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Structure Determination from Powder X-ray Diffraction Data of Black Azo (Hydrazone) Pigments

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Crystal structures of two black monoazo (hydrazone) pigments have been determined from powder X-ray diffraction data combined with DFT calculations. The DFT calculations suggested the molecules are in hydrazone forms but not in azo forms in both crystal structures. The molecular arrangements in the crystal structures suggested Davydov splitting may occur by excitonic interactions and it causes the red absorption band shift in the crystalline state leading to the characteristic black colors.

Azo compounds are widely used as organic dyes and pigments which usually show yellow to red color.[1] Characteristic colors of azo compounds come from a large π-electronic conjugation system which is extended by an N=N with conjugated polyene moieties. In solid state, colors of organic pigments are known to be altered by their crystal structures (i.e. molecular arrangement). For example, diketopyrrolopyrrole derivatives are known to change their color from vivid red to yellowish red depending on the molecular arrangement in their crystal structures, even though they show no spectral difference in solutions.[2] Such color change by crystallization is attributed to the excitonic interaction. In this background, crystal structure is very important for understanding the nature of the color of the pigments in the solid state.

Recently, we have succeeded in preparing new black monoazo pigments, 1-(4-dimethylaminophenylazo)-3-(naphtho[1,2-*d*]thiazol-2-yl)naphthalen-2-ol (**1**) and 1-(4-dimethylaminophenylazo)-3,6-bis(naphtho[1,2-*d*]thiazol-2-yl)naphthalen-2-ol (**2**), which are black in the solid state (Figure 1). Monoazo pigments are usually yellow to red, and characteristic black colors of these compounds would be due to the molecular arrangements in their crystal structures, in addition to their broadly extended π-conjugation systems inducing narrowing of the HOMO–LUMO gap which provides a red shift of light absorption and hopefully allowing a variety of electron transitions. However, unfortunately, we failed to prepare single crystals of these compounds because of their low solubility and no sublimation property, and we cannot clarify their crystal structures. In such case, techniques for carrying out structure determination directly from PXRD data (ab initio PXRD analysis) are clearly essential to reveal crystal structures without preparation of single crystals. Ab initio PXRD analysis for organic molecular materials has been developed in recent years.[3–5] In the present letter, we report the crystal structures of **1** and **2** which have been determined by ab initio PXRD analysis combined with density functional theory (DFT) calculation.

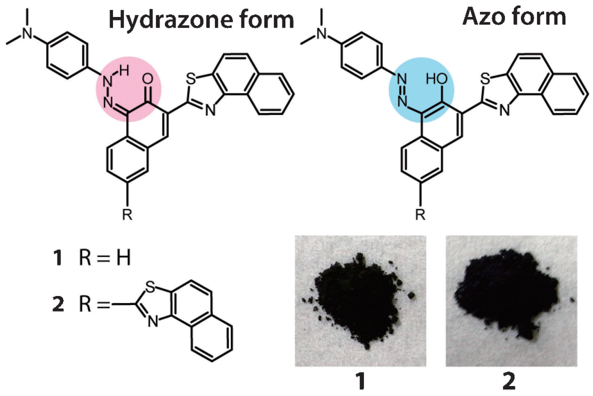

Figure 1. Molecular structures of **1** and **2** in azo forms (upper right) and hydrazone forms (upper left). The pictures show powdery solids of these compounds.

The monoazo-type pigments **1** and **2** were synthesized according to the procedures described in the Supporting Information. Synchrotron X-ray powder diffraction data of black powdery products of **1** and **2** were recorded under ambient conditions on beamline 4B2 (Multiple Detector System) at the Photon Factory, Tsukuba, Japan, with a wavelength of 1.196734(3) Å. The samples were introduced into 2 mm diameter borosilicate glass capillaries and were used for the measurements. The data collection time was 7 h.

Indexing of the powder X-ray diffraction data was carried out using the program X-cell[6] for **1** and DICVOL04[7] for **2**. The structure solution calculations were carried out using the program DASH[8] followed by the Rietveld structural refinement[9] by the GSAS[10] program. In the structural refinement, standard restraints were applied to the bond lengths and bond angles, and a global isotropic displacement parameter was used. There are two possible tautomeric forms for **1** and **2** (azo and hydrazone forms) and it is difficult to distinguish the difference from the powder X-ray diffraction data. Also, the IR spectra of **1** and **2** did not give a clear answer to the tautomeric forms (Figure S1 in the Supporting Information). Therefore, DFT calculations (B3LYP with a 6-31G* basis set) were carried out using the program SPARTAN'08 (Wavefunction, Inc.) to estimate the energy difference of both tautomeric forms. The energy differences were calculated to be 3.92 kcal mol^{-1} for **1** and 3.93 kcal mol^{-1} for **2** and the hydrazone forms have lower energies than the azo forms in both molecules. The detailed investigation using single-crystal X-ray diffraction combined with DFT calculation on the azo–hydrazone tautomerization of similar compounds suggested the hydrazone forms were generally more favorable than azo forms.[11] In addition, the literature reported that the energetic difference more than ca. 1 kcal mol^{-1} gave complete ordering of the tautomer. In addition, the calculated UV–vis spectra of the hydrazone forms (green

