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Direct Observation of Different Reaction Pathways by X-rays in the Photoisomerization of Cobaloxime Complexes with Diphenylboron Bridging

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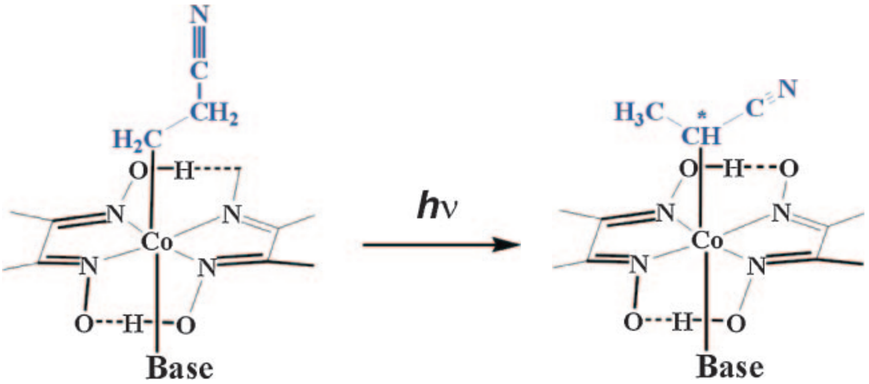
The 4-cyanobutyl groups of (4-cyanobutyl)(dimethylglyoximato)[*O*-(diphenylboranylium)dimethylglyoximato]-(pyridine)cobalt(III) and (4-cyanobutyl)(dimethylglyoximato)[*O*-(diphenylboranylium)dimethylglyoximato](4-ethylpyridine)cobalt(III) were isomerized to the 3-cyanobutyl groups with retention of the single-crystal form on exposure to visible light for 24 h. When the pyridine complex crystal was further irradiated for 48 h, the photoproduced 3-cyanobutyl group was transformed to a 1-cyanobutyl group with retention of the single-crystal form. However, the 3-cyanobutyl group of the 4-ethylpyridine complex was not further isomerized. Such different reaction pathways are clearly elucidated with the size and shape of the reaction cavity for the 4-cyanobutyl group in the crystal before photoirradiation.

Since it was found that the 2-cyanoethyl group bonded to the cobalt atom in the bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes with different axial base ligands were isomerized to the 1-cyanobutyl group in the solid state on exposure to visible light as shown in Scheme 1,[1] the relation between the crystal structure and reaction rate has been examined for various cobaloxime complexes.[2] For the complexes with 3-methylpyridine, 4-methylpyridine, and *N*-(2-hydroxyethyl)isonicotinamide as axial base ligands, the isomerization proceeded with retention of the single-crystal form.[3,4] The chirality of the produced 1-cyanoethyl group depended on the shape of the reaction cavity for the 2-cyanoethyl group before photoirradiation. When the 2-cyanoethyl group was replaced with 2-(methoxycarbonyl)ethyl and 2-(ethoxycarbonyl)ethyl groups, the powdered samples of the cobaloxime complexes were isomerized to 1-(methoxycarbonyl)ethyl and 1-(ethoxycarbonyl)ethyl groups, respectively, on exposure to visible light. The size of the reaction cavity for each reactive group in the crystal structure was found to have a great influence on the isomerization rate.[5]

The 3-cyanopropyl group bonded to the cobalt atom in the cobaloxime complexes with different base ligands were also isomerized to the 1-cyanopropyl group in the solid state as shown in Scheme 2. The isomerization rate was controlled by the size of the reaction cavity for the 3-cyanopropyl group before photoirradiation.[6] For the 3-cyanopropyl complex crystal with (*R*)-1-phenylethylamine as an axial base ligand, the isomerization proceeded with retention of the single-crystal form. The chirality of the photoproduced 3-cyanopropyl group was well explained by the shape of the reaction cavity.[6] The mechanism of the isomerization was clarified using neutron diffraction.[7]

However, the cobaloxime complex with the 4-cyanobutyl group was isomerized only to the 3-cyanobutyl group with retention of the single-crystal form as shown in Scheme 3. The crystal structure after 66 h exposure indicated that about 20% of 4-cyanobutyl group was transformed to the 3-cyanobutyl group, which was not disordered but had only one enantiomer at one site around an inversion center. The NMR data of the



Scheme 1. Photoisomerization of the 2-cyanoethyl group bonded to the cobalt atom in the cobaloxime complexes with different axial base ligands.

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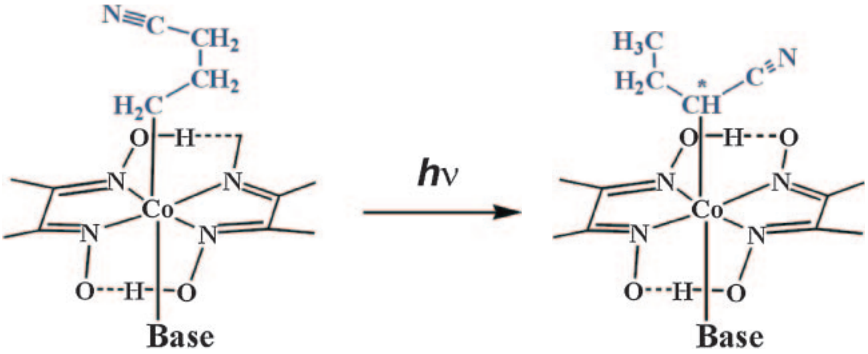
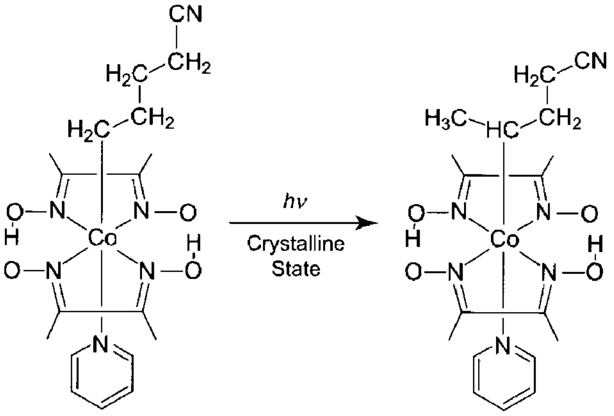


