Hydrogen Bond Donor Ability α_2^H Is a Good Index for Finding an Appropriate Color Developer for the Molecular Design of Functional Thermal Paper

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Thermal paper, which is comprised of sulfonylurea molecule $R^1SO_2NH–CO–NH–R^2$ (color developer) and the leuco-dye, can develop strong black color, and the developed color is durable. This is because sulfonylurea functional group has sufficient hydrogen bond donor ability to stabilize a π-delocalized carbocation generated from the leuco-dye due to heat-induced lactone ring opening. Thus, the color-developing complex (**CDC**) that appears can be stabilized by hydrogen-bond formation between two N–H bonds of the sulfonylurea and the carboxylate anion from the leuco-dye. The hydrogen bond donor ability of the color developer can be evaluated in terms of the α_2^H parameter proposed by Abraham. ^{1}H NMR chemical shift values of the N–H protons in the sulfonylurea and HPLC retention times of the sulfonylurea on a silica column show a good correlation with the α_2^H parameter values. The essential factors necessary for the sulfonylurea to give rise to high color developing by forming a stable hydrogen-bond complex are also discussed on the basis of the structure and the electronic properties of the sulfonylureas.

Thermal paper[1] is a very popular print media widely used in various ways in our daily life. Essential components of the thermal paper for color developing are a dye precursor, such as fluoran compounds, and a color developer. Heating a part of the surface area of the thermal paper by a thermal head leads to black color formation because of a chemical reaction due to the melting of component molecules, such as fluoran dye precursor, color developer, and color sensitizer. A popular fluoran dye precursor used in the thermal paper on the market is 2′-anilino-6′-(*N*-ethylisopentylamino)-3′-methylspiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one (**S-205**). The origin of black color developing is assumed to be a π-delocalized stabilized carbocation generated from the fluoran dye precursor by thermally induced cleavage of a lactone ring. This lactone ring-opened molecular framework can be an intense chromophore with absorption maxima at around 450 and 590 nm.[2,3] The role of the color developer is to stabilize the π-delocalized carbocation generated from the fluoran dye precursor. In our previous paper,[4] we have proposed that hydrogen-bond formation between an open-form fluoran dye precursor and a color developer is an essential factor for efficient color developing. If the ability to form hydrogen bonds between an open-form fluoran dye precursor and a color developer molecule can be evaluated, molecular design of a functional color developer for manufacturing thermal paper with high color developing and high durability will be possible. A good color developer for thermal papers that is actually on the market is a sulfonylurea compound.[5,6] Thermal paper, comprised of sulfonylurea and **S-205**, have been reported to show black color developing and its color durability is better than that of the previously used thermal papers, in which phenol-type color developer molecules are used.

In this paper, the hydrogen bond donor ability of a series of sulfonylurea compounds has been evaluated in terms of the α_2^H parameter[7] by measuring the UV–visible spectra of a solution containing the sulfonylurea (color developer) and **S-205**, and a correlation between the color developing of the solution expressed by absorbance at $\lambda_{max} = 580$ nm and the hydrogen bond donor ability of the sulfonylurea was investigated. Chemical implication of the determined α_2^H values of the sulfonylurea is discussed from the correlation analyses between the experimental data obtained from ^{1}H NMR N–H proton chemical shift and HPLC retention time measurements and α_2^H. Structural factors for black color developing were investigated from color developing UV–vis experiments involving various types of sulfonylurea compounds $R^1SO_2NH–CO–NH–R^2$ (R^1, R^2 = alkyl, aryl). Specific structural features of these sulfonylurea compounds were also determined by X-ray crystallographic experiments to determine the structural changes due to different R^1 and R^2 moieties. On the basis of these experimental results, essential factors for black color developing and durability of the developed color for preparing the good thermal paper were studied. The parameter α_2^H was found to be useful and effective for determining good color developer molecules for preparing functional thermal paper.

Results and Discussion

Evidence of Color Developing Complex Formation via Hydrogen Bond between the Sulfonylurea and Lactone Ring-Opened Form of S-205. Color-developing complex (**CDC**) was isolated as a black precipitate by dissolving both **S-205** and color developer sulfonylurea in hot toluene and rapidly cooling down the toluene solution in an ice bath. The black precipitate was quickly filtered, washed with cold tol-

