doi:10.1246/cl.2012.795
Published on the web July 28, 2012

Novel Solid-state Photochromic Reaction of Azobenzene Derivative Controlled by Appended Photoreactive Group

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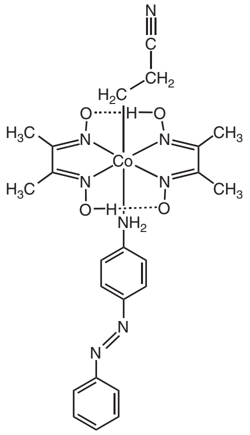
Photochromic solid-state trans–cis isomerization of the 4-aminoazobenzene moiety was observed for the first time in (*trans*-4-aminoazobenzene)(β-cyanoethyl)bis(dimethylglyoximato)cobalt(III) after β–α isomerization of the β-cyanoethyl group on exposure to UV light. The UV spectra revealed that β–α isomerization occurred first, followed by the trans–cis transformation. When the crystal was exposed to visible light, only the β–α isomerization of the cyanoethyl group occurred, with retention of the single-crystal form. The crystal structure before and after the β–α photoisomerization showed that the isomerization is important in this photochromic trans–cis transformation.



Scheme 1. (4-Aminoazobenzene)(β-cyanoethyl)cobaloxime.

(a) (b) (c)

Figure 1. Color change of **1** on photoirradiation.

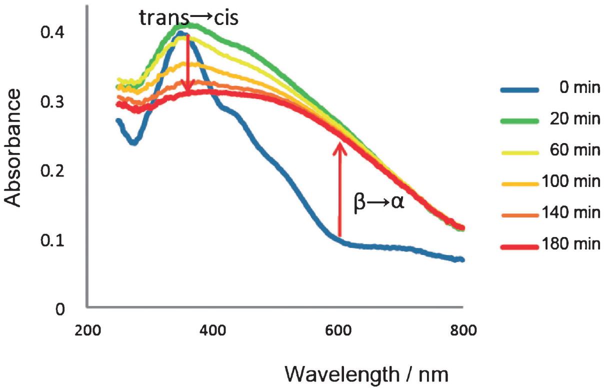


Figure 2. UV–vis spectra of **1** under UV irradiation.

In recent decades, organic photochromic materials have attracted much attention because of their potential applications in optical glasses, storage devices, electric displays, and optical switches. Many photochromic chromophores have been synthesized, and their properties have been examined.[1] The photochromic reactivity depends on the initial structure, and control of the photochromic properties has been considered to be impossible. Azobenzene derivatives are well-known photochromic compounds and have recently been used in molecular machines in solutions and liquid crystals.[2] In the solid state, however, the photochromic trans–cis transformation of azobenzene derivatives is difficult because of the large structural change in the closely packed crystal lattice. A crystalline powder of *trans*-4-aminoazobenzene, for example, showed no photoreactivity,[3] although Koshima et al. reported that crystals of *trans*-4-dimethylaminoazobenzene showed trans–cis isomerization, in 0.62% yield, on the surface of the crystal.[4]

We considered that the trans–cis transformation should occur if another photoreactive group is appended to the azobenzene derivative. A variety of crystalline-state photoreactions of (β-cyanoethyl)(base)bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes have been investigated,[5] and the complex **1** with 4-aminoazobenzene as an axial base was prepared and is shown in Scheme 1; the photoreactivity was examined.

The solid-state photoreactivity of **1** was examined under irradiation with a high-pressure Hg lamp (SANEI UVF-352S, 350 W). Figure 1 shows the color changes of the complex during the photoreaction in the solid state. The orange color of **1** before photoirradiation (a) became dark brown after exposure for 3 h (b). The sample was then stored in the dark for 24 h (c). The color changed to light brown.

Figure 2 shows the changes in UV–vis spectra of the complex before and after photoirradiation for 20, 60, 100, 140, and 180 min. The absorption at ca. 600 nm after exposure for 20 min (green curve) indicates that the β-cyanoethyl group was isomerized to an α-cyanoethyl group, based on the corresponding spectral changes of related cobaloxime complexes,[6] and the β–α isomerization of the cyanoethyl group was almost complete after 20 min exposure. Then the peak intensity resulting from the *trans*-4-aminoazobenzene ligand, at ca. 360 nm, gradually decreased.[7] This indicates that the *trans*-azobenzene was transformed to the cis isomer. The trans–cis isomerization continued up to 180 min.