Scheme 2. Photoisomerization of the 3-cyanopropyl group bonded to the cobalt atom in the cobaloxime complexes with different axial base ligands.



Scheme 3. Photoisomerization of the 4-cyanobutyl group bonded to the cobalt atom in the cobaloxime complexes with pyridine as an axial base ligand. Only a small portion of the 4-cyanobutyl group was isomerized to the 2-cyanobutyl group through the 3-cyanobutyl group in the solid state.

photoproduct in $CDCl_3$ solution however, indicated that about 6% of 4-cyanobutyl group was transformed to the 2-cyanobutyl group, although no peaks due to the produced 2-cyanobutyl group were observed in the difference map of the structure after photoirradiation.[8] In order to analyze the isomerization mechanism more precisely, it is necessary to observe the reaction process with retention of the single-crystal form. It seemed necessary to expand or control the reaction cavity for the 4-cyanobutyl group since the group is too large to be isomerized with retention of the single-crystal form.

Although the host–guest complex formation between the cobaloxime complexes with the 2-cyanoethyl group and dibenzylamines was successfully applied to expand and control the reaction cavity,[9,10] it was unsuccessfully applied to a cobaloxime complex with the 4-cyanobutyl group. Another method is the insertion of bulky substituents in the vicinity of the reactive group. Among cobalt complexes with modified oxime bridges,[11–13] a complex with diphenylboron bridging appeared to be very attractive since one of the phenyl groups may have parallel conformation with the axial alkyl group and may have great influence on the motion of the axial group bonded to the cobalt atom. For the 2-cyanoethyl group in the diphenylboron cobaloxime complexes, the reaction rates were comparable with those of the corresponding cobaloxime complexes without diphenylboron bridging.[14]

In the previous paper it was reported that the 4-cyanobutyl group of a diphenylboron cobaloxime complex, (4-cyanobutyl)(dimethylglyoximato)[*O*-(diphenylboranylium)dimethylglyoximato](3,4-lutidine)cobalt(III) (**1**) was isomerized to the 1-cyanobutyl complex with retention of the single-crystal form as shown in Scheme 4. In order to elucidate the isomerization mechanism, two hydrogen atoms of the 4-cyanobutyl group were replaced with deuterium atoms as shown in the left-side figure of Scheme 5. Using neutron diffraction analysis, the process of the 4-cyanobutyl group to the 1-cyanobutyl group was directly exemplified as shown in Scheme 5.[15] The reaction process is called "alkyl turn mode." It was proposed that the process is caused by the shape of the reaction cavity for the 4-cyanobutyl group in the crystal structure before irradiation.

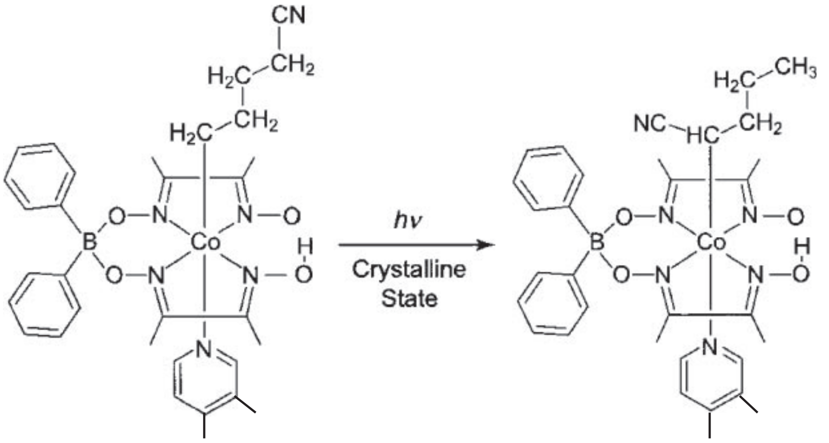
The present paper reports the isomerization processes of two diphenylboron cobaloxime complexes with the 4-cyanobutyl group and different axial base ligands, (4-cyanobutyl)(dimethylglyoximato)[*O*-(diphenylboranylium)dimethylglyoximato](pyridine)cobalt(III) (**2**) and (4-cyanobutyl)(dimethylglyoximato)[*O*-(diphenylboranylium)dimethylglyoximato](4-ethylpyridine)cobalt(III) (**3**) which are called "alkyl slide mode" and are completely different from the mode of **1**.