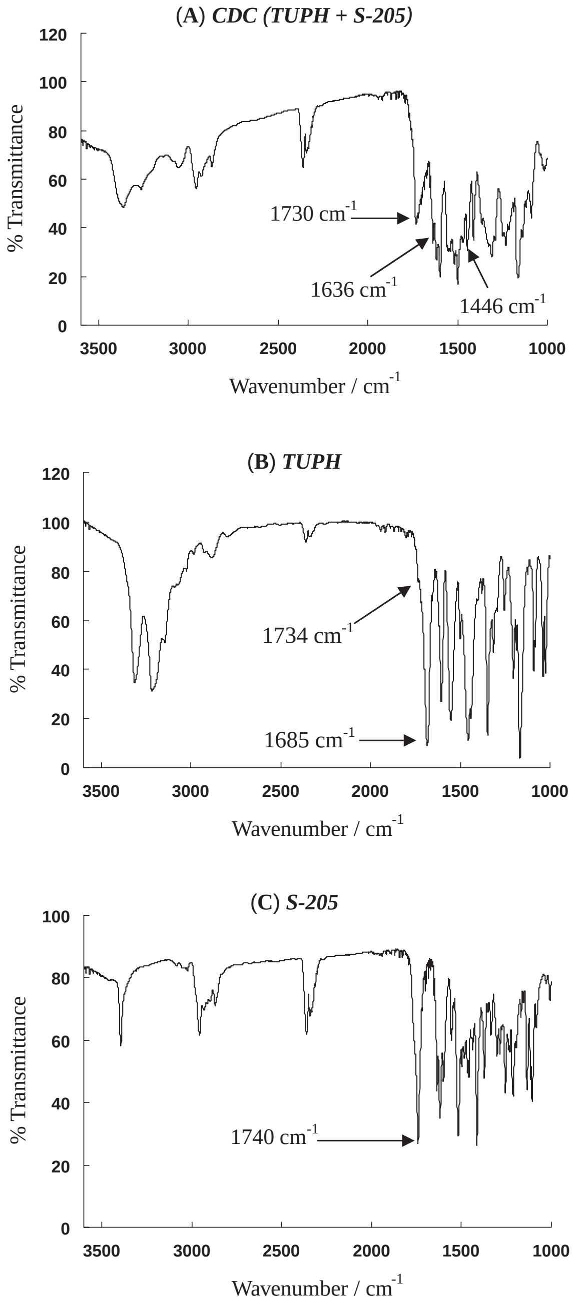


Fig. 1. IR spectra of the **CDC** composed of **S-205** + **TUPH**, and its relevant molecules in KBr disc. Two peaks found around 2340–2360 cm^{-1} are due to gaseous CO_2 in the spectrometers, and should be neglected.

uene with suction, and then dried in vacuo to give a black powder. This black powder is stable as long as it is in the solid state. The IR spectrum as a KBr disc of the **CDC** thus prepared from *N*-phenyl-*N*′-*p*-tolylsulfonylurea (TUPH), and **S-205** is shown along with spectra of **TUPH** and **S-205**, in Fig. 1.

