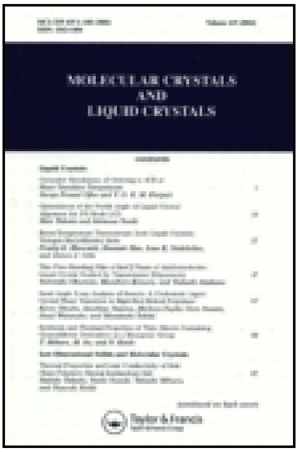

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Akira Uchida [b] & Jack D. Dunitz [a]

[a] Laboratory of Organic Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092, Zurich, Switzerland

[b] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152, Japan

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CALCULATED REACTION PATHS FOR A SOLID-STATE REACTION: RACEMIZATION OF CHIRAL CRYSTALLINE COBALOXIME COMPLEXES BY EXPOSURE TO X-RAYS.

Akira Uchida* and Jack D. Dunitz
Laboratory of Organic Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Abstract By means of point-to-point calculation of the packing potential energy (PPE), reaction paths and differences in activation energies were obtained for the racemization of chiral cyanoethyl groups in crystalline cobaloxime complexes. The results of the calculations are generally compatible with the experimental results and throw some light on the details of the reaction paths.

Introduction

It has been found that chiral cyanoethyl groups in a series of cobaloxime complex crystals invert the sense of chirality without loss of crystallinity.[1] The examples known so far can be grouped into three classes, depending on the type of crystal structure (Figure 1). In the first class, the initial chiral crystal structure contains one independent molecule per asymmetric unit and the final crystal structure is disordered.[2] In the second class, the initial chiral crystal contains two sets of independent molecules related by a pseudo inversion center, and the final crystal structure, in which only one of the two molecules inverts, is an ordered racemate with a centrosymmetric space group.[3-5] In the third class, the asymmetric unit of the initial chiral structure again consists of two independent molecules related by a pseudo inversion center per asymmetric unit

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*On leave from Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo 152, Japan.

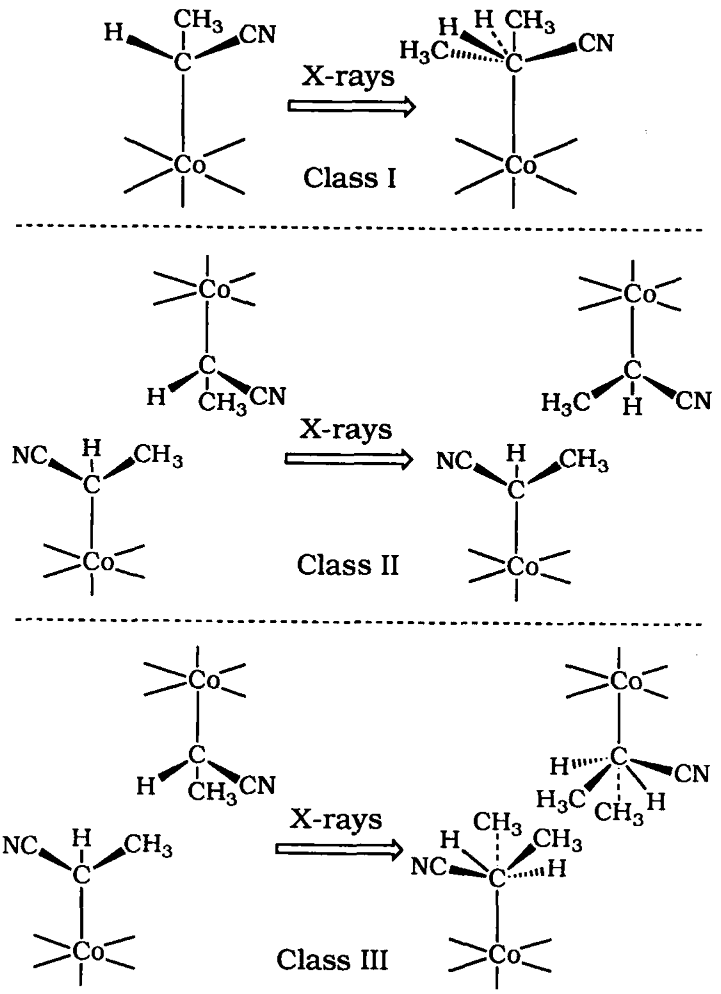


Figure 1. Schematic drawings of racemization process in the crystals of the three classes.

but now both cyanoethyl groups can invert to yield a disordered racemate as the final structure.[6]

It has been reported that reaction rates of racemization vary, depending on crystal structures, and that there is a positive correlation between the reaction rate and the volume of the "reaction cavity".[4] Although the volume of the cavity is a simple and good guide for understanding the crystalline-state racemization, we would like to gain more insight into the details of the reaction path. We attempt to follow the coupling among the various types of atomic motion that must take place during the course of the racemization. These motions include at least: (a) translation of the cyanoethyl group away from the Co atom to produce the elongation of the Co to C interatomic distance (Δl) associated with initial homolytic rupture of the Co-C bond; (b) change in pyramidality of the resulting 1-cyanoethyl radical (P); (c) rotation of the radical about the C-Co vector (θ_1, positive for clockwise rotation looking along this vector); (d) rotation of the radical about the C-CN vector (θ_2, positive for clockwise rotation looking along this vector). These motions are illustrated in Figure 2.