Experimental

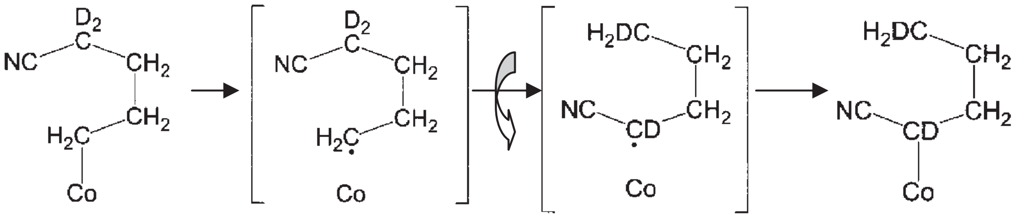
Preparation. Compounds **2** and **3** were synthesized in a way similar to **1**, which was reported previously.[15]

Photoirradiation. A halogen lamp was placed at a distance of 5 cm from a crystal of **2**, which was on a cool plate (NISSAN Cool Plate NCP-2215) at 0 °C. Two filters were inserted between the crystal and the lamp; an R-68 filter (TOSHIBA) cutting off light shorter than 680 nm and a heat absorbing water filter. This means light with the wavelengths between 680 to 1350 nm was exposed to the crystal. The crystal data and three-dimensional intensity data of the crystal **2** were obtained under the same conditions at three stages; before photoirradiation, after 24 h and after 72 h photoirradiation, which are called crystal data **II**, **II***, and **II****, respectively. For the crystals of **3**, the intensity data were collected before photoirradiation and after 24 h irradiation, which are called crystal data **III** and **III***, respectively.

FT-IR Spectrometry. The photoreaction was monitored with an FT-IR spectrometer (BIO-RAD FT3000 IR spectrom-



Scheme 4. Photoisomerization occurred directly from the 4-cyanobutyl group to the 1-cyanobutyl group in the solid state in **1**.



Scheme 5. “Alkyl turn mode” from the 4- to 1-cyanobutyl group in the photoisomerization of **1**.

eter). Several KBr pellets about 1 mm thick were mounted in a pellet holder and were irradiated with light under the above conditions at room temperature. At appropriate time intervals, successive FT-IR measurements of the pellets were carried out one by one. The conversion rate in each step was estimated from the intensity change of the stretching vibration mode of the C–N triple bond of the 4-cyanobutyl group at early stages (within 40 min). Assuming first-order kinetics, the reaction rate constants for **1**, **2**, and **3** are 19.0×10^{-3}, 6.2×10^{-3}, and $9.5 \times 10^{-3}\,s^{-1}$, respectively. For the crystal of **1**, the conversion rates of the original 4-cyanobutyl and the produced 1-cyanobutyl and 2-cyanobutyl groups were measured till 1400 min after the photoirradiation. Since the C–N triple bond of the 4-cyanobutyl group for **1** has a similar absorption band to that of the 3-cyanobutyl group, the obtained conversion rate is a sum of 4-cyanobutyl and 3-cyanobutyl groups. However, the conversion rate indicates only the decrease of 4-cyanobutyl group, since it was already found that the 4-cyanobutyl group of **1** was directly transformed to the 1-cyanobutyl group.[15]

Crystal Structure Analyses before Photoirradiation. Graphite-monochromated Mo Kα radiation was used with Rigaku rotating-anode X-ray generator and the temperature was controlled by a Rigaku cryostat system. The diffraction data of **II** and **III** were collected on a *Rigaku R-AXIS RAPID* diffractometer at 223 and 173 K, respectively. Empirical absorption correction was calculated with the ABSCOR program.[16] The crystal structure was solved by a direct method using the SIR-92 program[17] and was refined by full-matrix least-squares using the SHELX-97.[18] All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were obtained geometrically and were refined with the riding model. The crystal data and the refinement details are listed in Table 1.

Crystal Structure Analysis after Photoirradiation. The diffraction data of **II***, **II****, and **III*** were taken and analyzed under the same conditions as those before photoirradiation, introducing the photoproduced structures as a disordered model. In the early stages of the least-squares refinement, the disordered structures were constrained to have the original bond distances and angles, or the ideal ones for the photoproducts, since the disordered atoms come too close in the refinement. It was difficult to remove a part of the constraints at the final stage. The crystal data and the refinement details for **II***, **II****, and **III*** are also listed in Table 1.

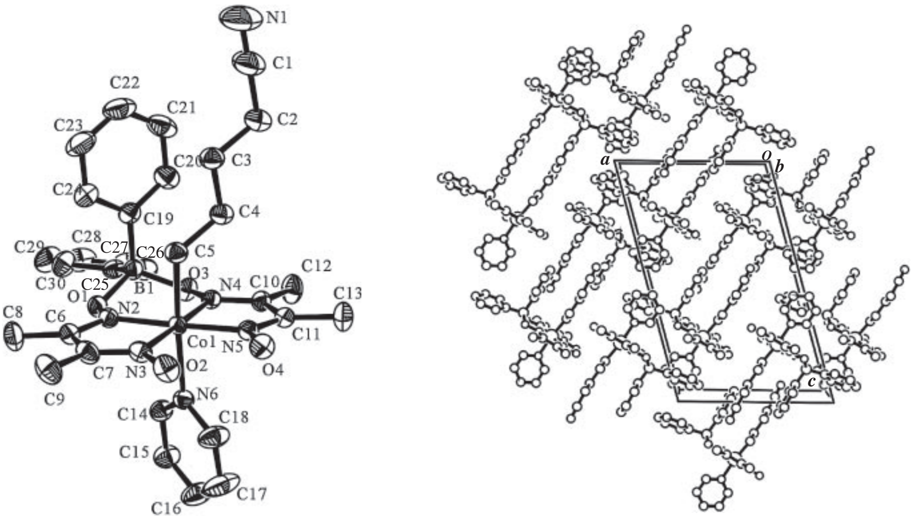
The crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC 807032–807036 for **II**, **II***, **II*****, **III**, and **III***. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; FAX: +44 1123 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results

