

## Perkin Communications

### X-Ray Structural Study of a 1:1 Complex of 4-Methoxy-1-methylpyridone and (*R,R*)-(-)-1,6-Bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol the Irradiation of which gives Optically Pure $\beta$ -Lactam

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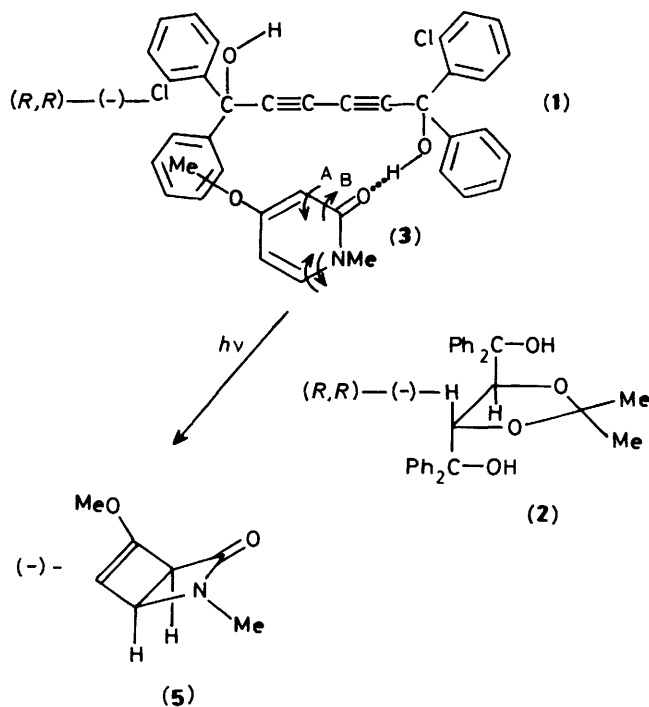
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A 1:1 complex of 4-methoxy-1-methylpyridone and (*R,R*)-(-)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol, on irradiation, gives a pure  $\beta$ -lactam. The mechanism for this photoconversion has been studied by means of an X-ray crystallographic analysis of the complex.

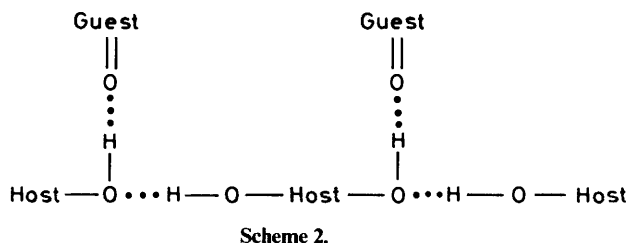
Recently we found that, upon irradiation, the 1:1 complexes of pyridone with (*R,R*)-(-)-1,6-bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (1) or (*R,R*)-(-)-*trans*-4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane (2) in the solid state underwent enantioselective conversion to give optically active  $\beta$ -lactams.<sup>1</sup> For example, irradiation of the 1:1 complex (4) of (1) and 4-methoxy-1-methylpyridone (3) in the solid state gave (-)-5-methoxy-2-methyl-2-azabicyclo[2.2.0]hex-5-en-3-one (5) of 100% e.e.<sup>1</sup> The mechanism of the



stereocontrol was investigated by means of an X-ray crystal structure determination of (4).

A large crystal of (4), cut to 0.30 × 0.40 × 0.50 mm, was used for X-ray diffraction measurements on a Rigaku AFC-5 diffractometer using Cu-K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation.<sup>†</sup>

As shown in Figure 1, the crystal structure is characterized by a layer structure along the *c*-axis. One layer arises from host-



guest and host-host hydrogen bonding (see Scheme 2) and the other by hydrophobic interaction *i.e.*  $\pi$ - $\pi$  bonding (3.65  $\text{\AA}$ ) between the host benzene rings and host-guest van der Waals contacts.

Figure 2 shows a selective part of the structure in the host-guest crystalline complex. The thin arrow indicates that the guest molecule is fixed with the host hydrogen bonding between

<sup>†</sup> Crystal data for C<sub>30</sub>Cl<sub>2</sub>H<sub>20</sub>O<sub>2</sub>·C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub> (4):  $F_w = 622.55$ ,  $F(000) = 1296$ , orthorhombic,  $P2_12_12_1$ ,  $Z = 4$ ,  $a = 18.387(2)$ ,  $b = 22.378(2)$ ,  $c = 7.885(1) \text{ \AA}$ ,  $V = 3244.6(7) \text{ \AA}^3$ ,  $D_x = 1.275$ ,  $D_m = 1.310(5) \text{ Mg m}^{-3}$  by flotation with aqueous citric acid,  $\mu = 21.32 \text{ cm}^{-1}$ . Unit cell parameters were obtained by the least-squares fit using 20 reflections with  $55^\circ < 2\theta < 60^\circ$ . Intensity data were collected up to  $2\theta = 125^\circ$ , including Bijvoet pair:  $0 \leq h \leq 21$ ,  $-25 \leq k \leq 25$ ,  $-9 \leq l \leq 0$ , by the  $\omega$ - $2\theta$  technique with a scan speed of  $4^\circ/\text{min}$  in  $\omega$  and background counts for 4 s. A total of 5769 reflections were obtained, in which 4906 with  $F_o > 3\sigma(F_o)$  were used of the analysis. The structure was solved by the direct method SIR85<sup>2</sup> using reflections with  $h, k \geq 0$ , and  $l \leq 0$ . The refinement was carried out by the block-diagonal least-squares method with isotropic temperature factors and a unit weight for all reflections. The absolute structure was determined by all reflections with Bijvoet and  $f' = 0.348$ ,  $f'' = 0.702$  for the Cl atom; the least-squares refinements were done on two independent sets of the positional parameters: ( $x y z$ ) and ( $-x y z$ ), with anisotropic temperature factors. The  $R$  values converged at  $R = 0.071$ ,  $w_R = 0.074$  for the former set and 0.080, 0.081 for the latter, respectively; the former showed good relations in magnitudes of  $F_o$  and  $F_c$  between Bijvoet pairs. All hydrogen atoms were obtained on a difference Fourier map. The final  $R$  value converged at  $R = 0.054$ ,  $w_R = 0.055$ . All the computations were done on an IBM 3081-GX3 machine at the Information Processing Center of Shimane University. Atomic co-ordinates, bond lengths and angles, and thermal parameters are available on request from the Cambridge Crystallographic Data Centre.\*