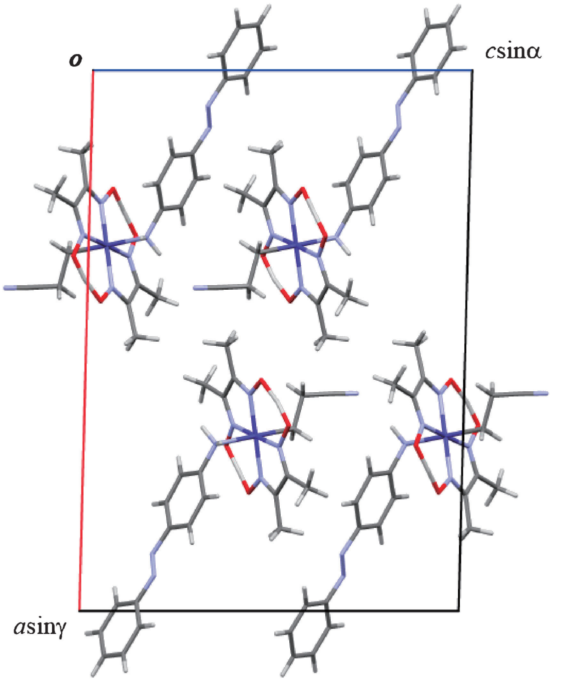


Figure 3. Crystal structure of **1**.

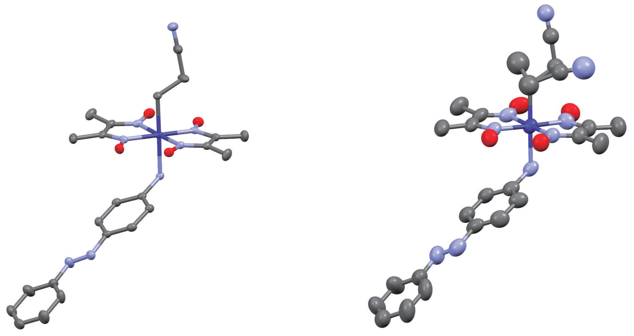
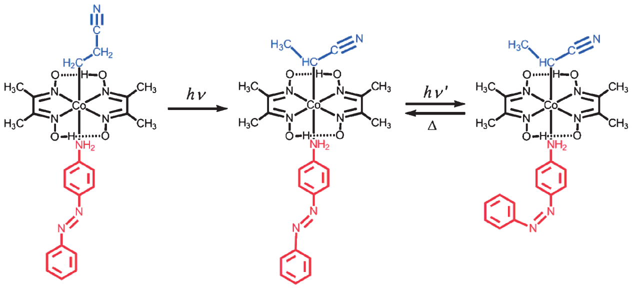


Figure 4. Molecular structure of **1** before (left side) and **1′** after photoirradiation (right side) with a Xe lamp. The cyanoethyl group for **1′** has disordered structure of β- and α-cyanoethyl. Hydrogen atoms are omitted for clarify.



1 **1’** **1”**

Scheme 2. Photoisomerization and photochromism of **1**.

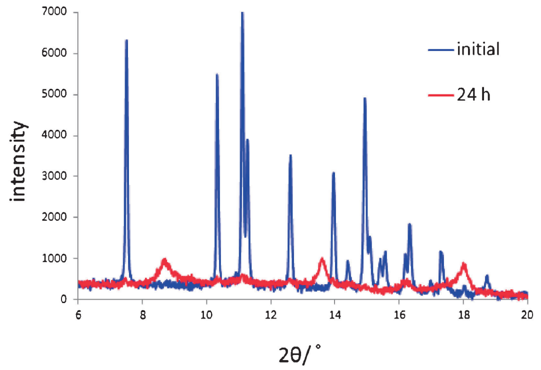


Figure 5. X-ray powder pattern of **1** before and after UV photoirradiation.

When the sample was kept in the dark for 24 h, the UV spectra showed a similar pattern to that after 20-min exposure (green curve). This means that the produced *cis*-4-aminoazobenzene reverted to the original trans isomer, but the α-cyanoethyl group did not revert to the original β-cyanoethyl group. The NMR spectra[8] confirmed that the *cis*-4-aminoazobenzene ligand formed after 180-min exposure reverted to the original *trans*-4-aminoazobenzene after 24 h in the dark.