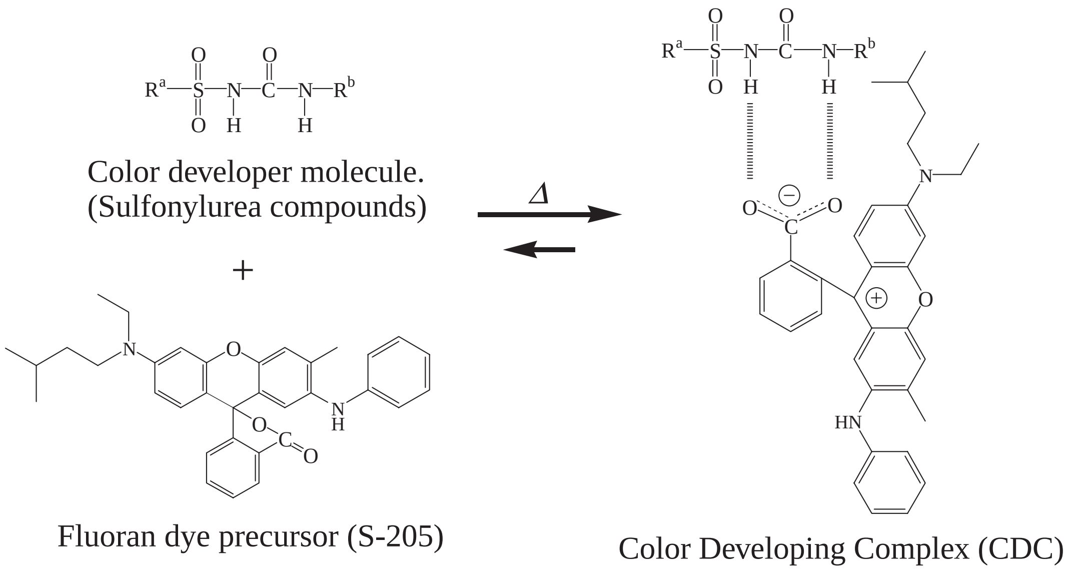
The IR spectrum of the **CDC** has characteristic absorptions inherent to the COO^- group at 1636 cm^{-1} (anti-symmetrical mode) and at 1446 cm^{-1} (symmetrical mode) suggesting that lactone ring opening may be stabilized by the formation of a hydrogen bond with **TUPH**. Hydrogen-bond formation between sulfonylurea N–H groups and carboxylate functional group is indicated by broader bands in the N–H region (3050–3350 cm^{-1}). On the other hand, **S-205** has a carbonyl stretching band at 1740 cm^{-1} characteristic of an ester functional group of a lactone ring. The IR spectra indicate that **CDC** is a hydrogen-bonded complex between **S-205** and sulfonylurea compound as shown in Scheme 1. Around the carbonyl-stretching region, another rather intense absorption peak at 1730 cm^{-1} was observed in the **CDC** spectrum. This peak was assumed to come from a free carbonyl group that does not participate in a formation of the hydrogen bond in **TUPH**. From the X-ray crystallographic analysis discussed later, it was shown that the sulfonylurea, such as **TUPH**, is likely to aggregate[8] and exists in dimeric form in the unit cell by forming intermolecular hydrogen bond between two N–H groups and carbonyl/sulfonyl oxygen atoms (Fig. 2).[9] Thus, in IR spectrum of **TUPH** as a KBr disc, two types of carbonyl C=O stretching bands were observed. One is the peak as shown at 1685 cm^{-1} characteristic to the hydrogen-bonded sulfonylurea carbonyl group, and the other is the shoulder peak at 1734 cm^{-1} ascribed to the free C=O group.

When **CDC** was formed between the lactone ring-opened **S-205** and **TUPH**, hydrogen-bond formation between carboxylate anion COO^- and two N–H groups in sulfonyl urea occurred via penetration of the **S-205** molecule into the dimeric structure of **TUPH**, resulting in the collapse of the hydrogen-bond network formed among **TUPH** molecules. Therefore, the shoulder peak for the free carbonyl group in **TUPH** was found at 1730 cm^{-1} in the IR spectrum of **CDC**. The IR spectrum of **TUPH** in CCl_4 also showed two carbonyl peaks at 1727 (free form) and 1683 cm^{-1} (dimeric hydrogen-bonded form). In the N–H stretching[10] vibrational region (3150–3400 cm^{-1}) of **TUPH**, two rather intense peaks were observed. These peaks were identified as the sulfonylurea N–H stretching mode absorptions, which come from the free and hydrogen-bonded forms of sulfonylurea.

^{1}H NMR measurements have shown that **CDC** is composed of **S-205** and sulfonylurea with a mole ratio of 1:2. When a black-colored **CDC** was dissolved in solvents containing hydroxy groups, such as methanol, the solutions became colorless indicating dissociation of **CDC**. The colorless solution showed a spectrum, on which the spectra of each component molecule of **CDC** could be superimposed and of which integration gave a molar ratio of **S-205**:sulfonylurea of 1:2.

From the determined crystal structure of the **TUPH** (in Fig. 2),[9] it was found that the distance between the two amino hydrogen atoms in the sulfonylurea functional group (R^1SO_2-N$\underline{H}$–CO–N$\underline{H}$–R^2) is 2.199 Å and is almost the same as the distance between the two carboxylate oxygen atoms ($\underline{O}$–C(carbonyl)–$\underline{O}$). The reported O···O distances for the carboxylate functional group, which are compiled in the Cambridge Structural Database[11–13] and the calculated values by fully optimized ab initio calculations, are about 2.22 Å. Structurally, the sulfonylurea functional group and carboxylate group are a good fit, contributing to facile hydrogen-bond formation.

Hydrogen Donor Ability (α_2^H) Values of the Sulfonylurea Molecules. The IR spectrum investigation of **CDC** and X-ray crystallographic study of sulfonylurea molecules indicate that **CDC** is a hydrogen-bonded complex of **S-205** and a sulfonylurea, e.g., **TUPH**, with a molar ratio of 1:2. It



Scheme 1.