\* See 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. I*, 1989, Issue 1.

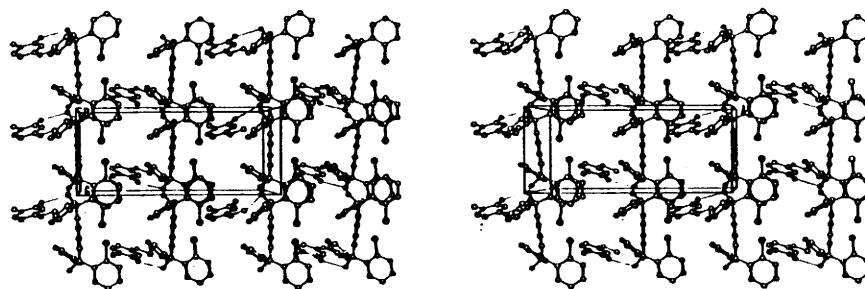


Figure 1. A PLUTO<sup>3</sup> drawing of the crystal structure of (4) along the *b*-axis. The Cl atoms are indicated by solid circles and hydrogen bonds by thin lines

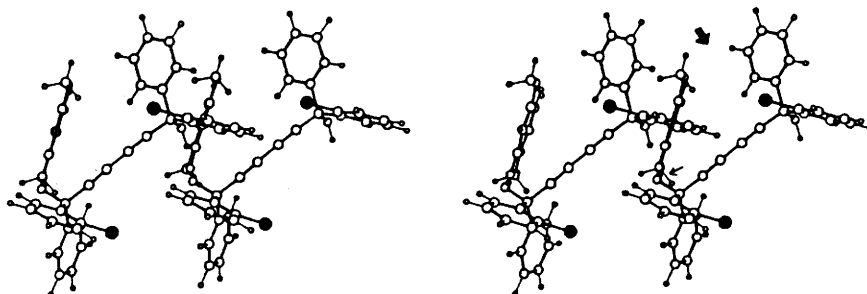


Figure 2. A part of the crystal structure of (4)

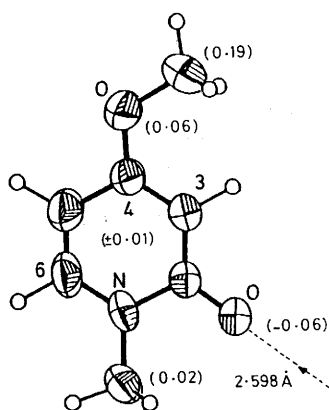
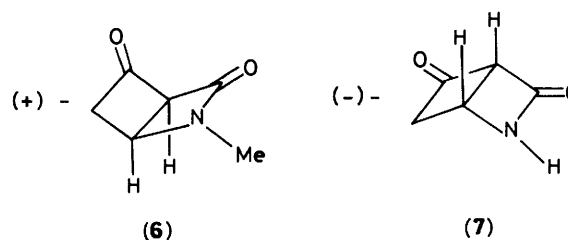


Figure 3. Molecular structure of (3) in (4). The pyridine ring is fairly planar with maximum deviation of 0.01 Å, the other deviations of atoms from the ring plane are indicated in parentheses

the carbonyl oxygen atom of (3) and the hydroxy group of (1). The thick arrow indicates that the methoxy group of (3) is in close van der Waals contact with the benzene ring of (1). The molecular structure of (3) in (4) is shown in Figure 3. The pyridine ring is planar (maximum deviation of 0.01 Å) whilst the methyl carbon, carbonyl oxygen, methoxy oxygen, and methoxy carbon atom deviate 0.02, -0.06, 0.06, and 0.19 Å from the plane, respectively. The large deviation of the methoxy group, especially the methoxy methyl carbon atom of 0.19 Å from the plane toward the reader may be attributed to the close van der Waals contact between the methoxy group and host benzene ring. In other words, the methoxy group cannot shift far from the reader. The carbonyl oxygen atom accepts the hydrogen bond of 2.589 Å from the hydroxy group of (1).



Although two directions (A and B) are possible in the photochemical disrotatory ring closure of (3) to (5) (Scheme 1), the steric constraints discussed above allow cyclisation only in the A direction (towards the reader): this should produce (5) of *S,S* configuration. In order to confirm the configuration of (5), which is an oil, an *X*-ray analysis of a 1:1 complex of (1) and (5) was carried out. Unfortunately, since there is considerable disorder in (5) its absolute configuration was not determined directly: it was, however, estimated to be *S,S* by the following method. Hydrolysis of (5) gave (+)-2-methyl-2-azabicyclo[2.2.0]hexane-3,5-dione (6). Since the configuration of (-)-2-azabicyclo[2.2.0]hexane-3,5-dione (7) has been reported to be *R,R*,<sup>4</sup> that of (6) and thus its precursor (5) must be *S,S*.

## References

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