Structural Change of 2. Molecular and crystal structures of **II** are shown in Figures 1a and 1b, respectively. One phenyl group of the diphenylboron group is almost perpendicular to the cobaloxime plane whereas another one is almost parallel to the cobaloxime plane. The conformation of the 4-cyanobutyl group is all *trans* and is approximately parallel to the perpendicular phenyl group. The 4-cyanobutyl and perpendicular phenyl groups of the two molecules make a pair around an inversion center. The pair stacks parallel to the (10–2) plane and forms a sheet structure.

Table 1. Crystal Data and Experimental Details

Parameter	**II**	**II***	**II****	**III**	**III***
Formula	$C_{30}H_{36}BCoN_6O_4$	$C_{30}H_{36}BCoN_6O_4$	$C_{30}H_{36}BCoN_6O_4$	$C_{32}H_{40}BCoN_6O_4$	$C_{32}H_{40}BCoN_6O_4$
Formula weight	614.39	614.39	614.39	642.44	642.44
Temperature/K	232(2)	232(2)	232(2)	173(2)	173(2)
Wavelength/Å	0.71069	0.71069	0.71069	0.71069	0.71069
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal	tetragonal
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P4/n$	$P4/n$
a/Å	13.2895(2)	13.6189(6)	13.5393(5)	26.856(1)	26.654(1)
b/Å	11.3141(1)	11.3758(4)	11.3286(4)	26.856(1)	26.654(1)
c/Å	21.4778(3)	21.3462(9)	21.2050(8)	9.209(8)	9.2155(4)
α/°	90	90	90	90	90
β/°	105.218(1)	105.574(2)	105.713(1)	90	90
γ/°	90	90	90	90	90
Volume/Å^3	3116.13(7)	3185.7(2)	3130.9(2)	6642(8)	6547.1(6)
Z	4	4	4	8	8
D_{calcd}/Mg m^{-3}	1.31	1.281	1.303	1.285	1.304
μ/mm^{-1}	0.595	0.582	0.592	0.561	0.569
F(000)	1288	1288	1288	2704	2704
Crystal size/mm^3	0.25 × 0.20 × 0.05	0.25 × 0.20 × 0.05	0.25 × 0.20 × 0.05	0.50 × 0.05 × 0.05	0.50 × 0.05 × 0.05
θ range/°	2.05–27.48	2.37–27.49	2.53–27.48	3.03–27.45	3.06–27.48
Refrections collected/unique	44280/7145	27010/7278	27327/7155	40912/7540	84870/7493
R(int)	0.0516	0.0738	0.069	0.0533	0.0666
Data/retraints/parameters	7145/0/383	7278/8/376	7155/17/399	7500/3/349	7493/6/392
GOF	1.088	1.041	1.066	1.027	1.036
$R1(I > 2\sigma(I))$	0.0447	0.1146	0.0895	0.0833	0.0962
$wR2(I > 2\sigma(I))$	0.1074	0.3006	0.24	0.2476	0.2548
$R1$(all data)	0.056	0.1733	0.1314	0.1034	0.1136
$wR2$(all data)	0.1135	0.3434	0.2676	0.2605	0.2707
$\Delta\rho_{\max}/\Delta\rho_{\min}$/e Å^{-3}	0.384/−0.383	0.569/−0.620	0.556/−0.485	0.937/−0.744	1.533/−3.858



(a) (b)

Figure 1. (a) Molecular structure of **II**. Thermal ellipsoids are drawn at 50% probability level. (b) Crystal structure of **II** viewed along the b axis. Hydrogen atoms are omitted for clarity.

The molecular structure of **II*** is shown in Figure 2. Since the crystallinity is retained, the crystal structure, of course, is nearly the same as that of Figure 1b. It is clear that the 3-cyanobutyl group shown in red was produced on exposure to light. The occupancy factor of the produced 3-cyanobutyl group is 0.24(1). Only one enantiomer of the chiral carbon C4B was obtained at one site around an inversion center during photoisomerization. Since the crystallinity was retained after 24 h exposure, the photoirradiation was continued for further 48 h. It must be emphasized that the cell volume of **II*** increased by 69.6 Å^3 due to the formation of the 3-cyanobutyl group but the cell volume of **II**** decreased by 54.8 Å^3, as

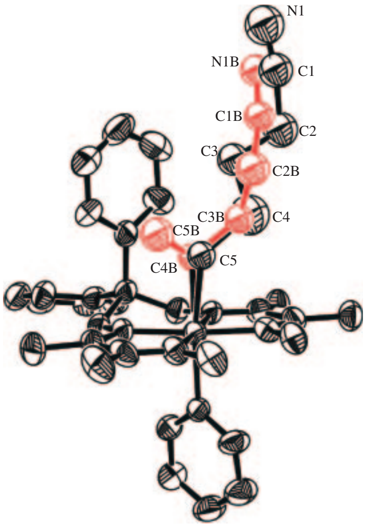


Figure 2. Molecular structure of **II***. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Red atoms show the photoproduced 3-cyanobutyl group.

