of symmetry. Even with the limited cases discussed here, it turns out that the dimer formed in all the photoreactive complexes with the chiral host (Ib) is mirror symmetric. Further, the results demonstrate that the chiral diol is a much better system than the achiral one in achieving photodimerization of reactive guest molecules with good yield. The large dimer yield is suggestive of the fact that the voids are big enough to permit reorientation of guest molecules upon excitation so as to achieve better overlap of π-orbitals of the reacting centers. The photodimerization reaction reported here appears to be the first case where the chiral diol has been successfully used.

Experimental Section

Preparation of Inclusion Complexes. The complexes of coumarins with Ia and Ib were formed by dissolving 2:1 equiv of guest and host, respectively, in chloroform or methanol and evaporating the solvent at room temperature over a period of 2 days. The complexes were characterized by melting points and broadening of the OH stretching frequency in the IR spectra owing to hydrogen bonding with the carbonyl group of the guest coumarins.

Photolysis and Characterization of Dimers. The powdered samples were irradiated by Rayonet lamps ($\lambda > 320$ nm) at room temperature with occasional shaking. The appearance of multiplets for the cyclobutyl protons of the dimers in the ^1H NMR spectrum of the irradiated mixture was followed at different intervals of time. The dimers of coumarin (II) and 7-methoxycoumarin (IV) were isolated by extracting the irradiated mixture with ethanol in which the host and guest dissolve but not the dimer. The dimer of 7-methylcoumarin was isolated by PTLC by elution with 10% ethyl acetate in hexane. The dimers were characterized by comparing the multiplicity pattern of cyclobutyl protons in the ^1H NMR spectrum with those already reported in the literature[12] and by mass spectral analysis. Percentage of conversions were deduced from the integrations of olefinic and cyclobutyl protons in the NMR spectrum of the irradiated complex.

X-ray Crystallographic Data. 1,1-Bis(*o*-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol–Coumarin (1:2) $[C_{30}H_{20}O_2Cl_2\text{-}2C_9H_6O_2]$. Single crystals amenable for X-ray crystallography were grown by slow evaporation of the solution of 2:1 equiv of II and Ib in a 1:1 mixture of CH_2Cl_2 and CCl_4. The crystals were orthorhombic, space group $P2_12_12_1$, $a = 8.451$ (1), $b = 19.746$ (2), and $c = 22.775$ (2) Å. The calculated density is 1.355 g cm^{-3} for $Z = 4$. The data were collected on an Enraf nonius CAD-4 diffractometer with Cu Kα (1.5418 Å) radiation using a $\omega/2\theta$ scan mode up to $\theta \leq 65°$. A total of 2737 reflections were significant $[|F_o| \geq 3\sigma(|F_o|)]$. The direct methods program MULTAN87[18] was used for structure solution. The refinement of positional and anisotropic thermal parameters of non-hydrogens and positional and thermal parameters of hydrogens by full matrix least-squares procedures using SHELX76[19] converged to a final R value of 0.058. The final difference Fourier map was featureless with $\rho_{max} = 0.28$ and $\rho_{min} = -0.25$ e/Å^3.

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Registry No. Ia, 20583-04-4; Ia·2II, 136538-04-0; Ia·2III, 136538-06-2; Ia·2IV, 136538-08-4; Ia·2V, 136538-10-8; Ia·2VI, 136538-12-0; Ia·2VII, 136538-14-2; Ib, 86436-20-6; Ib·2II, 136538-05-1; Ib·2III, 136538-07-3; Ib·2IV, 136538-09-5; Ib·2V, 136538-11-9; Ib·2VI, 136538-13-1; Ib·2VII, 136538-15-3; II, 91-64-5; II (dimer a), 5248-11-3; III, 2445-83-2; III (dimer a), 93097-92-8; IV, 531-59-9; IV (dimer a), 37818-63-6; IV (dimer b), 37786-10-0; V, 14002-89-2; VI, 14002-90-5; VII, 17831-88-8.

Supplementary Material Available: Full details of the X-ray analyses of host and guest molecules (21 pages). Ordering information is given on any current masthead page.

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[18] Debaerdemaeker, T.; Germain, G.; Main, P.; Tate, C.; Woolfson, M. M. MULTAN87, "A system of computer programs for the automatic solution of crystal structures from X-Ray diffraction data", Universities of York, England, and Louvain, Belguim.

[19] Sheldrick, G. M. SHELX, Program for Crystal Structure Determination, University of Cambridge, 1976.

Additions and Corrections

Vol. 56, 1991

F. M. Menger. The Negative Rate Constants of Breslow and Huang.

Page 6251. The following passage was inserted by the author during galley proofs and did not appear in the version of the manuscript that was approved for publication by the Editor:

"Dr. Albert Haim of Stony Brook simultaneously and independently uncovered a variety of other problems with the Breslow manuscripts (e.g., the reported rate constants and equations do not fit the theoretical plots). His analysis will be published elsewhere. Neither of us was permitted to publish our work in the journal where the errors originated."

The Editors would not have permitted the manuscript to be published with this passage, had it been in the version of the manuscript that was accepted.