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β–α Photoisomerization of Cobaloxime Complexes in the Solid State. 6.[1] Asymmetric Induction Due to Chiral Crystal Environment

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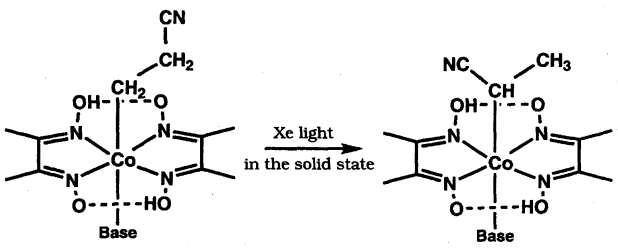
The crystal structure of (*S*)-*s*-butylamine(2-cyanoethyl)cobaloxime was determined by X-ray analysis ; the crystal is monoclinic, and the space group is *C*2, $Z=4$ with $a=15.656(2)$, $b=11.699(2)$, $c=11.553(1)$ Å, $\beta=96.979(9)°$ and $V=2100.5(5)$ Å^3. The structure was refined by a full-matrix least-squares method to the final *R* value of 0.052 for 1678 observed reflections. The 2-cyanoethyl group takes a perpendicular conformation to the cobaloxime plane and has disordered conformations (A, B, and C) around the Co–C bond. The occupancy factors of A, B, and C are 0.48, 0.34, and 0.18, respectively. The crystalline sample was irradiated with a xenon lamp. The (*R*)-1-cyanoethyl group is preferentially produced from the (*S*)-*s*-butylamine complex. The conversion rates, which were determined by HPLC analysis using the chiral stationary phase, were obtained to be 1.17×10^{-5} and 0.59×10^{-5} s^{-1} for the (*R*)- and (*S*)-1-cyanoethyl groups, respectively. The diastereomeric excess is 27%. Such asymmetric induction is well explained by the shape of the reaction cavity for the 2-cyanoethyl group, and is also in good agreement with a packing-energy calculation by molecular mechanics.

It was found that the 2-cyanoethyl group which bonded to the cobalt atom in some bis(dimethylglyoximato)cobalt(III), cobaloxime, complexes was isomerized to the 1-cyanoethyl group in the solid state, as shown in Scheme 1.[2] Extensive studies have been carried out to change the axial base ligands.[3—6] Three factors were found to effect the rate of the above-mentioned 2→1 photoisomerization : hydrogen bond, conformation and cavity volume of the 2-cyanoethyl group.[1,7] If the former two factors are the same, it was clarified using four different crystal forms of the (2-cyanoethyl)-(triphenylphosphine)cobaloxime complex, that the reaction rates are quantitatively dependent on the cavity volume.[8]

In this isomerization the chiral 1-cyanoethyl group was produced from the achiral 2-cyanoethyl group. This gave an idea that the asymmetric induction would be observed if the isomerization proceeded in the chiral crystal environment. Several complex crystals with chiral space groups were prepared and the powdered samples were irradiated with a xenon lamp. The specific rotation of the chloroform solution of the samples solved after irradiation clearly indicated that asymmetry was introduced to the product due to the chiral crystal environment.[9] However, a serious criticism was offered to concerning the above observation, since the produced 1-cyanoethyl group should be racemized upon exposure to a xenon lamp. Since many examples of crystalline-state photoracemization were observed for the 1-cyanoethyl group of the cobaloxime complexes by us,[10] we thought further experiments should be necessary to propose asymmetric induction.



Scheme 1.

Recently, a very high optical yield was obtained using (*R*)-2-amino-2-phenylethanol as an axial base ligand.[11] Furthermore, it was found that the isomerization proceeded with a retention of the single-crystal form in a centrosymmetric unit cell. The shape of the reaction cavity of the 2-cyanoethyl group in the initial crystal suggested that the configuration of the produced 1-cyanoethyl group at one site was in accord with the asymmetric environment around the 2-cyanoethyl group.[12]

In order to examine the above-mentioned asymmetric induction more precisely, the cobaloxime complex with *s*-butylamine as an axial base ligand was prepared, since the amine is the simplest chiral and the two equivalent experiments may be performed independently using (*R*) and (*S*) isomers. This paper reports on the mechanism of asymmetric induction.