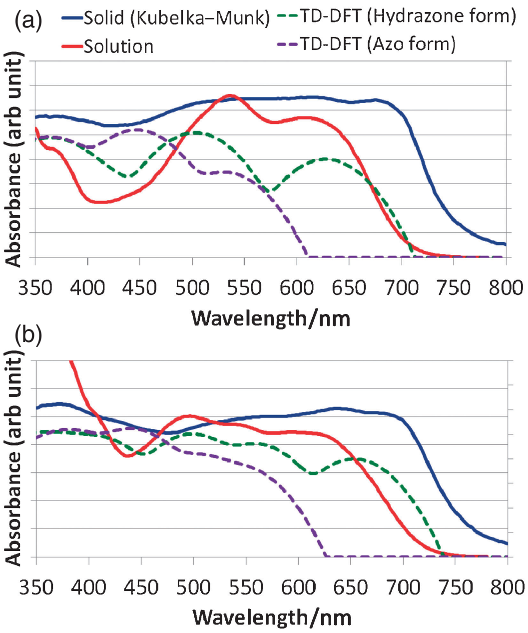

Figure 2. UV–vis spectra of (a) **1** and (b) **2**.

dash lines in Figure 2) obtained by time-dependent DFT (TD-DFT) calculations gave better agreement with those in the solution (red lines in Figure 2) than azo forms (purple dash lines in Figure 2). Here the B3P86 functional with a 6-31G* basis set was used for the TD-DFT calculations because it can give better results than the B3LYP functional.[12] From these considerations, we concluded that the molecules are in the hydrazone forms in both crystals. The final Rietveld structural refinements were, therefore, carried out with the hydrazone forms. The final results are shown in Table 1.

The crystal structure of **1** (Figure 3a) contains two independent molecules (blue and green) in the unit cell. Both molecules are almost flat and are alternatively stacked along the *b* axis giving a herring bone packing motif. There are no intermolecular hydrogen bonds and only an intramolecular hydrogen bond is found at the hydrazone.

The molecule in the crystal structure of **2** (Figure 3b) is also flat. The molecules arrange parallel to the *ab* plane giving sheet motifs which are stacked along the *c* axis. There is a large vacant channel along the *c* axis at the (0, 0, *z*) in the crystal structure of **2** (blue dash lines in the center of Figure 3b). The volume of the void is calculated to be 422 $Å^3$/unit cell and it is possible to incorporate solvents in them. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were simultaneously measured on a Rigaku Thermo Plus 2 instrument. 3.219 mg of **2** were heated at a rate of 5 °C min^{-1} and the TG curve was recorded from 40 to 300 °C in a dry nitrogen atmosphere with a flux of 20 mL min^{-1}. The TGA data of **2** showed no mass decrease (less than 0.3% weight loss) by heating which eliminate the possibility of containing the solvents in their crystal packing (Figure 4). In addition, the structural analysis gave a good quality fitting between the experimental and calculated data (Figure 3b). Therefore, the large channel does not contain any ordered molecules and it may be filled by air. As well as for **1**, there is no intermolecular hydrogen bond and only intramolecular hydrogen bond is found at the hydrazone in the crystal structure of **2**.

Table 1. Crystallographic data of **1** and **2**

	1	**2**
Formula	$C_{29}H_{22}N_4OS$	$C_{40}H_{27}N_5OS_2$
Formula weight	474.58	657.80
Crystal system	Monoclinic	Hexagonal
Space group	$P2_1/c$	$P6_1$
a/Å	21.9743(4)	23.1191(6)
b/Å	7.46291(7)	23.1191
c/Å	30.6772(7)	10.67304(15)
α/°	90	90
β/°	114.2703(11)	90
γ/°	90	120
V/$Å^3$	4586.19(17)	4940.39(25)
Temperature/°C	27	27
Z	8	6
Z'	2	1
R_{wp}	0.0528	0.0752
$R_F{}^2$	0.0630	0.0725

UV–vis spectra of both **1** and **2** were measured in the solid state (Kubelka–Munk conversion of the diffuse reflectance spectra) and the solution (these compounds can slightly dissolve in *N*-methylpyrrolidone). The absorption bands in the solid state (blue lines in Figure 2) are shifted to longer wavelength (i.e. red shift) compared to the spectra in solution (red lines in Figure 2). The red shift of the absorption by crystallization may attribute to the molecular arrangement of the crystal structures. It is known that compounds which have high absorption coefficient show absorption shift by excitonic interaction.[14] The positions and orientation of two molecules are important for the absorption shift. In the present case, the transition dipoles (calculated by TD-DFT) have oblique arrangements (Figure S2 in the Supporting Information). Such condition is known to lead a Davydov splitting and it would cause the red absorption band shifts in both **1** and **2**.

In this work, we have revealed the crystal structures of black azo pigments **1** and **2** from powder X-ray diffraction data combined with the (TD-)DFT calculations. The DFT calculations suggested the molecules are in hydrazone forms in both crystal structures. Therefore these pigments are actually not azo-type pigments. Both structures consist of highly planar molecules having largely extended π-conjugation systems which can cause wide range absorption. The molecular arrangements in the crystal structures suggested the Davydov splitting may occur by the excitonic interactions which cause broadening of the optical absorption bands including thier red shifts in the crystalline state leading the characteristic black colors.