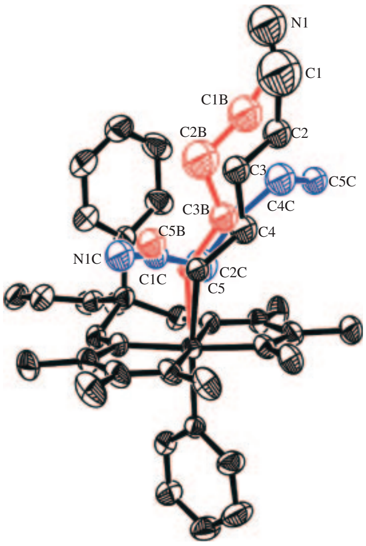


Figure 3. Molecular structure of **II****. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Red and blue atoms show the photoproduced 3-cyanobutyl and 1-cyanobutyl groups, respectively.

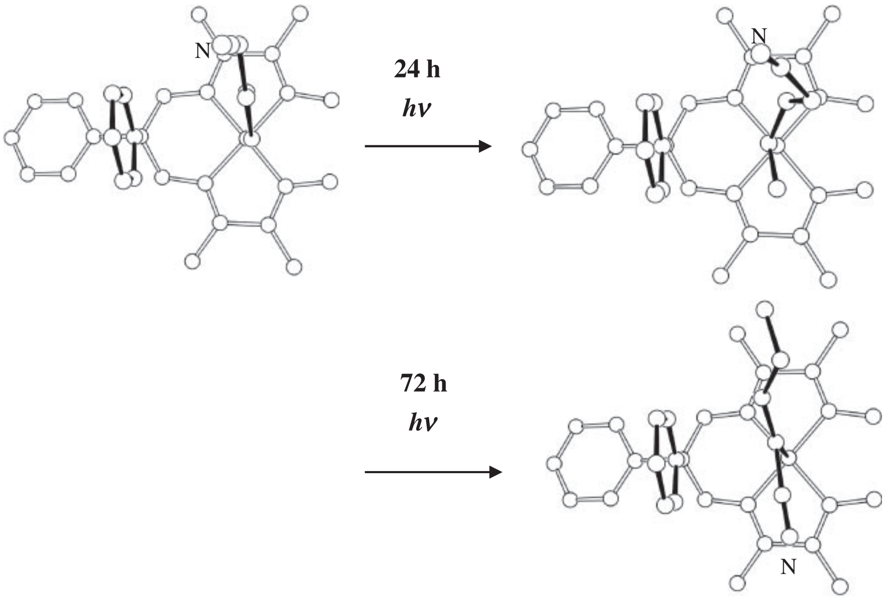


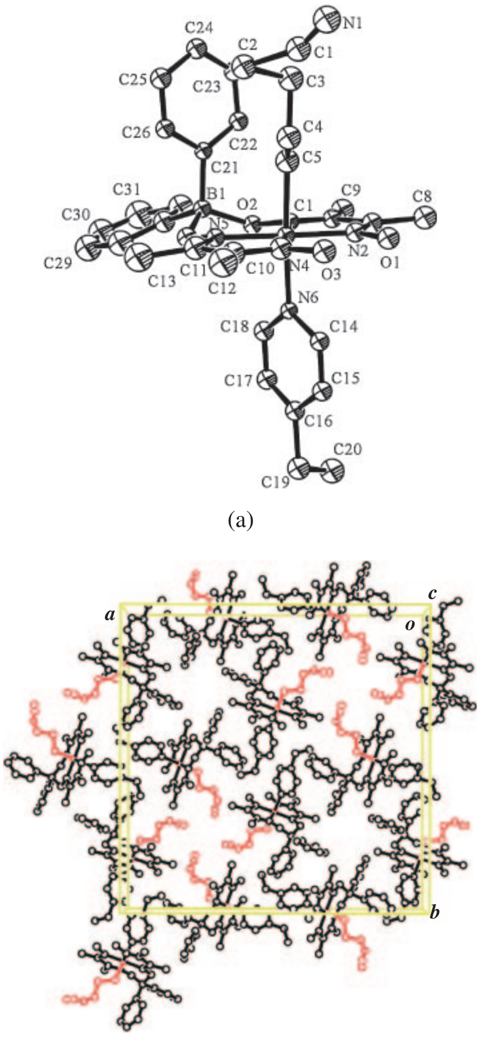
Figure 4. Conformational change of the 4-cyanobutyl group in the photoisomerization of **II**. The N atom of the cyano group is indicated.

shown in Table 1. The molecular structure of **II**** is shown in Figure 3. It is clear that the blue 1-cyanobutyl group was produced after the prolonged photoirradiation in addition to the 4- and 3-cyanobutyl groups. Only one enantiomer of the chiral carbon, C2C, was observed at one site of an inversion center. The occupancy factors of 4-, 3-, and 1-cyanoethyl groups became 0.69(1), 0.15(1), and 0.16(1), respectively. Although the change from 4-cyanobutyl to 3-cyanobutyl groups is small, about a half of the 3-cyanobutyl group was changed to the 1-cyanobutyl group. It is clear that the decrease of cell volume is caused by the transformation from the 3-cyanobutyl to 1-cyanobutyl group.

In order to examine the conformational change of the cyanobutyl group in the photoisomerization, the structures of the original and photoproduced cyanobutyl groups viewed along the normal to the cobaloxime plane are shown in Figure 4. The photoproduced cyanobutyl groups take conformations almost parallel to the perpendicular phenyl ring.