Experimental

Crystal Structure Determination. A complex of (*S*)-*s*-butylamine(2-cyanoethyl)cobaloxime and its enantiomer were prepared in a way similar to that reported previously.[13] Orange crystals suitable for an X-ray experiment were obtained from acetone/hexane solutions. The X-ray data were collected on a Rigaku AFC7S diffractometer. Mo $K\alpha$ radiation monochromated with graphite was used. The structure was solved by the Patterson method with the program SAPI 91[14] and refined with the program SHELXL 93.[15] In the process of the refinement, the 2-cyanoethyl group was found to have three disordered conformations around the Co–C bond. The

bond distances and the torsion angles around the C–C bond of the disordered 2-cyanoethyl groups were restrained to have fixed values in the further refinement cycles. All of the hydrogen atoms were calculated geometrically and refined with a riding model. Non-hydrogen atoms were refined with the anisotropic temperature factors, except for the disordered atoms, which were refined isotropically. The absolute configuration was determined to coincide with that of the *s*-butylamine, which was consistent with that obtained from the Flack χ parameter in the refinement. The atomic-scattering factors were taken from International Tables for Crystallography.[16] The crystal data and experimental details are given in Table 1. The final atomic coordinates with the equivalent isotropic temperature factors for non-hydrogen atoms are given in Table 2.

Photoisomerization and HPLC Analysis. Crystals scattered onto a Petri dish were irradiated with a xenon lamp at ambient temperature (ca. 300 K). After irradiation, an HPLC analysis of the crystals was carried out using the chiral stationary phase in order to determine the diastereoselectivity. The HPLC system used was a HITACHI L-7000 series system equipped with a CHIRALPAK-AD column (Daisel Chem.) maintained at 300 K and with a Model L-7420 UV-vis absorbance detector monitored at 242 nm. The mobile phase consisted of hexane with 10% v/v ethanol, and its flow rate was 1.0 ml min^{-1}. Quantification was performed by integrating the peak area using an internal standard, benzyl alcohol. No leading or tailing around the peaks corresponding to (*R*)- and (*S*)-1-cyanoethyl complexes was observed in the chromatogram. This indicates that the produced 1-cyanoethyl group was not inverted to the opposite configuration when it migrated in the chiral stationary phase of HPLC. The retention time of the (*R*)-1-cyanoethyl and (*S*)-1-cyanoethyl complexes was measured at 10.11 and 13.67 min, respectively. These two peaks were perfectly divided.

Results and Discussion

Crystal and Molecular Structure. The crystal structure viewed along the *c*-axis is shown in Fig. 1. An ORTEP drawing[17] of the molecular structure with the numbering of atoms is shown in Fig. 2. The 2-cyanoethyl group takes a perpendicular conformation to the cobaloxime plane, and has disordered conformations (A, B, and C) around the Co–C bond. The occupancy factors of A, B, and C are 0.48, 0.34, and 0.18, respectively. The disordered 2-cyanoethyl group contacts with the chiral *s*-butylamine ligands of neighboring molecules, which causes a chiral environment around the 2-cyanoethyl group. The 2-cyanoethyl groups along the *b*-axis loosely contact with each other. This brings about a fairly large cavity for the 2-cyanoethyl group. The 2-cyanoethyl group makes no hydrogen bond with the neighboring molecules.

In order to examine the reason why the occupancy factors of A, B, and C are different, the packing energy of the 2-cyanoethyl group around the Co–C bond was calculated in the crystalline lattice using the program Cerius^2 [18] with the Universal Force Field parameter.[19]

The calculated conformer of the 2-cyanoethyl group having the lowest packing energy is in good agreement with the observed structure within 0.3 degree of the Co–C bond rotation (torsion angle). The packing-energy profile of the 2-cyanoethyl group rotating about the Co–C bond by 5° is shown in Fig. 3, in which the torsion angle and packing energy indicate the deviations from the most stable conformer, A. The wide range of the bottom profile well explains the disorded conformers and their occupancy factors.