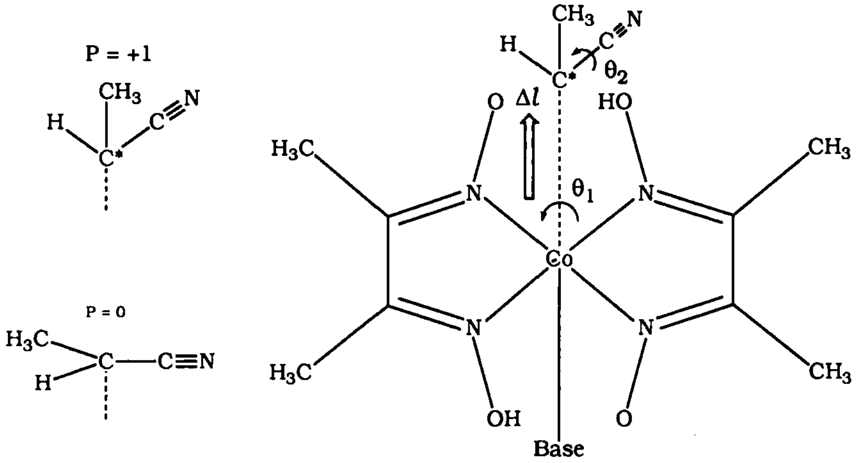
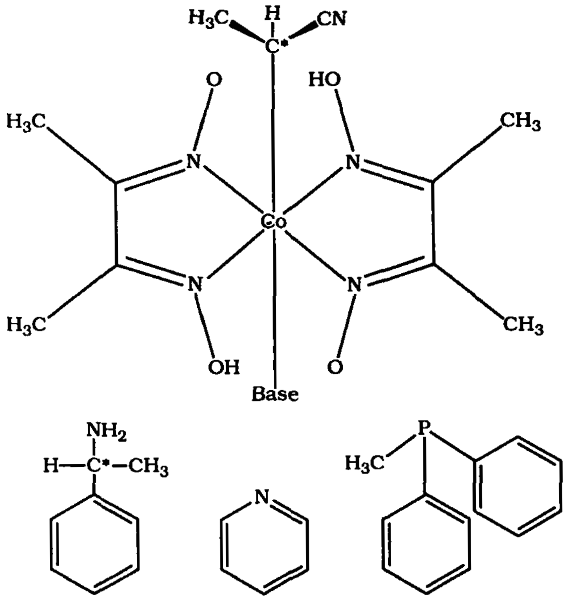


Figure 2. Diagrammatic illustration of the atomic motions involved in these calculations.

Point-to-point calculation of the packing potential energy (PPE) was made with the computer program OPEC (organic packing energy calculations)[7] for typical examples of the three classes (Figure 3). In these calculations we consider only the change in packing energy, that is, we ignore the energy changes associated with the purely "chemical" aspects of these reactions, the rupture of the Co-C bond, the inversion of the cyanoethyl group, and the reformation of the Co-C bond.[8]