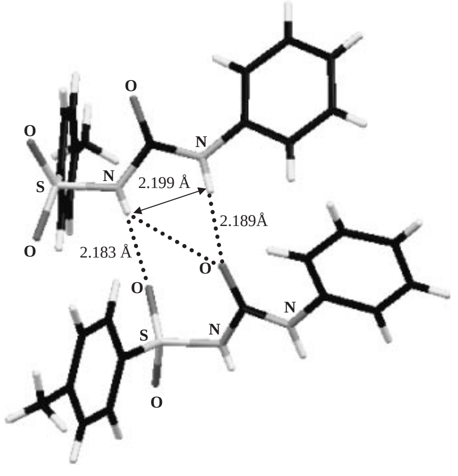


Fig. 2. Crystal structure of the **TUPH**.

Table 1. The Reported $\alpha_2{}^H$ Values[7] of Hydrogen Bond Donor Molecules, and the Absorbance Values for the Solutions of (**S-205** + Hydrogen Bond Donor Molecules with a Molar Ratio of 1:2) at $\lambda_{max} = 580$ nm Determined by UV–Vis Experiments

Compounds	α_2^H	$\log(A_{\text{S-205+Color Developer}})$
4-Nitrophenol	0.824	−0.023
4-Cyanophenol	0.787	−0.435
4-Iodophenol	0.679	−0.907
4-Bromophenol	0.674	−1.137
4-Chlorophenol	0.670	−0.928
4-Fluorophenol	0.629	−1.377
Phenol	0.596	−1.620
2,2,2-Trifluoroethanol	0.567	−1.721
N-Methylacetamide	0.383	−2.328
4-Bromoaniline	0.308	−3.092

is intriguing to evaluate quantitatively $\alpha_2{}^H$ of the sulfonylurea molecules by comparing with other kind color developer molecules, such as substituted phenols. An appropriate scale of hydrogen bond donor ability must take into account the feasibility of measuring it experimentally. Among reported various parameters for hydrogen bond donor abilities, $\alpha_2{}^H$ proposed by Abraham et al.[7] seems to be universal and trustworthy because the $\alpha_2{}^H$ values have been derived from reliable equilibrium constant values for many acid–base complexes determined experimentally by using various spectroscopic methods. We determined the $\alpha_2{}^H$ values for sulfonylurea molecules by measuring the absorbance (**A**) of solutions containing **S-205** and the sulfonylurea molecules (**S-205**:sulfonylurea = 1:2) at $\lambda_{max} = 580$ nm with a UV–vis spectrometer.[14] The chemical species for developing black color has also been assumed to be a zwitterionic form of **S-205**[2,4] stabilized by hydrogen bond donor molecules, such as 2,2,2-trifluoroethanol ($\alpha_2{}^H = 0.567$), by UV–vis experiments.

The UV–vis spectrum of this chemical species has two absorption maxima at $\lambda_{max} = 468$ and 580 nm, which cause the black color developing. The reflection UV–vis spectrum of a black color image[4] on the thermal paper composed of **S-205** and bisphenol A showed the same absorption peaks. As the peak at $\lambda_{max} = 580$ nm is stronger in absorbance than that at $\lambda_{max} = 468$ nm, it is better to monitor the absorbance at $\lambda_{max} = 580$ nm to evaluate the black color developing. On the basis of the reported $\alpha_2{}^H$ values[7] for the hydrogen bond donor molecules, such as alcohols and substituted-phenols, in Table 1, the plot was drawn as shown in Fig. 3. The derived linear regression line was expressed as in Eq. 1.

$$\log(A_{\text{S-205+Color Developer}}) = 5.465 \times \alpha_2{}^H - 4.700 \qquad R^2 = 0.971. \tag{1}$$

Equation 1 was used to determine the $\alpha_2{}^H$ values of various sulfonylurea molecules by measuring the absorbance **A** of **S-205** + sulfonylurea (molar ratio; 1:2) solution in 1:1 (V/V) acetonitrile/toluene. The $\alpha_2{}^H$ values for the sulfonylurea molecules (R^1SO_2NH–CO–NH–R^2) are compiled in Table 2. It is apparent that sulfonylurea molecules that have aryl groups attached directly to both terminal atoms in the sulfonylurea group (R^1, R^2 = aryl), are better hydrogen-bond donors with $\alpha_2{}^H$ values ranging from 0.896 (compound **8**) to 1.089 (compound **1**) and can develop a stronger black color. In contrast, sulfonylureas that have alkyl group/groups at either or both terminal ends (R^1 and/or R^2 = alkyl; compounds **9–11** and **13**) have weaker color-developing abilities (0.669 to 0.845).