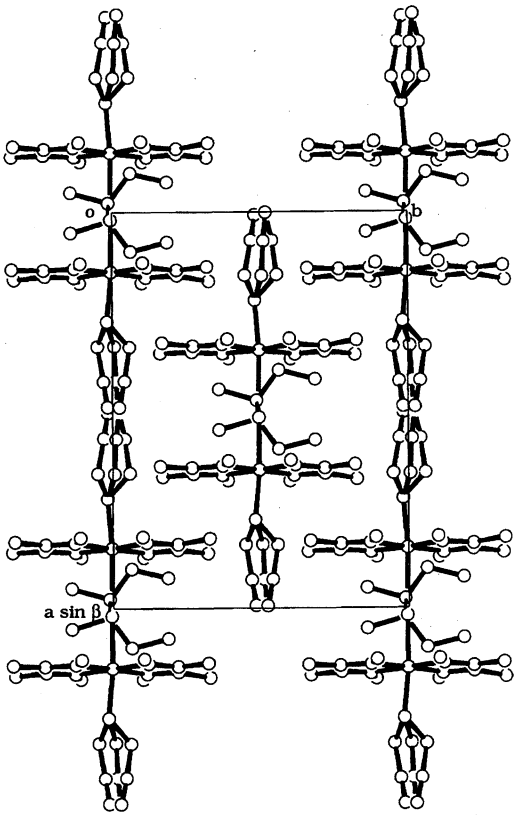


Fig. 1. Crystal structure viewed along the *c* axis.

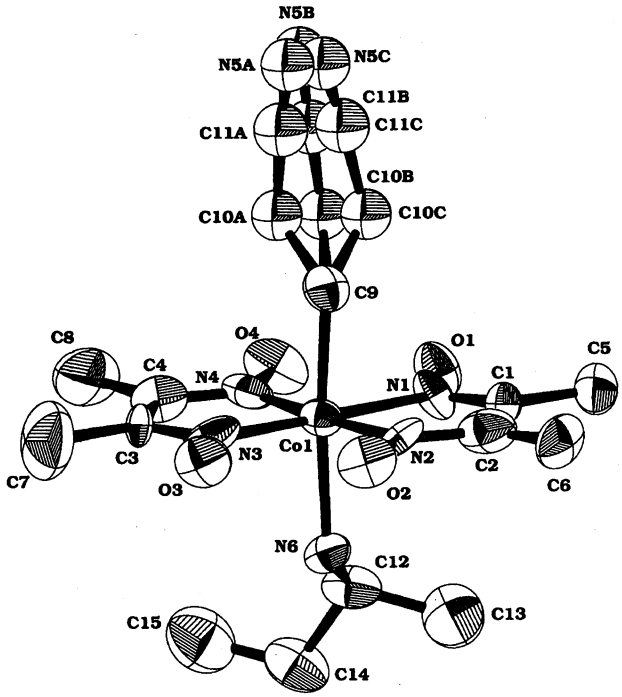


Fig. 2. ORTEP drawing of the molecule with the numbering of the atoms. The thermal ellipsoids are 50% level. The 2-cyanoethyl group has three disordered conformations.

Table 1. Crystal Data and Experimental Details

Crystal data	
Chemical formula	$[Co(C_4H_7N_2O_2)_2(C_3H_4N)(C_4H_{11}N)]$
Formula weight	416.37
Cell system	Monoclinic
Space group	$C2$
a/Å	15.656(2)
b/Å	11.699(2)
c/Å	11.553(1)
β/°	96.979(9)
V/Å^3	2100.5(5)
Z	4
D_x/ Mg m^{-3}	1.317
$F(000)$	880
Radiation type	Mo $K\alpha$
Wavelength/Å	0.71073
No. of reflections for cell parameters	25
θ range/°	10-15
μ / mm^{-1}	0.847
Temperature/K	296
Crystal form	Prismatic
Crystal size/mm	0.2 × 0.2 × 0.2
Crystal color	Orange
Data collection	
Diffractometer	AFC-7S
Data collection method	ω–2θ
Scan rate/° min^{-1}	8
Absorption correction	ψ scan
T_{min}	0.9396
T_{max}	1.000
No. of measured reflections	2630
No. of independent reflections	2539
No. of observed reflections	1678
Criterion for observed reflections	$I > 2\sigma(I)$
θ_{max}/°	27.48
Range of h, k, l h	$0 \rightarrow 20$
k	$0 \rightarrow 15$
l	$-15 \rightarrow 14$
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Intensity decay /%	0.2
Refinement	
Refinement on	F^2
$R[I > 2\sigma(I)]$	0.0521
$wR(I)$	0.1267
S	1.158
No. of reflections used in refinement ($I > 0$)	2226
No. of parameters used	247
H-atom treatment	Calculated
Weighting scheme	$w = 1[\sigma^2(F_o^2) + (0.0756P)^2 + 0.1912P]$. where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.149
$\Delta\rho_{max}$/eÅ^{-3}	0.380
$\Delta\rho_{min}$/eÅ^{-3}	−0.607
Extinction correction	None
Flack χ parameter	−0.0016(466)

