visible region, which shifts to lower energy and intensifies with increasing pressure in compensation for the original ultraviolet absorption band. They identified this piezochromic peak as the thermochromic peak under atmospheric pressure, thus describing the pressure effect as a driving force for the proton-transfer equilibrium towards the keto form.

In the case of BSP, the shift in the absorption edge with pressure was also observed. However, the magnitude (0.17 eV by 33 kbar) was larger than that observed for the systems studied by Hockert and Drickamer (less than 0.1 eV by 30 kbar for the absorption peak). On the other hand, the emission spectral changes with pressure for BSP (Fig. 8) indicate only a small maximum shift to lower energy. This is in contrast to the finding of the above-mentioned authors that the energy difference between the piezochromic band and the emission band for N-5-bromosalicylideneaniline remains fairly constant over a wider pressure range. It is also noticed that the pressure dependence of the emission intensity of BSP is different from that of other derivatives studied by Hockert and Drickamer[23] and by ourselves;[11] the pressure dependence of the intensity cannot be fitted by a single exponential function in the case of BSP. Thus, the apparent emission spectral changes can only be qualitatively accounted for by an increase in the probability of quenching due to the level crossing resulting from the change of potential surface and/or increase of the reabsorption accompanied by the red shift of absorption. At any rate, the distinctive behavior of BSP must be associated with the existence of a stronger intermolecular interaction in this compound.
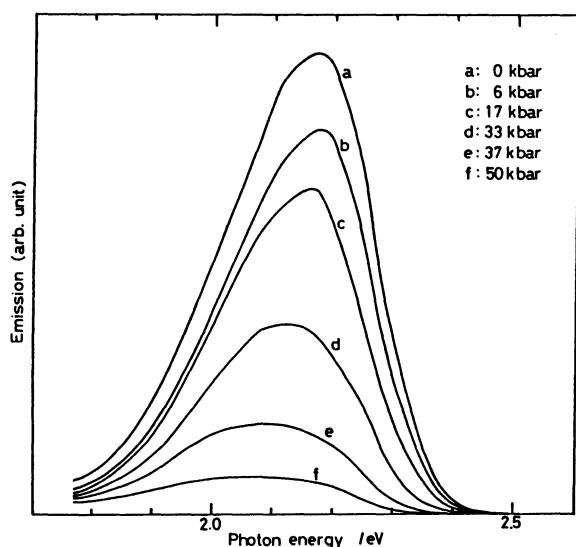

Fig. 8. Single crystal emission spectral changes with pressure for BSP.

Summary

Thermochromic BSP single crystals have been studied both structurally and optically. From the structural study it has been found that the interplanar distance is shorter than in other thermochromic salicylideneanilines, while retaining the normal one-dimensional packing of molecules. Since the keto form of the BSP molecule consists of donor and acceptor portions, it is suggested that the charge-transfer interaction operates in the crystalline state as an intermolecular interaction. The infrared spectroscopic study clearly demonstrates the presence of OH stretching absorption for the first time among the salicylideneanilines and is interpreted in the regime of strong hydrogen bonds. The effect of the thermal proton transfer on the proton vibrational spectra has not been characterized, but additional information on microscopic or dynamic aspects will facilitate the understanding.

The visible absorption and emission spectra are basically understandable in terms of the ground state and the excited-state proton transfer, respectively, as for other salicylideneanilines previously studied. We would like to point out, however, that unconventional interpretations are possible for some detailed aspects noted in this study. Firstly, the absorption band has a long low-energy tail at temperatures below ca. 80 K where thermochromic absorption is not highly visible. Secondly, the emission band edge coincides the edge of this absorption tail edge at 2.4 eV, where the thermochromic absorption also shows up. With regard to the low-energy absorption tail, it is possible that quantum mixing of enol and keto ground states due to proton tunneling results in a significant amount of the population in the latter, even at low temperatures. Another possibility is that this weak absorption is due to non-Frank-Condon type transitions from the enol ground state to the keto excited state cannot be ruled out. This would mean that the optical electronic excitation simultaneously causes the proton transfer, and implies that the excited state of this system has a potential surface close to a single minimum well. Another interesting feature observed in the absorption and emission spectra of BSP is that all spectra related to the proton transfer have phonon structures due to the coupling with the vibrational modes involved in the skeleton of the hydrogen-bonded chelate ring. This becomes particularly important when the coupling between the electronic properties of solids and proton transfer is to be considered. Further studies on extended systems which are designed to introduce the stronger intermolecular charge-transfer interaction are being made, and preliminary results indicate that the equilibrium position of hydrogen atoms is fairly sensitive to the electronic state of the system. Systematic studies of the structure and optical properties of extended systems should help clarify the nature of the

proton transfer and, especially, its coupling with the electronic state.

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