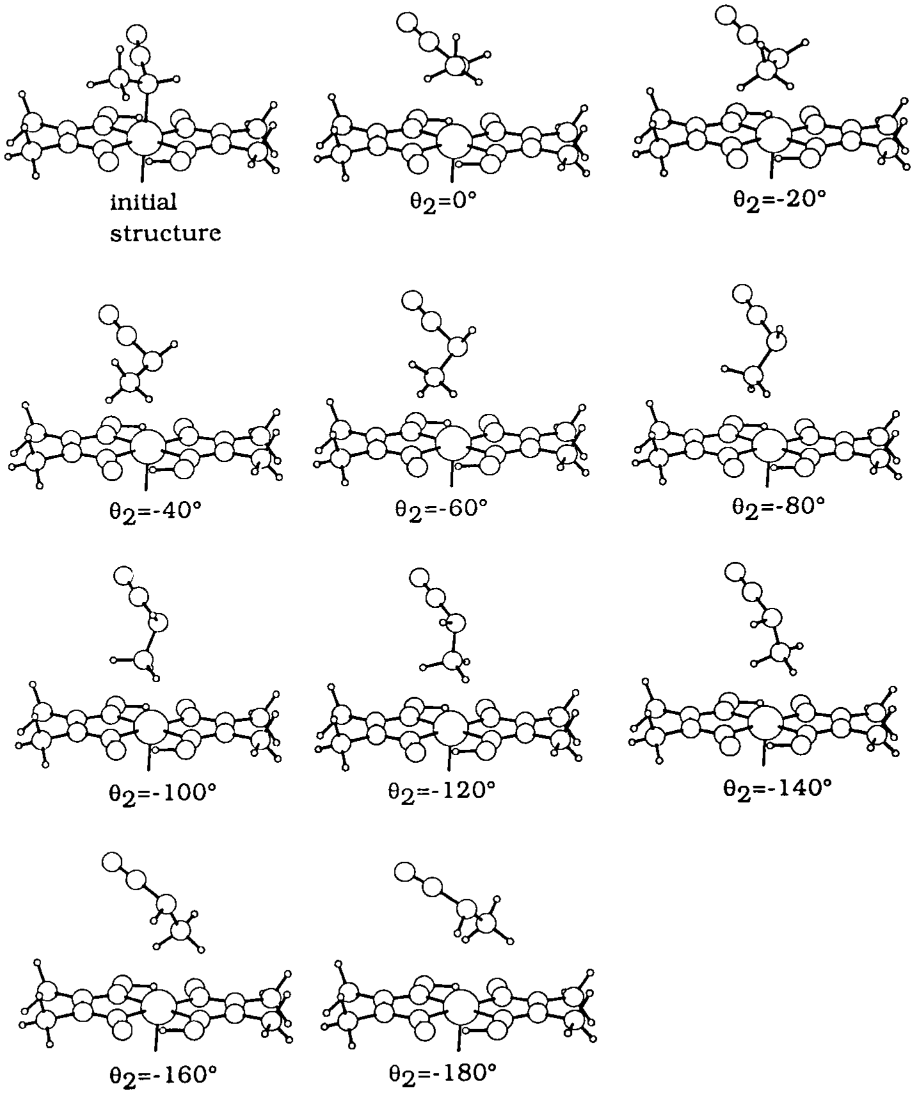
1 2 3

Figure 3. Cobaloxime complexes with **1**; (S)-α-methylbenzylamine, **2**; pyridine and **3**; diphenylmethylphosphine as axial ligands.

The first class of racemization: 1

Figure 4 shows movements of the cyanoethyl radical of **1** along the reaction path with minimum PPE. For the initial crystal structure ($P = +1$, $\Delta l = \theta_1 = \theta_2 = 0$) before rupture of the Co-C bond, the PPE was calculated to be -44 kcal mol^{-1}. As the radical rotates anticlockwise in θ_2, the value of PPE increases gradually. A pass is located at -120 to -140° in θ_2 (PPE = -27 kcal mol^{-1}). The path then continues downhill to a structure with $\theta_2 = 180°$ (PPE = -33 kcal mol^{-1}). But at this point the cyanoethyl group is still pyramidal with its initial configuration ($P = +1$).

The PPE for the planar cyanoethyl radical ($P = 0$) is generally higher; at the pass ($\theta_2 = -80°$) it is about 10 kcal mol^{-1} higher. The planarization of the cyanoethyl group leads to an increase in the non-bonded repulsions between the two molecular fragments and an increase in the non-bonded repulsions between the cyanoethyl group and the surrounding molecules.



initial structure

θ_2=0°

θ_2=-20°

θ_2=-40°

θ_2=-60°

θ_2=-80°

θ_2=-100°

θ_2=-120°

θ_2=-140°

θ_2=-160°

θ_2=-180°

Figure 4. Crystal **1**; sequence of structures along the path of minimum PPE with the cyanoethyl group held in its initial configuration (P = +1)

The second class of racemization: 2

As shown in Figure 1, crystals which belong to the second class contain two independent molecules in the initial structures. In the experimental study these were designated A and B, only the latter being reactive. Separate calculations were made for the motion of the two symmetry-independent molecules in the initial structure. The PPE for this crystal structure ($P = +1$, $\Delta l = \theta_1 = \theta_2 = 0$) before rupture of the Co-C bond is -88 kcal mol^{-1}.

Figure 5 shows sequence of structures of molecule B along the path of minimum PPE with the planar cyanoethyl group ($P = 0$). The clockwise rotation of the planar radical was calculated to have a pass with $\theta_2 = 100°$ (PPE = -65 kcal mol^{-1}).