Asymmetric Induction. Table 3 shows the reaction yield and diastereomeric excess of the produced 1-cyanoethyl complex with the irradiation time. The reason why the value of diastereomeric excess gradually increased with the irradiation time from 16 to 256 min is probably due to the fact that isomerization would occur from the surface of the crystal, where the lattice control may be looser than that in the inner part of the crystal. The diastereomeric excess converged to 27% after 256 min. The conversion rates of the 2-cyanoethyl group to the (*R*)-1-cyanoethyl and (*S*)-1-cyanoethyl groups are shown in Fig. 4. The conversion rates during the early stages (less than 256 min) seem to be explained by first-order kinetics. The rate constants were calculated to be 1.17×10^{-5} and 0.59×10^{-5} s^{-1} for the (*R*)- and (*S*)-1-cyanoethyl groups, respectively. These results strongly suggest that the epimerization of the complex or the racemization of the 1-cyanoethyl group does not occur during the process of photoisomerization. Moreover, the (*R*)-1-cyanoethyl group is preferentially produced when (*S*)-*s*-butylamine is used as an axial base ligand.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2)

Atom	x	y	z	U_{eq} [a)]
Co1	0.34914(5)	0.5036(2)	0.79642(6)	0.035
O1	0.3220(6)	0.6106(7)	0.5774(9)	0.058
O2	0.3711(6)	0.6079(8)	1.0185(9)	0.056
O3	0.3726(6)	0.3965(9)	1.021(1)	0.061
O4	0.3209(6)	0.3999(8)	0.5704(8)	0.062
N1	0.3353(6)	0.6290(8)	0.6924(8)	0.041
N2	0.3587(6)	0.6275(8)	0.9028(9)	0.040
N3	0.3608(6)	0.382(1)	0.9024(9)	0.053
N4	0.3347(6)	0.386(1)	0.686(1)	0.047
N5A	0.0067(8)	0.477(2)	0.794(2)	0.064
N5B	0.0008(9)	0.479(2)	0.731(3)	0.064
N5C	0.007(2)	0.516(6)	0.762(6)	0.064
N6	0.4810(3)	0.505(1)	0.7945(3)	0.042
C1	0.3390(9)	0.727(1)	0.738(2)	0.051
C2	0.354(1)	0.731(1)	0.863(1)	0.063
C3	0.3532(8)	0.2816(9)	0.858(1)	0.042
C4	0.339(1)	0.280(1)	0.727(1)	0.051
C5	0.3312(8)	0.8314(9)	0.658(1)	0.059
C6	0.3576(8)	0.838(1)	0.927(1)	0.061
C7	0.361(1)	0.179(1)	0.938(2)	0.115
C8	0.325(1)	0.173(1)	0.659(2)	0.099
C9	0.2232(3)	0.517(1)	0.8018(5)	0.048
C10A	0.1588(6)	0.442(2)	0.730(2)	0.059
C10B	0.1607(6)	0.493(4)	0.692(1)	0.059
C10C	0.159(1)	0.551(6)	0.698(3)	0.059
C11A	0.0725(6)	0.459(2)	0.765(2)	0.067
C11B	0.0730(6)	0.488(3)	0.722(2)	0.067
C11C	0.0714(8)	0.530(6)	0.723(3)	0.067
C12	0.5234(4)	0.512(1)	0.6875(5)	0.054
C13	0.5510(8)	0.639(1)	0.677(1)	0.086
C14	0.5992(7)	0.437(1)	0.6883(8)	0.070
C15	0.5762(9)	0.314(1)	0.685(1)	0.101

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$. Occupancy factors A: 0.48(2); B: 0.34(3); C: 0.18(3).