Structural Change of 3. The molecular and crystal structures of **III** are shown in Figures 5a and 5b. One phenyl group of the diphenylboron group is almost perpendicular to the cobaloxime plane whereas another one is almost parallel to the cobaloxime plane. The structure of the diphenylboron is essentially the same as those of **1** and **2** before photoirradiation.

The conformation of the 4-cyanobutyl group on the other hand, is *trans*, *gauche*, and *gauche* around the C5–C4, C4–C3, and C3–C2 bonds, respectively, which is different from that of **II**, that is all *trans*-conformation. Moreover, the 4-cyanobutyl group takes a conformation perpendicular to the phenyl group which is perpendicular to the cobaloxime plane. This is because comparatively large void space exists around the 4-fold axis in the tetragonal unit cell and the 4-cyanobutyl groups related by the 4-fold axis occupy the space.



(a)

(b)

Figure 5. (a) Molecular structure of **III**. Thermal ellipsoids are drawn at 50% probability level. (b) Crystal structure viewed along the *c* axis. The red atoms indicate the 4-cyanobutyl group. Hydrogen atoms are omitted for clarity.

The molecular structure of **III*** is shown in Figure 6. Only the 3-cyanobutyl group appeared. Although the occupancy factor of the 3-cyanobutyl group became 0.71(1), there was no indication of the 2- or 1-cyanobutyl group. The cell volume decreased by 95 Å^3 in the photoreaction, which is different from **II***. Further exposure was impossible due to the degradation of the crystallinity. Only one enantiomer of the chiral carbon, C4B, was observed at one site around an inversion center. The structural change from 4-cyanobutyl to 3-cyanobutyl viewed along the normal to the cobaloxime plane is shown in Figure 7.

Discussion

Reaction Rate and Produced Structure Based on the Reaction Cavity. The reaction cavities[19] for the 4-cyanobutyl group were calculated in the crystals of **1**, **2**, and **3** before photoirradiation. The cavity volume and the isomerization rate constant at early stages for the three crystals are listed in Table 2. Since the 4-cyanobutyl groups of **2** and **3** are isomerized to 3-cyanobutyl groups at early stages, the rate

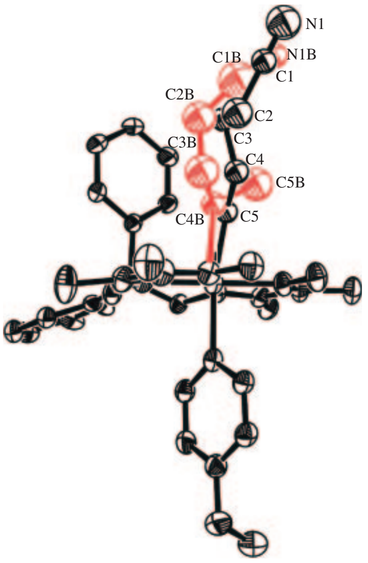


Figure 6. Molecular structure of **III***. Thermal ellipsoids are drawn at 50% level. Hydrogen atoms are omitted for clarity. Red atoms indicate the photoproduced 3-cyanobutyl group.

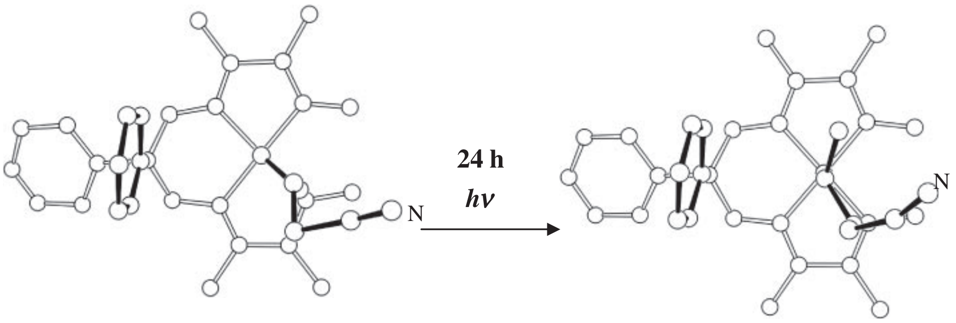


Figure 7. Conformational change of the 4-cyanobutyl group in the photoisomerization of **III**. The N atom of the cyano group is indicated.

Table 2. Rate Constant, Size of Reaction Cavity, and the Photoproduced Group in the Early Stages of Photoisomerization of **1**, **2**, and **3** (0–40 min)

Compound	Rate constant /s^{-1}	Cavity volume /$\mathrm{\AA}^3$	Photoproduced group
1	19×10^{-3}	32.7	1-cyanobutyl
2	6.2×10^{-3}	38.1	3-cyanobutyl
3	9.5×10^{-3}	49.2	3-cyanobutyl

constant has a good correlation with the size of the reaction cavity. In spite of the small cavity, the rate constant of **1** is significantly greater than those of **2** and **3**. This is caused by the different process of isomerization in **1**, in which the 4-cyanobutyl group is not transformed to the 3-cyanobutyl but to the 1-cyanobutyl group. As discussed in the previous paper,[15] the motion of cyanobutyl radical following the alkyl turn mechanism as shown in Scheme 5 can occur very easily in spite of its small cavity.