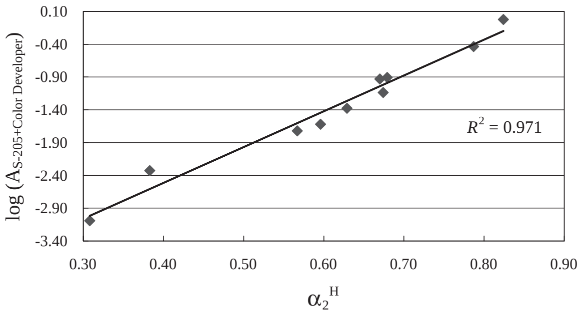


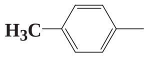
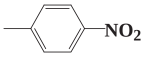
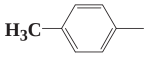
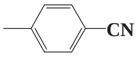
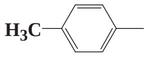
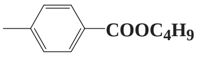
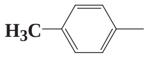
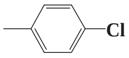
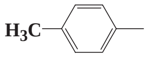
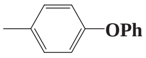
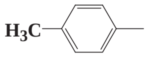
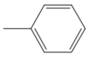
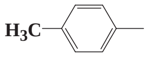
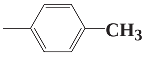
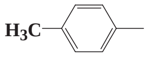
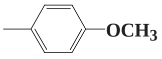
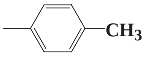
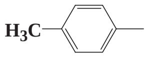
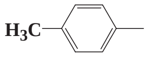
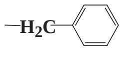
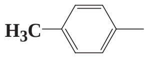
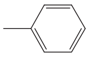
Fig. 3. Linear regression line to evaluate $\alpha_2{}^H$ values determined from experimental $\log(A_{\text{S-205+Color Developer}})$ vs $\alpha_2{}^H$ plot on the basis of the reported $\alpha_2{}^H$ values[7] for alcohols and substituted phenols.

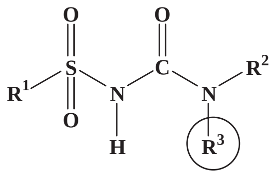
It should be noted that two N–H groups on the sulfonyl group are needed to form **CDC**. When the one of the N–H group in the sulfonylurea is substituted with alkyl group (compound **12**), black color developing was depressed because of a decrease in the hydrogen bond donor ability ($\alpha_2{}^H$(compound **6**) = 0.917, $\alpha_2{}^H$(compound **12**) = 0.684).

Why does $\alpha_2{}^H$ become lower in the case of alkylsulfonylureas compared to the arylsulfonylureas? This is because that alkylsulfonylureas have a higher LUMO energy level than the arylsulfonylureas due to the smaller range π-electrons delocalization around the sulfonylurea functional group. By increasing the LUMO energy level of the sulfonylureas, the acquired stabilization energy from hydrogen-bond formation between the carboxylate anion moiety of **S-205** and the sulfonylurea functional group may decrease. The stabilization energy can be approximately expressed with the inverse of the E_{HOMO}(**S-205**) − E_{LUMO}(sulfonylurea) as shown in Eq. 2.[15]

$$\Delta E = -\frac{Q(\text{HB}_{\text{donor}})Q(\text{HB}_{\text{acceptor}})}{\varepsilon R} + \frac{2(c(\text{HB}_{\text{acceptor}})c(\text{HB}_{\text{donor}})\beta)^2}{E_{\text{HOMO}}(\text{HB}_{\text{acceptor}}) - E_{\text{LUMO}}(\text{HB}_{\text{donor}})}. \quad (2)$$

Table 2. The Determined $\alpha_2{}^H$ Values for the Sulfonylurea Molecules with ^{1}H NMR Chemical Shifts (δ) of the Sulfonylurea N–H Proton in CD_3CN at 30 °C and the HPLC Retention Times (R.T.) to Silica Column with CH_3CN as an Eluent

Compounds	R^1	R^2	R^3	α_2^H	$\delta_{\text{N–H}}$/ppm	R.T./min
1			H	1.089	8.10	6.35
2			H	1.052	7.96	7.14
3			H	1.000	7.92	5.32
4			H	0.963	7.75	6.20
5			H	0.941	7.72	5.57
6			H	0.917	7.72	5.28
7			H	0.899	7.64	5.54
8			H	0.896	7.60	5.10
9	H_3C–		H	0.845	7.68	—
10		$–CH_2CH_2CH_3$	H	0.742	5.97	—
11			H	0.711	6.41	3.91
12			CH_3	0.684	—	4.11
13	H_3C–	$–CH_2CH_2CH_3$	H	0.669	5.81	—



