

Supramolecular Photochemistry of Crystalline Host–Guest Assemblies: Absolute Asymmetric Photorearrangement of the Host Component

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The design of new host molecules for applications in molecular recognition and materials science is a topic of much current interest.¹ Weber and Czugler² have delineated some of the features of good hosts: they should be bulky and pack inefficiently with voids, and they should contain appended sensor groups that will coordinate to the guests ("coordinatoclatrates"). One of the most important types of coordination is hydrogen bonding, and Etter and co-workers have carried out important studies in this area, including the demonstration that triphenylphosphine oxide, an excellent hydrogen-bond acceptor, forms crystalline complexes with a wide variety of hydrogen-bond donors.³

It occurred to us that it might be possible to combine the concepts of Weber and Etter in one molecule: a bulky "roof-shaped" ² coordinatoclatrate with appended diphenylphosphine oxide sensor groups (compound **2**, Scheme I). In this communication we report on the preparation of **2** and its ability to form crystalline host–guest complexes. Because host molecule **2** is a potential di- π -methane reactant,⁴ a second goal of our work was to investigate the photochemistry of these complexes. The intriguing results of these experiments, in which the ethanol complex of **2** was found to undergo an "absolute asymmetric" solid-state photorearrangement in high enantiomeric excess, are also reported herein.

The coordinatoclatrate **2** was prepared in 80–90% yield by Diels–Alder addition of ethynediylbis(diphenylphosphine oxide) (**1**)⁵ to anthracene (Scheme I).⁶ Compound **2** forms crystalline 1:1 inclusion complexes with a wide variety of solvent molecules, including acetone, 2-butanone, 2-pentanone, 3-pentanone, methyl vinyl ketone, tetrahydrofuran, dimethoxyethane, ethyl acetate, acetic acid, methanol, ethanol, 1-propanol, and 2-propanol. Solvents that failed to form crystalline complexes included benzene, acetophenone, and dioxane. The complexes were prepared by recrystallizing the host from the appropriate solvent and were characterized (with the exception of the acetic acid and methanol complexes, which decompose upon standing in air at room temperature) by IR, NMR, and elemental analysis. Thermally, the complexes begin to effloresce at approximately

120 °C, and eventually the empty host melts at 237–238.5 °C. For the ethanol and ethyl acetate complexes, the crystal and molecular structures were determined by X-ray diffractometry.⁷ A stereodigram of the 2-EtOH complex is shown in Figure 1. Evidently, from the variety of molecules complexed, hydrogen bonding is not essential for complex formation.

As expected,⁸ compound **2** undergoes the di- π -methane photorearrangement, both in solution ($\Phi = 0.28$, CDCl₃) and in its crystalline complex form. The photoproduct, dibenzosemi-bullvalene derivative **3**, was characterized spectroscopically as well as by reduction to the corresponding bis(phosphine) **4**, whose structure was established by X-ray crystallography.⁷ The finding that the ethanol complex of host molecule **2** crystallizes in a chiral space group ($P2_12_12_1$) offered the opportunity for carrying out an absolute asymmetric di- π -methane photorearrangement in the solid state.⁹ Accordingly, single crystals of the ethanol complex were irradiated through Pyrex, and the chiral photoproduct **3** was tested for optical activity by polarimetry and chiral HPLC. Strikingly, this indicated an enantiomeric excess of 89% (84% conversion, room temperature); even higher enantiomeric excesses could be achieved at lower temperatures and lower conversions.¹⁰ By way of contrast, samples of compound **3** derived from solution-phase photolyses of **2** or from irradiation of its crystalline ethyl acetate complex (achiral space group $P2_1/c$) proved to be racemic.