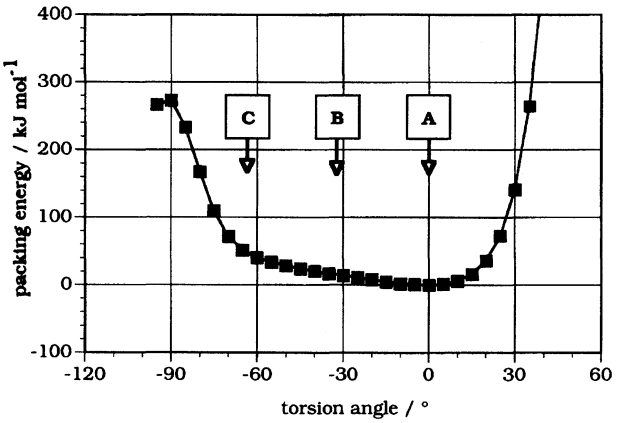


Fig. 3. Packing energy variation of the 2-cyanoethyl group with the rotation angle around the Co–C bond. The energy was calculated in a constant interval of 5°. The values of the energy and angles are deviations from the most stable confomer, A.

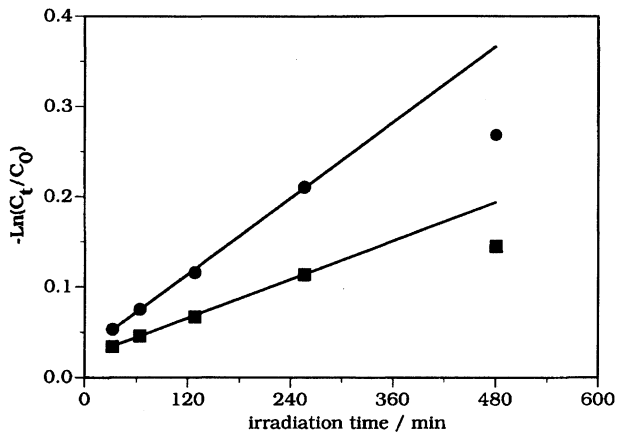


Fig. 4. Conversion of the 2-cyanoethyl group to the (*R*)- and (*S*)-1-cyanoethyl groups with the irradiation time. In the irradiation time to 256 min, the conversions are expressed by first-order kinetics, which are drawn in solid lines. The rate constants are 1.17×10^{-5} and 0.59×10^{-5} s^{-1} for the (*R*)- and (*S*)-1-cyanoethyl group. The values of C_0 and C_t indicate the amounts of 1-cyanoethyl complex at the irradiation time, 0 and *t*, respectively.

Cavity Shape of the 2-Cyanoethyl Group. In order to explain the reason why the (*R*)-isomer is produced when the (*S*)-*s*-butylamine is used, the reaction cavity for the 2-cyanoethyl group in the initial crystal structure was drawn,

and its volume was calculated in the same way as previously reported.[13] Figure 5 shows the reaction cavities for the three disordered conformers. In a calculation of the cavities, all of the conformations were included in the neighboring 2-cyanoethyl groups because a cavity with a similar shape and volume was obtained, even if any one of the three conformers was fixed to those of the neighboring 2-cyanoethyl groups. To examine the asymmetric shape, the cavity was divided into two parts by the average plane comprising the C–C–C–N atoms of the 2-cyanoethyl group. The volumes of the two parts were also calculated, and are given in Fig. 5, in which the C–C–N moiety of each conformer is drawn so as to occupy the same position to each other.