These results indicate that the *trans*-4-aminoazobenzene showed photochromism as a result of a trans–cis transformation when it was coordinated to the cobalt atom of (β-cyanoethyl)cobaloxime as an axial ligand. However, the trans–cis transformation occurs after β–α isomerization of the cyanoethyl group. Although the produced *cis*-azobenzene reverted to the original trans isomer, the α-cyanoethyl group did not revert to the original β-cyanoethyl group. The trans–cis photochromisms (from (b) to (c), and the reverse, in Figure 1) occurred repeatedly.

In order to examine the structural changes, an orange crystal of **1** ($0.18 \times 0.15 \times 0.10\,\text{mm}^3$) suitable for X-ray measurements was obtained from ethanol solution. The intensity data were collected using a Rigaku RAPID IP diffractometer equipped with a Rigaku liquid-nitrogen cooling system, at 173 K. The crystal structure viewed along the *b* axis is shown in Figure 3. Then the crystal was irradiated with a Xe lamp (SANEI, SUPER BRIGHT 152S, 150 W) on the diffractometer. The cell dimensions gradually changed, with retention of the single-crystal form. After 86 h exposure, the change became insignificantly small, and the crystallinity deteriorated somewhat. The crystal **1′** has increased cell volume by 44.4(5) Å.[3,9]

The molecular structures before and after irradiation are shown in Figure 4. After 86 h exposure, the β-cyanoethyl group was isomerized to the α-cyanoethyl group, in 24% yield, in the crystalline state. It must be emphasized that the 4-aminobenzene has the trans conformation during the reaction.

The above results clearly indicate that the β–α photoisomerization should initiate the trans–cis photoisomerization, since the unit-cell volume increases by 44.4(5) Å^3 after the β–α photoisomerization, and this volume expansion should make space for the trans–cis transformation. The reaction is summarized in Scheme 2.

Although it was impossible to achieve the photoreaction from **1** to **1′** with retention of the single-crystal form, the X-ray powder diffraction pattern of **1** showed that the tiny crystal of **1** gradually decomposed on exposure to UV light and a new pattern from **1″** appeared, as shown in Figure 5. The red line shows **1″** after 24-h irradiation under UV light in Figure 5, and at that stage the cis isomer produced with 40% yield which was confirmed by ^{1}H NMR spectra. Structural analysis of **1″** from the powder pattern was impossible because the peaks are too broad.

To our knowledge, this is the first example showing that a nonphotochromic compound can be changed to a photochromic one by appending another photoreactive group, that is, by β–α photoisomerization of the cyanoethyl group of the cobaloxime complex. This work provides new opportunities for in situ control of solid-state photochromism by using crystal environment changes in crystalline-state photoreactions.

This work was supported by a Grant-in-Aid for Scientific Research in Priority Areas “New Frontiers in Photochromism (No. 471)” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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6 See Figure S1. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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8 ^{1}H NMR spectra (300 MHz, $(CD_3)_2SO$, r.t.) peaks were observed at 6.72 and 5.88 ppm for (b) and 6.67 and 6.09 ppm for (c). See Figure S2. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 *Crystal data for* **1**: $C_{23}H_{29}N_8O_4Co$, $M_r = 540.47$, $a = 23.3410(19)$ Å, $b = 6.5350(7)$ Å, $c = 16.911(3)$ Å, $\beta = 91.508(6)°$, $V = 2578.6(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.392$, monoclinic, space group $P2_1/c$, $T = 173(2)$ K, R $[I > 2\sigma(I)] = 0.0536$, Rw $[I > 2\sigma(I)] = 0.1304$, goodness-of-fit = 1.051. *Crystal data for* **1′**: $C_{23}H_{29}N_8O_4Co$, $M_r = 540.47$, $a = 23.6610(6)$ Å, $b = 6.5420(5)$ Å, $c = 16.9540(14)$ Å, $\beta = 91.8220(11)°$, $V = 2622.99$ (19) Å^3, $Z = 4$, monoclinic, space group $P2_1/c$, $T = 173(2)$ K, R $[I > 2\sigma(I)] = 0.0755$, Rw $[I > 2\sigma(I)] = 0.2211$, goodness-of-fit = 1.100.