Because phosphorus is a sufficiently heavy atom to give rise to measurable anomalous dispersion ($\Delta f'' = 0.434$ for Cu K α radiation) during X-ray crystallographic analysis, the absolute configuration of compound **2** in its ethanol complex as well as that of optically pure product **4** could be determined with a high degree of certainty by the Bijvoet method.¹¹ Making the reasonable assumption that the absolute configuration of photoproduct **3** does not change upon reduction to **4**, the absolute configurations of *pro*-(+)-**2** and (+)-**3** can be depicted as shown in Scheme I. From this information, and assuming the standard Zimmerman mechanism for the di- π -methane rearrangement,⁴ we can deduce that initial benzo–vinyl bridging occurs between C(11) and C(10a) and/or C(12) and C(9a). The situation is represented by partial structure **5** in Scheme I. The absolute value of the P(1)—C(11)=C(12)—P(2) dihedral angle is +23.9°, which predisposes the molecule to C(11)–C(10a) bridging (or its stereochemical equivalent, C(12)–C(9a) bridging) owing to better orbital overlap between the interacting orbitals as well as to a diminution of the steric interaction between the bulky diphenylphosphine oxide substituents in the transition state. In the alternative pathways leading to the unobserved enantiomer, the diphenylphosphine oxide groups would be driven *toward* each other during benzo–vinyl bridging. A similar explanation has successfully accounted for the absolute steric course of three other solid-state di- π -methane photorearrangements^{12,13} and can provisionally be taken as being general.

(7) Complex 2-EtOH: $P2_12_12_1$; $a = 17.983(2)$ Å, $b = 20.682(3)$ Å, $c = 9.384(6)$ Å; $Z = 4$; $R = 3.8\%$. Complex 2-EtOAc: $P2_1/c$; $a = 18.223(2)$ Å, $b = 9.435(3)$ Å, $c = 21.946(2)$ Å; $\beta = 103.430(7)^\circ$; $Z = 4$; $R = 4.9\%$. Bis(phosphine) **4**: $P2_12_12_1$; $a = 17.381(4)$ Å, $b = 18.414(3)$ Å, $c = 9.591(2)$ Å; $Z = 4$; $R = 3.1\%$.

(8) Chen, J.; Scheffer, J. R.; Trotter, J. *Tetrahedron* 1992, 48, 3251.

(9) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* 1986, 108, 5648.

(10) Both photoproduct enantiomers were formed depending on the enantiomorph photolyzed. By seeding of ethanol solutions of **2** with crystals known to give rise to (+)-**3** upon photolysis, large quantities of crystalline *pro*-(+)-**2** enantiomorph could be formed. In a similar way, a substantial stock of the *pro*-(–)-**2** enantiomorph could be prepared.

(11) Bijvoet, J. M.; Peerdeman, A. F.; Van Bommel, J. A. *Nature* 1951, 168, 271. For 2-EtOH, $\Delta R = 4.6\% - 3.8\% = 0.8\%$; for bis(phosphine) **4**, $\Delta R = 3.8\% - 3.1\% = 0.7\%$.

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(2) Weber, E.; Czugler, M. *Top. Curr. Chem.* 1988, 149, 45.

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(4) For reviews on the di- π -methane photorearrangement, see: (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Chapter 16. (b) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, Chapter 1.

(5) Ethynediylbis(diphenylphosphine oxide) (**1**) was prepared according to a published procedure: Von Hartmann, H.; Beermann, C.; Czempik, H. *Z. Anorg. Allg. Chem.* 1956, 287, 261.

(6) A previous example of the use of compound **1** as a dienophile with α -pyrone is known: Kyba, E. P.; Rines, S. P.; Owens, P. W.; Chou, S.-S. P. *Tetrahedron Lett.* 1981, 22, 1875.