For conformers A and B, the left part of the cavity is

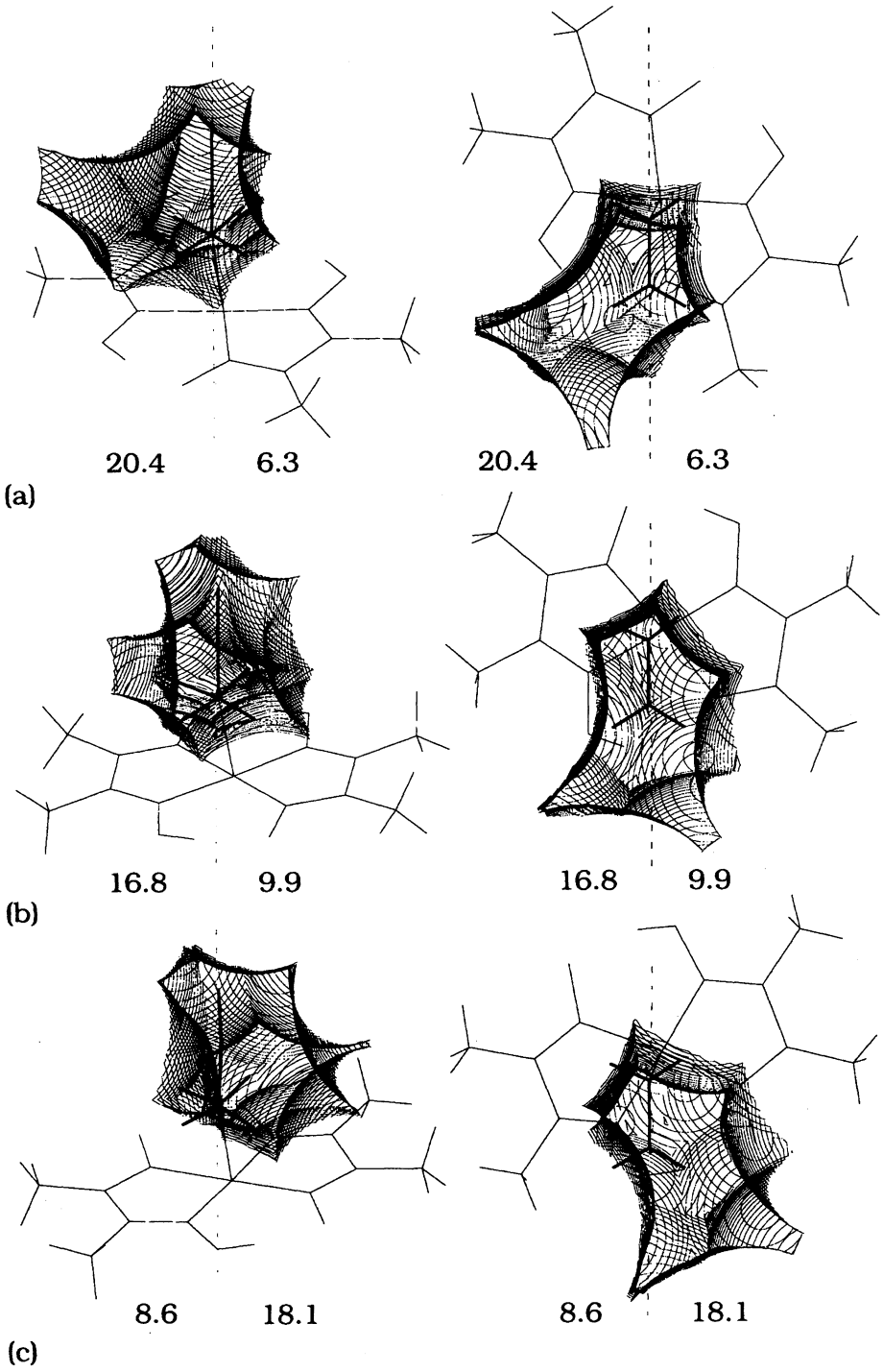


Fig. 5. Reaction cavity for the 2-cyanoethyl group, viewed along the central C–C bond of the group (left) and viewed along the normal to the cobaloxime plane (right); (a) conformer A, (b) conformer B, and (c) conformer C. The contours are drawn at an interval of 0.2 Å. Each cavity divided into two parts by the average plane composed on the C–C–C–N bond. The cavity volumes (Å^3) of left and right halves are also given.