In order to make clear the reason why the 4-cyanobutyl group of **2** is finally isomerized to 1-cyanobutyl whereas the 3-cyanobutyl is the final product for **3**, the reaction cavities for the 4-cyanobutyl group for **2** and **3** before photoirradiation are drawn in Figures 8 and 9, respectively. For **2**, there is void space in the neighborhood of the chiral carbon atom bonded to the cobalt atom, A and B in Figure 8. When the 4-cyanobutyl group is changed to 3-cyanobutyl, the methyl and cyanopropyl groups can occupy the space A and B, respectively. After 72 h exposure, the cyano and propyl groups are accommodated in the space A and B, respectively. This also indicates that the ethyl group is too small for the space A when the 2-cyanobutyl group is produced. It seems adequate to consider that the 2-cyanobutyl group was not observed in the intermediate stages because it is very unstable due to steric repulsion.

For the crystal of **3**, there is no space around the chiral carbon atom bonded to the cobalt atom except a wide space along the cyanopropyl group, A, in Figure 9. This wide space is due to a fairly loose contact of 4-cyanobutyl groups around the 4-fold axis as shown in Figure 5b. In order to continue further isomerization, it is necessary to accommodate either of the cyano, cyanomethyl, or propyl group in the space B. However, this space is too small to accommodate any of the groups. This may be a reason why only 3-cyanobutyl was made in the photoisomerization. As discussed in the previous paper, the reaction cavity for the 4-cyanobutyl group in the crystal of **1** has enough space for the produced cyanobutyl radical to rotate upside down in the cavity. It is clear that the shape of the cavity controls the reaction pathway from 4-cyanobutyl to 1-cyanobutyl group directly.

Formation of the Intermediate 2-Cyanobutyl Group in a Crystal of 1. It is clear considering from the shape of the reaction cavity that the intermediate 2-cyanobutyl group cannot be observed in the crystals of **2** and **3** as discussed above. However, it seems possible to accommodate the 2-cyanobutyl group in the cavity for crystal **1**, although it is smaller than those of **2** and **3**. As shown in Figure 10, there is a void space indicated as A in the cavity of **1** before irradiation. The cyanomethyl group may be accommodated using the void space A and the ethyl group can occupy the axial position instead of the propyl group.

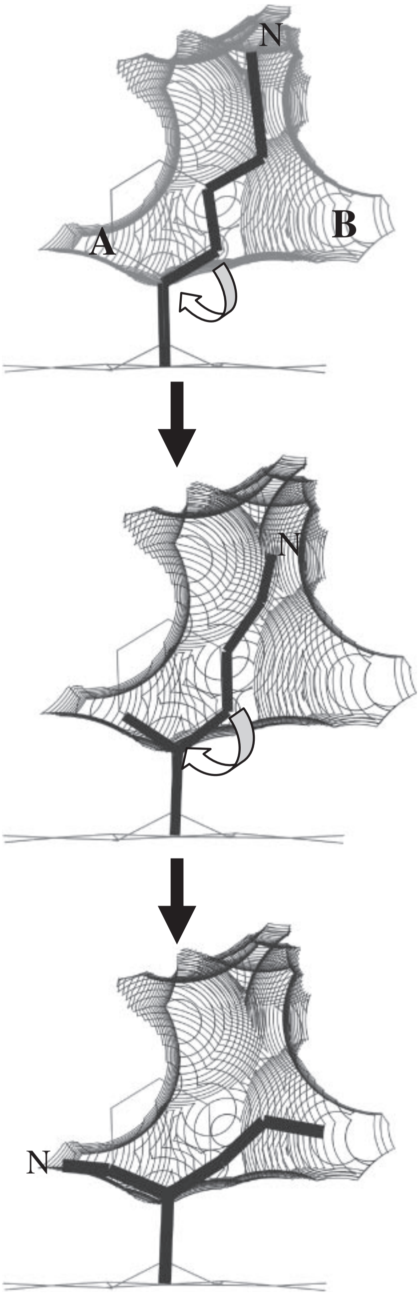


Figure 8. Reaction cavity for the 4-cyanobutyl group in **II** viewed along the cobaloxime plane. The original 4-cyanobutyl group and the photoproduced 3-cyanobutyl and 1-cyanobutyl groups are drawn in the upper, middle, and lower figures, respectively. The N atom of the cyano group is indicated.

The reaction process for the powdered crystal of **1** was examined by the measurement of IR spectra using a KBr pellet on exposure to light, which is shown in Figure 11. Since the 4-cyanobutyl and 3-cyanobutyl groups have nearly the same spectra, the merged amount of the two groups is shown as circles. However, most of the merged value should be due to the 4-cyanobutyl group, because the 4-cyanobutyl group is directly changed to the 1-cyanobutyl group at early stages of **1**. It is clear that the 1-cyanobutyl group increases as the 4-cyanobutyl group decreases at the early stages. The photoconversion of the