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Supporting Information is available electronically on J-STAGE.

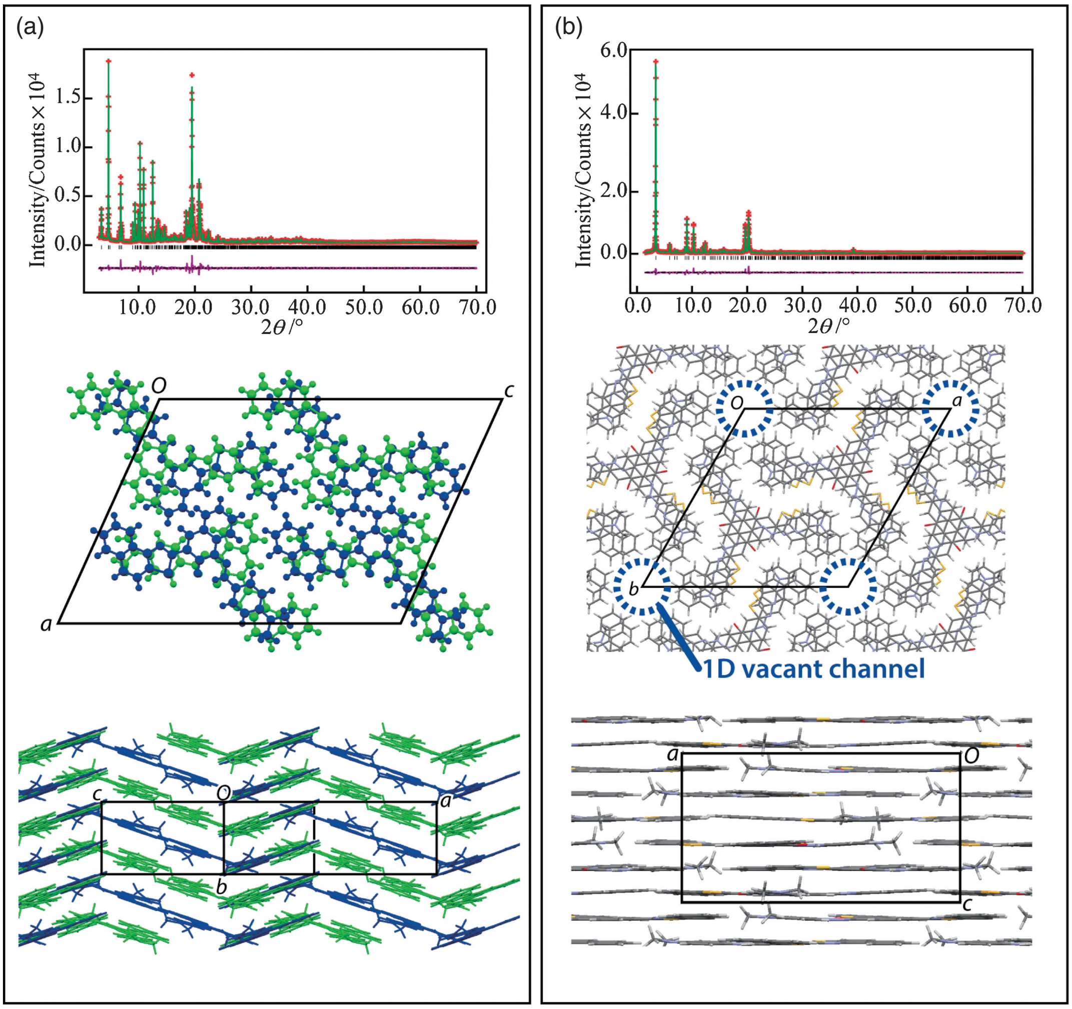

Figure 3. Final Rietveld refinement and crystal structures of (a) **1** and (b) **2**. The experimental powder X-ray diffraction pattern (red + marks), calculated powder X-ray diffraction pattern (green solid line) and difference profile (black line) are shown. The tick marks indicate the peak positions. Two independent molecules in (a) are drawn in different colors (blue and green).[13]

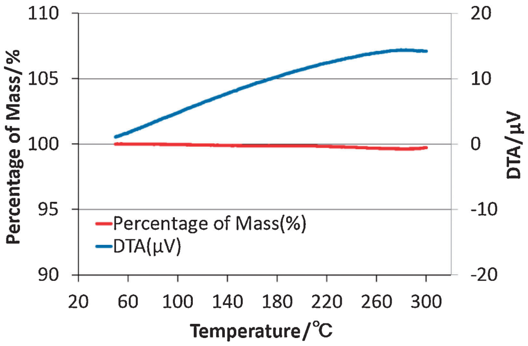

Figure 4. TGA/DTA plot of **2**.

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13 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1043710 and 1043711. Copies of the data can be obtained free of charge via 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; or deposit@ccdc.cam.ac.uk).

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