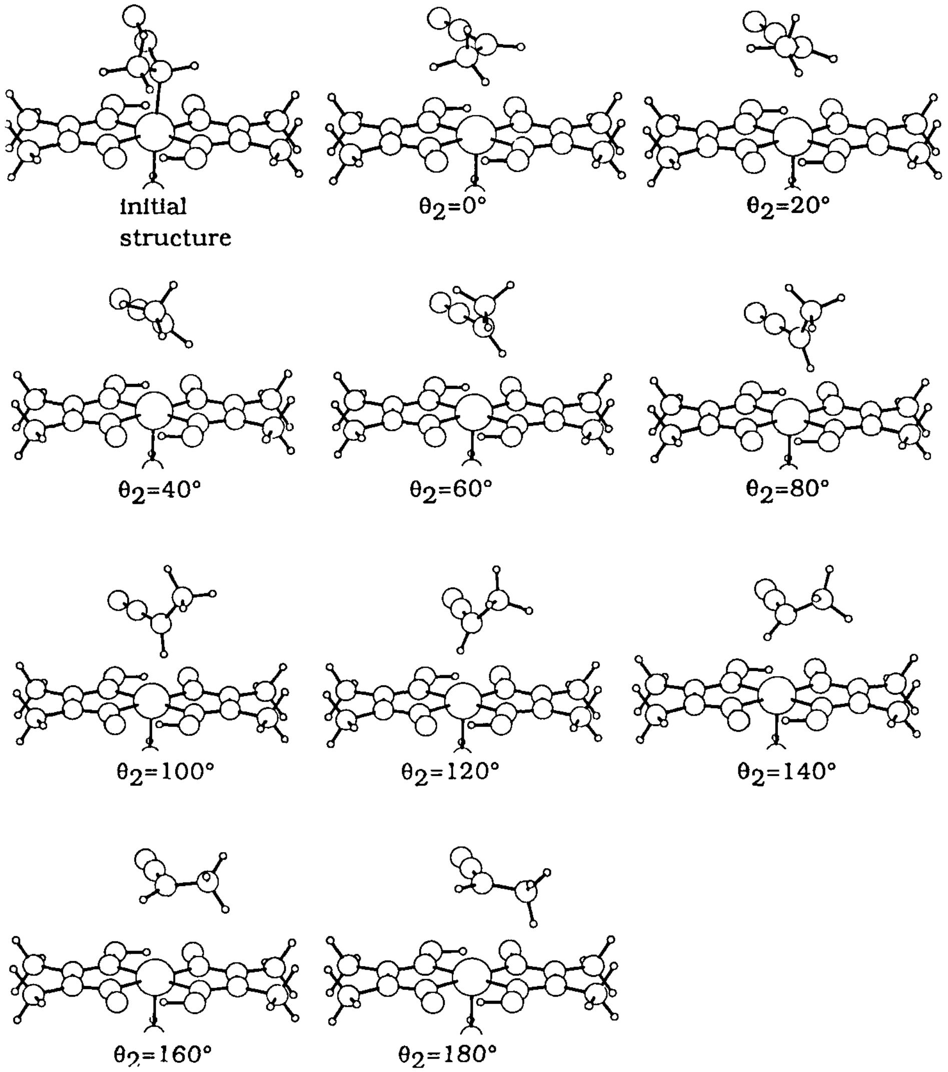
On the other hand, regardless of the sense of the θ_2 rotation and of the pyramidality of the radical, molecule A was calculated to have a much higher activation energy for inversion of configuration than molecule B.

The third class of racemization: 3

In the third class, the initial chiral crystal structure also contains two sets of independent molecules, A and B, but now both sets of molecules are reactive. The PPE for this crystal structure in its initial state ($P = +1$, $\Delta l = \theta_1 = \theta_2 = 0$) was calculated to be -101 kcal mol^{-1}. For molecule A, anticlockwise rotation of the planar cyanoethyl radical was calculated to have a pass with $\theta_2 = -80°$ (PPE = -82 kcal mol^{-1}) and clockwise rotation was calculated to have a pass with $\theta_2 = 140°$ (PPE = -92 kcal mol^{-1}).

On the other hand, regardless of the sense of the θ_2 rotation and of the pyramidality of the radical, molecule B was calculated to have a much higher activation energy (circa 50 kcal mol^{-1}) than molecule A, which is irreconcilable with the observed racemization of both molecules at comparable rates.

In the search for a lower energy path for molecule B, translation of the cyanoethyl group along the long axis of the cobaloxime fragments was introduced. The calculations showed that



initial structure

$\theta_2=0^\circ$

$\theta_2=20^\circ$

$\theta_2=40^\circ$

$\theta_2=60^\circ$

$\theta_2=80^\circ$

$\theta_2=100^\circ$

$\theta_2=120^\circ$

$\theta_2=140^\circ$

$\theta_2=160^\circ$

$\theta_2=180^\circ$

Figure 5. Crystal **2** (molecule B); sequence of structures along the path of minimum PPE with the planar cyanoethyl group (P = 0)

there is a pass (PPE = -85 kcal mol^{-1}) for clockwise rotation in θ_2 and a somewhat higher one (PPE = -75 kcal mol^{-1}) for anticlockwise rotation.

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