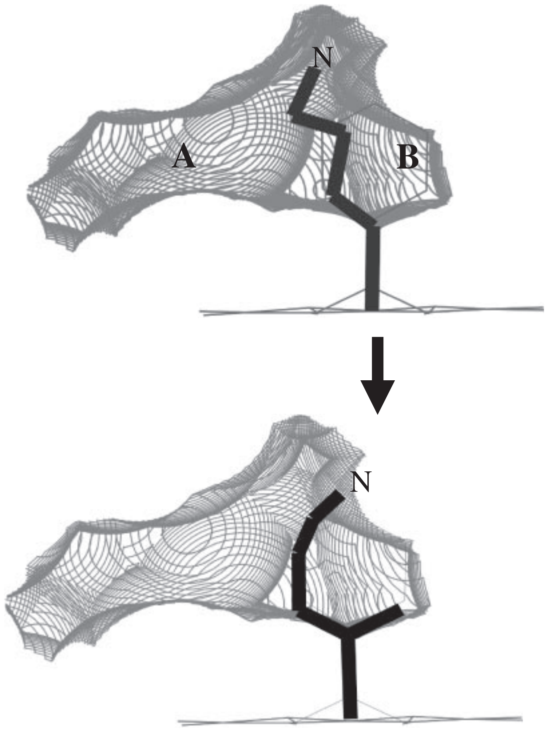


Figure 9. Reaction cavity for the 4-cyanobutyl group in **III** viewed along the cobaloxime plane. The 4-cyanobutyl group and the photoproduced 3-cyanobutyl group are drawn in the upper and lower figures, respectively. The N atom of the cyano group is indicated.

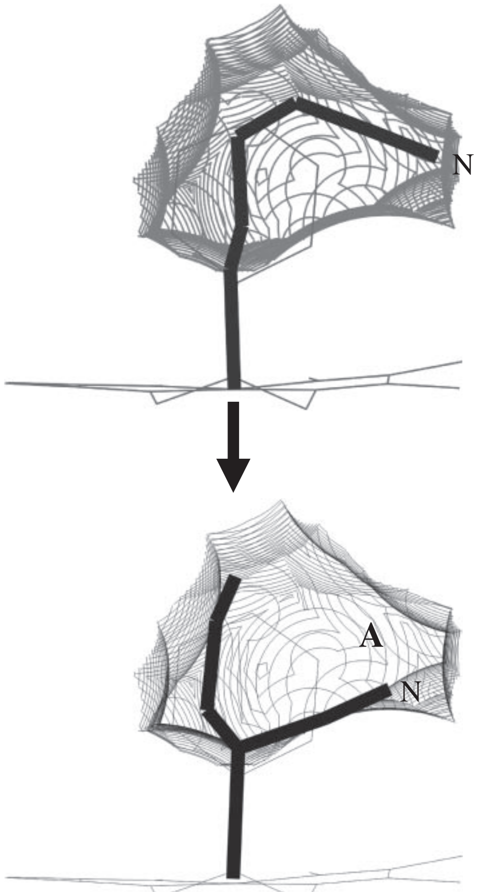


Figure 10. Reaction cavity for the 4-cyanobutyl group in **I** viewed along the cobaloxime plane. The 4-cyanobutyl group and the photoproduced 1-cyanobutyl group are drawn in the upper and lower figures, respectively. The N atom of the cyano group is indicated.

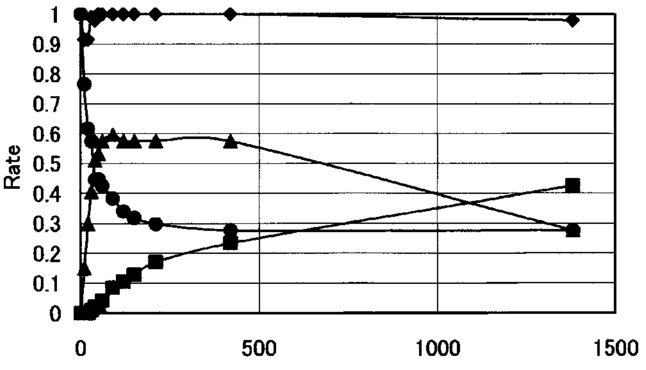


Figure 11. Reaction rates of 4-cyanobutyl (circle), 2-cyanobutyl (square), and 1-cyanobutyl (triangle) groups and their total value (diamond) with the exposure time.

4-cyanobutyl group converges to about 0.28 after 450 min whereas the amount of the 1-cyanobutyl group decreases after 450 min. On the other hand, the 2-cyanobutyl group gradually increases from the initial stage and becomes greater than the 1-cyanobutyl group after 1100 min. This fact indicates that the 4-cyanobutyl group is isomerized to the 2-cyanobutyl group through the 1-cyanobutyl group in the crystal of **1** and the 2-cyanobutyl group may be the final product for **1**. This is brought about by the different reaction cavity and conformation of the 4-cyanobutyl group in **1** compared with those of **2** and **3**. The similar IR spectra due to the 2-cyanobutyl group were not observed for the crystals of **2** and **3**. This indicates that the 4-cyanobutyl group of **2** is isomerized to the 1-cyanobutyl group through the 3-cyanobutyl and 2-cyanobutyl groups. Since the 2-cyanobutyl group suffers from steric repulsion too heavily in the cavity and may be unstable, the IR spectra of the 2-cyanobutyl group were not observed for **2**. The similar isomerization of 3-cyanopropyl group from 3-cyanopropyl to 1-cyanopropyl through 2-cyanopropyl was already observed in the cobaloxime crystal as shown in Scheme 2. The existence of the intermediate 2-cyanopropyl was confirmed using neutron diffraction.[7] Therefore, it is reasonable to assume the intermediate 2-cyanobutyl group in **2** should be made in the same process as that of the 2-cyanopropyl group. This will be verified using the same neutron diffraction technique in the near future.

Conclusion

In summary, the reaction process and the final product are different in the solid-state reaction among the compounds with different axial bases, which are on the opposite side of the cobaloxime plane. This is caused by the different size and shape of the reaction cavity for the reactive group. If we can modify the reaction cavity by introducing substituents in the vicinity of the active site, it is possible to obtain different products in the solid state.

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