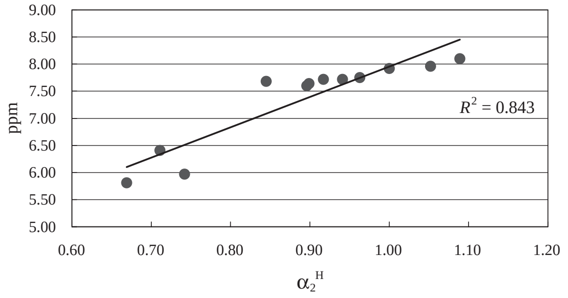


Fig. 4. Correlation plot between $\alpha_2{}^H$ and N–H proton (R^1SO_2NH–CO–N<u>H</u>–R^2) chemical shifts of the sulfonylurea molecules.

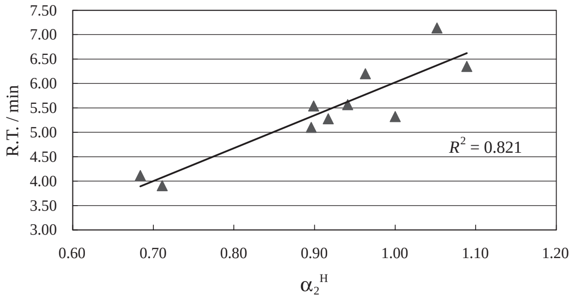


Fig. 5. Correlation plot between $\alpha_2{}^H$ and HPLC retention time of sulfonylurea molecules for silica column with CH_3CN as an eluent.

Where $Q(\mathrm{HB_{donor}})$, $Q(\mathrm{HB_{acceptor}})$ are electronic charges on HB (hydrogen bond) donor and HB acceptor atoms, respectively, R is distance between the centers of HB donor and HB acceptors, $E_{\mathrm{HOMO}}(\mathrm{HB_{acceptor}})$, $E_{\mathrm{LUMO}}(\mathrm{HB_{donor}})$ are HOMO and LUMO energies of HB donor and HB acceptor, respectively, ε is the dielectronic constant, β is the resonance integral, and c is the coefficient for the atom of HB acceptor or HB donor, respectively, in the HOMO and LUMO.

Preliminary studies involving the frontier orbital energy levels and the optimized structures of the sulfonylurea molecules used in the experiments were performed via Hartree–Fock[16] level ab initio calculations, and the results showed that sulfonylurea molecules with less black color developing ability have a higher LUMO energy level. Details will be reported in the next paper.

Chemical Implication of the $\alpha_2{}^H$ Parameter. To validate the $\alpha_2{}^H$ parameter values thus obtained for sulfonylurea, the relevant experimental results, such the spectral data, of the sulfonylureas were correlated to $\alpha_2{}^H$ values. In Table 2, ^{1}H NMR chemical shift values of the sulfonylurea N–H protons (R^1SO_2-NH–CO–N<u>H</u>–R^2) and the HPLC retention times (R.T.) of sulfonylurea molecules on a silica column with CH_3CN as an eluent are compiled with $\alpha_2{}^H$ values. Linear correlations of each experimental value versus $\alpha_2{}^H$ are shown in Fig. 4 (^{1}H NMR) and Fig. 5 (HPLC retention time). With regard to the ^{1}H NMR chemical shift of the sulfonylurea N–H proton located between carbonyl and R^2 group, there is a good linear correlation ($R^2 = 0.843$) because the chemical shifts move down-field dependent on the increase in $\alpha_2{}^H$ of the sulfonylureas. The chemical shift of N–H proton adjacent to SO_2 group changed less and no linear correlations were found. The retention times correlated well ($R^2 = 0.821$), i.e., retention times for the sulfonylureas increased with larger $\alpha_2{}^H$ values. These results confirmed that $\alpha_2{}^H$ is an appropriate parameter to evaluate the hydrogen bond donor ability of the sulfonylurea compounds. By comparing the $\alpha_2{}^H$ values of the phenol compounds (0.596–0.824) with aryl-type sulfonylurea molecules R^1SO_2NH–CO–NH–R^2 (R^1, R^2 = aryl) (0.896–1.089), thermal paper that uses aryl-type sulfonylureas as the color developer are better.