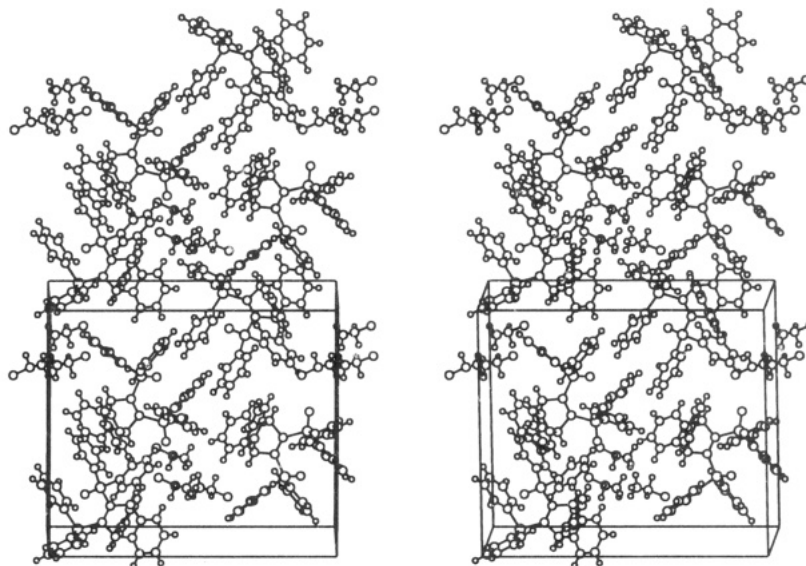
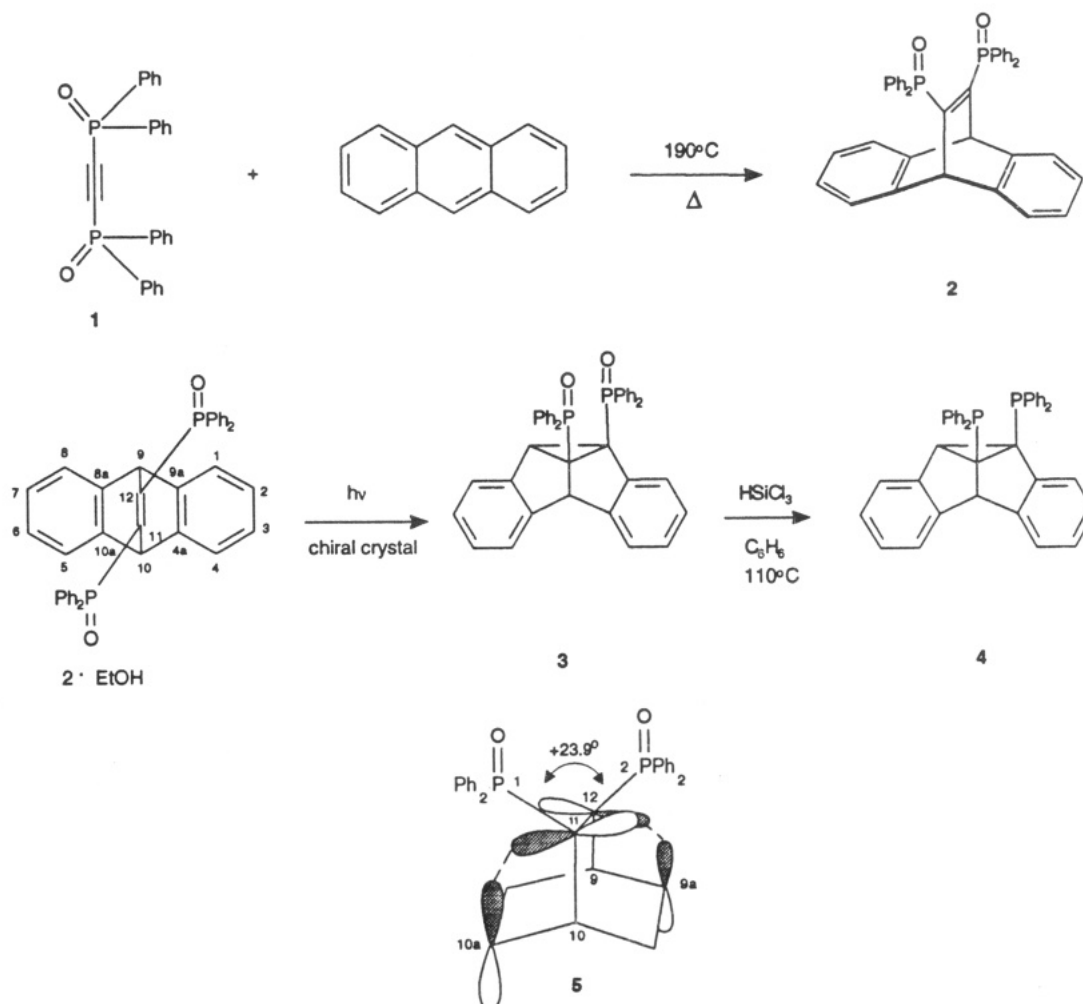


Figure 1. Stereoscopic view of the ethanol complex of 9,10-dihydro-9,10-ethenoanthracene 11,12-bis(diphenylphosphine oxide) (2).

Scheme I



The use of bis(phosphine) 4 as an optically active ligand for homogeneous transition metal catalysis is under investigation.

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