Table 3. The Diastereoselectivity in the Solid-State Photoisomerization of (*S*)-*s*-Butylamine(2-cyanoethyl)cobaloxime

Irradiatin time	Reaction yield	Major	Diastereomeric
min	%	configuration	excess (%de)[a]
8	2.1	*R*	22.2
16	3.7	*R*	20.8
32	8.9	*R*	21.5
64	12.5	*R*	23.3
128	19.2	*R*	25.6
256	35.3	*R*	27.5
480	46.3	*R*	27.1

a) $de = |RS - SS|/(RS + SS)$.

significantly greater than the right part. Since the CN group has a greater volume than the CH_3 group, it is favorable that the CN and CH_3 groups occupy the greater and smaller parts of the reaction cavity, respectively, after conversion to the 1-cyanoethyl group. This explains the reason why the (*R*)-1-cyanoethyl group is preferentially produced from the (*S*)-*s*-butylamine complex after 2→1 isomerization.

For conformer C, on the other hand, the right part is significantly greater than the left part. From conformer C, a 1-cyanoethyl group with the opposite configuration would be produced. This may be a reason why this complex showed a low optical yield.

Packing Energy Calculation. In order to examine the above discussion more quantitatively, the conformation and configuration of the produced 1-cyanoethyl group after irradiation were calculated by the molecular-mechanics method using the program Cerius^{2} [18] with the Universal Force Field (UFF)[19] parameter set. The UFF parameter set is applicable to organometallic compounds.[19,20] At first, the energy of the analyzed crystal structure was minimized with the rigid-body model. In this calculation, the 2-cyanoethyl group was treated as a disordered conformation similar to the results of the observed structure. Energy minimization was carried out by the conjugate-gradient method, at the end of which the value of the root-mean-square energy derivative of the atomic coordinates was less than 0.42 kJ mol^{-1}. The conformation of the (*R*)-1-cyanoethyl group was altered at a constant interval of 30° around the Co–C bond, and the model structure was minimized geometrically with the fixed unit-cell dimension. Figure 6 shows the structure of the (*R*)-1-cyanoethyl group with the lowest energy in the reaction cavity of the 2-cyanoethyl group.

The same calculation was performed for the (*S*)-1-cyanoethyl group. The lowest energy was higher by 10.33 kJ mol^{-1} than that for the (*R*)-1-cyanoethyl group. Although the energy difference is too high, based on the optical yield, this result is in good agreement with the observed configuration of the major part and the reaction model proposed based on the shape of the reaction cavity.

There remains a serious question, that is, why the produced 1-cyanoethyl group is not racemized upon exposure to a xenon lamp. A plausible answer is that the produced 1-cyanoethyl group does not have sufficient void space for the inversion. In a previous paper,[10] we proposed that the reaction cavity should be greater than 11.5 Å^3 when the 1-cyanoethyl group is inverted in the crystalline lattice. The produced 1-cyanoethyl group may be fixed in the cavity, since the shape of the cavity does not meet the 1-cyanoethyl group. A further investigation is in progress.

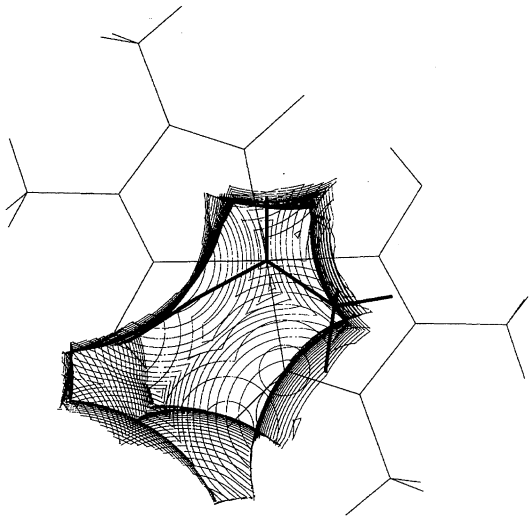


Fig. 6. Conformation of the (*R*)-1-cyanoethyl group with lowest energy calculated by molecular mechanics in the cavity of the initial 2-cyanoethyl group. The cavity is drawn in the same direction as that of the conformation A in Fig. 5(a).

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