With regard to IR frequencies of the sulfonylurea functional group, such as N–H and C=O stretching bands, only fair linear correlations with $\alpha_2{}^H$ values were obtained, though the IR data should correspond well to hydrogen bond donor abilities of the sulfonylurea molecules. This is partly because IR frequency numbers for N–H and C=O bands are sensitive to water in the solvents or finely ground KBr powder. Other problem in the IR experiments include the difficulty in assigning the sulfonylurea N–H and/or C=O peaks specificially and the low solubility of the sulfonylureas in CCl_4 solvent. In the IR spectra of **CDC** (**S-205** + sulfonylurea), multiple absorption peaks inherent to the N–H/C=O group were observed reflecting inter- or intra-molecular interactions in **CDC**. At present, it is rather difficult to identify accurately the vibrational mode of these multiple peaks.

Structural Factor to Form Favorable Hydrogen-Bonded Complex. In addition to the electronic features described above, structural factors may be important in order to form a hydrogen-bond complex effectively. On the basis of the crystal structures of sulfonylureas, shown in the dimeric form in Fig. 2, structural characteristics of the **CDC** formed by **S-205** and the sulfonylureas (R^1SO_2NH–CO–NH–R^2) have been investigated preliminary with an aid of computational chemistry using the force field. The estimated two **CDC**'s (**A**: R^1 = *para*-tolyl, R^2 = phenyl, **B**: $R^1 = -CH_3$, $R^2 = -CH_2CH_2$-CH_3) are displayed in Fig. 6. **CDC A**, in which the color developer is an arylsulfonylurea, is stabilized due to hydrogen bonds between the carboxylate anion and the two N–H groups in the sulfonylurea as designated by dotted lines. In the **CDC A**, the two terminal aryl groups in the sulfonylurea molecule are oriented to relieve steric hindrance between the aryl groups and neighboring substituents attached to the carboxylate group in the **S-205**. In the case of **CDC B**, there is steric repulsion between the terminal methyl group and **S-205**, as shown in the area surrounded by an ellipse, when sulfonylurea forms hydrogen bonds. Aryl groups located at R^1 and R^2 positions are better due to the electronic and stereochemical aspects for forming hydrogen bonds.

Conclusion

Sulfonylurea (R^1SO_2NH–CO–NH–R^2) is a good color developer for preparing functional thermal paper with high black color developing and durability of the developed color because two N–H groups in the sulfonylurea functional group are good donors forming a stable hydrogen-bonded complex with the carboxylate group (COO^-), which forms when the lactone ring of the leuco-dye opens. The hydrogen bond donor ability of the sulfonylurea molecules corresponded quantitatively with $\alpha_2{}^H$. The chemical validity of the $\alpha_2{}^H$ values for the sulfonylureas was established by correlating the experimental results (^{1}H NMR chemical shifts and HPLC retention time of the sul-

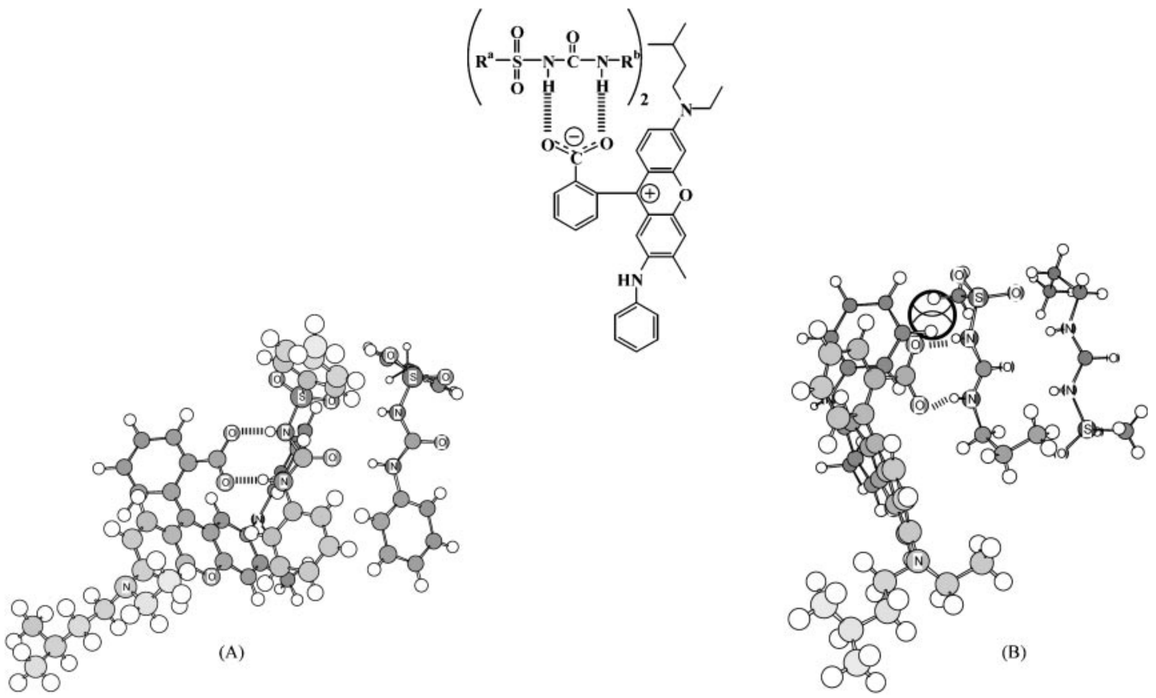
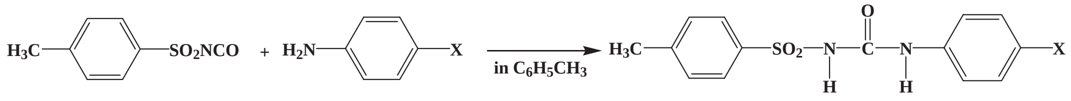
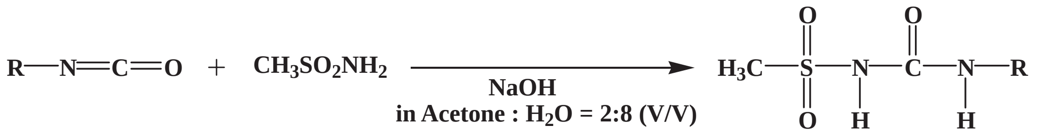


