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# Crystal Structure of a 1:1 Inclusion Complex of (R,R)-(-)-1,6-Bis(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol and (-)-(Z)-Benzylidene-2-(3-methylbutyl)azane Oxide

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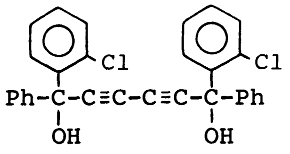
Crystal structure analysis of the title complex establishes the chirality of the (-)-(Z)-nitrone and the path of its photocylization to the corresponding optically active oxaziridine.

We recently reported that the irradiation of 1:1 complexes of (R,R)-(-)-1,6-bis(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (1) and nitrones in the solid state yielded optically active oxaziridines.1) For example, irradiation of a 1:1 solid complex (3) of 1 with racemic (-)-(Z)-benzylidene-2-(3-methylbutyl)-azane oxide (2) for 24 h gave oxaziridine 4 of 100% ee in 40% yield. The present X-ray analysis of 3 establishes the path of photocyclization (A or B) controlled by the chiralities of 1 and 2.



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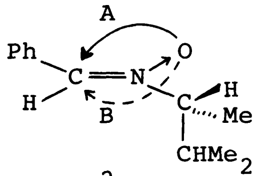

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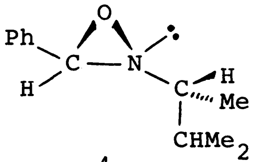

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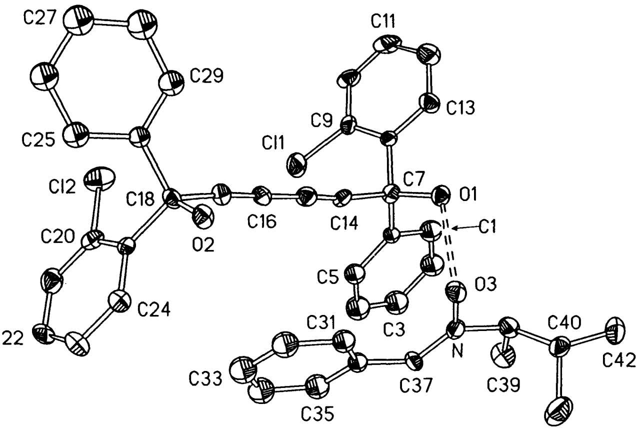
Crystal data of 3: $C_{30}H_{20}O_2Cl_2 \cdot C_{12}H_{17}NO$, mp 128 °C, FW = 674.66, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 12.190(2), b = 16.800(7), c = 17.081(8)Å, V = 3498(2)Å$^3$, $D_m$ = 1.275, $D_c$ = 1.281 g cm$^{-3}$, F(000) = 1416, monochromatized Mo-Kα radiation (λ = 0.71073Å), μ(Mo-Kα) = 2.23 cm$^{-1}$, crystal size 0.36 x 0.34 x 0.28 mm. Of the 3469 independent reflections collected using the ω-2θ technique (Nicolet R3m/V diffractometer, $2\theta_{max}$ = 50°, 2.02-8.37° min$^{-1}$, 1° below $K\alpha_1$ to 1° above $K\alpha_2$, stationary counts for one-half of scan time at each end of scan range), 1657 [$|F_o| > 4\sigma(|F_o|)$] were considered to be observed. The raw intensities were processed with the learnt-profile procedure, and absorption correction (transmission factors 0.895-0.908) was based on a pseudo-ellipsoidal fit to the ψ-scan data of 8 selected strong reflections over a range of 2θ-values. The structure was solved by direct phase determination guided by negative quartets. In view of the unfavorable data-to-parameter ratio, the three phenyl rings and three methyl groups were treated as rigid groups, and all H atoms were included in the calculation of structure factors. All other atoms were subjected to anisotropic refinement. Full-matrix least-squares refinement yielded *R* = 0.052 and *Rw* = 0.045 for 316 atomic parameters. All computations were done on a DEC MicroVAX-II computer with the SHELXTL PLUS package.[2)]



Selected bond distances (Å) and angles (°): C7-C14 1.499(10), C14-C15 1.172(10), C15-C16 1.376(11), C16-C17 1.185(10), C17-C18 1.492(10), C7-O1 1.432(8), C18-O2 1.431(8), C9-Cℓ1 1.733(8), C20-Cℓ2 1.738(8), N-O3 1.331(8), N-C37 1.297(10), N-C38 1.524(10); C7-C14-C15 171.0(8), C14-C15-C16 178.5(8), C15-C16-C17 177.7(8), C16-C17-C18 173.5(8), C36-C37-N 124.4(7), C37-N-O3 125.5(6), C37-N-C38 122.6(6), C38-N-O3 111.8(5).

Fig. 1. Perspective view of **3** showing both molecular components linked by a hydrogen bond.

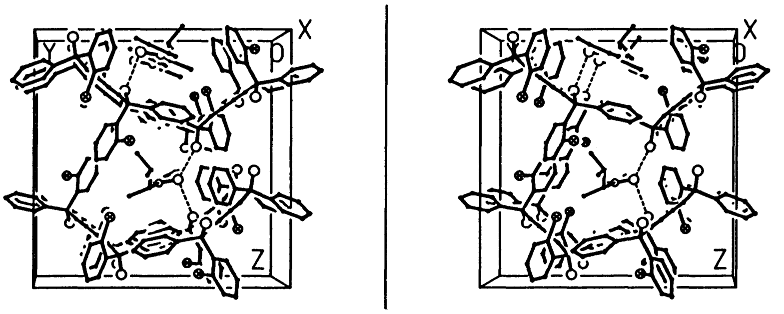


Fig. 2. Molecular packing in the crystal structure of **3**. The origin of the unit cell lies at the upper right corner, with *a* pointing towards the reader, *b* from right to left, and *c* vertically downwards.

Atom numbering in the asymmetric unit of complex **3** is shown in Fig. 1. Since the chirality of **1** is known, nitrone **2** has the *R* configuration, and its enantioselective photocyclization to **4** via path A in the solid state is clearly facilitated by the orientation of the chiral alkyl group. The diol (**1**) and nitrone (**2**) molecules which alternate along a $2_1$ axis parallel to *a* are linked by hydrogen bonds [O3...O1 = 2.788, O3...O2'(-½+*x*, 1½-*y*, -*z*) = 2.780Å, O1...O3...O2' = 122.0°] to form an infinite zigzag spiral chain (Fig. 2), such that the benzylidene and 3-methylbutyl moieties of guests **2** are aligned in a column bounded by phenyl and chlorophenyl groups of host molecules **1**.

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## References

1) F. Toda and K. Tanaka, Chem. Lett., 1987, 2283.

2) Experimental and computational details are as described in F. Toda, K. Okada, and T.C.W. Mak, Chem. Lett., 1988, 1829, and references cited therein. Atomic parameters have been deposited with the Cambridge Crystallographic Data Centre, and structure factors are available on request from the last author.

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