Fig. 6. The estimated structures of **CDC** on the basis of the crystal structures determined by X-ray crystallographic experiments. In the case of **A** (R^a = *p*-tolyl, R^b = phenyl), favorable hydrogen-bond interaction is possible as shown by ---- lines. To the contrary, steric hindrance occurred in the case of **B** (R^a = $-CH_3$, R^b = $-CH_2CH_2CH_3$) to avoid forming hydrogen bond.



Scheme 2.



Scheme 3.

fonylurea) vs $\alpha_2{}^H$ values. Among the sulfonylurea molecules, arylsulfonylureas ($R^1SO_2NH–CO–NH–R^2$:R^1 and R^2 = Ar) are better color developers than those in which R^1 and/or R^2 are alkyl groups because arylsulfonylurea is a better hydrogen-bond donor and the aryl groups can move to reduce steric repulsion when forming the hydrogen-bond complex.

Experimental

Arylsulfonylureas have been synthesized by a reaction of substituted anilines with *p*-toluenesulfonyl isocyanate in toluene as shown in Scheme 2.[17,18] **S-205** (Yamada Chemical) and *p*-toluenesulfonyl isocyanate are commercially available. The purity of the synthesized sulfonylurea was checked by measuring the melting points. Alkylsulfonylureas, such as $CH_3SO_2NH–CO–NH–CH_2CH_2CH_3$ (compound **13**), were synthesized by the reaction of 0.11 mol alkyl(R) isocyanate with an acetone H_2O solution (acetone:H_2O = 2:8 (V/V)) containing 0.10 mol methansulfonamide and 0.10 mol NaOH as shown in Scheme 3.[19]

IR spectra were measured on a Perkin-Elmer FT/IR spectrometer as a KBr disc or in CCl_4 solutions, if the sulfonylureas were soluble. UV–vis spectra were taken on a JASCO UVIDEC 610C UV–vis spectrometer. To measure absorbances (**A**) of black color solutions composed of **S-205** and the color developer molecules, such as sulfonylureas and substituted phenols, they were dissolved in an acetonitrile:toluene = 1:1 (V/V) mixed solvent. The molar ratio of **S-205**:color developer was adjusted to be 1:2, and the absorption intensities at λ_{max} = 580 nm were measured to evaluate the hydrogen bond donor abilities $\alpha_2{}^H$ of the color developer molecules. ^{1}H NMR measurements were carried out on a JEOL JNM-AL400 spectrometer in CD_3CN at 30 °C and referenced to a $(CH_3)_4Si$ standard.

HPLC experiments were performed with a Shimadzu LC-9A instrument attached to a Shimadzu SPD-6AV UV–vis spectrometric detector (detection wavelength: 260 nm) by using a TOSOH TSK-GEL Silica 60 column (4.6 mm diameter × 25 cm). The retention times of the sulfonylureas were measured with CH_3CN as an eluent and a flow rate of 1.0 mL min^{-1}.

X-ray crystallographic measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation at ambient temperature. The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. All calculations were performed using the teXsan[22] crystallographic software package of the Molecular Structure Cooperation.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-619831 for compound No. 6. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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