Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles for [1]PF_6 and an ORTEP drawing of the asymmetric part of the unit cell (9 pages); table of observed and calculated structure factors for [1]PF_6 (25 pages). Ordering information is given on any current masthead page.

The Chemical Consequences of Conformational Polymorphism: The Phase-Transition-Dependent Photochemistry of Crystalline 1,14-Cyclohexacosanedione

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It has been recognized for some time that polymorphic crystal modifications of organic compounds differ not only in packing arrangement but also frequently in the *shape* of the constituent molecules as well, a phenomenon that has been termed "conformational polymorphism" by Bernstein.[1] Only rarely, however, have such structural differences been exploited chemically, the idea being that by comparing the solid-state chemistry of conformational polymorphs, one can arrive at an increased understanding of the effects of conformation on chemical reactivity.[2] In the present communication we describe the case of a macrocyclic diketone that exhibits very different photochemical behavior from each of the two well-defined conformational polymorphs (dimorphs) whose structures have been determined by X-ray crystallography. The results are interpreted as arising primarily from the different conformations of the molecules in each dimorph rather than from their different packing arrangements.

As a continuation of our studies on the crystalline-phase photochemistry of macrocyclic "diametric" diketones,[3] we prepared 1,14-cyclohexacosanedione (**1**), the 26-membered ring homolog.[4] Careful recrystallization of this material at room temperature from a mixture of ethyl acetate and petroleum ether leads to clear plates which, upon heating, crack and become opaque at 54 °C and melt at 70 °C. The existence of an endothermic ($\Delta H \approx 6$ KJ/mol) solid–solid-phase transition at 54 °C was confirmed by differential scanning calorimetry. The phase transition is not reversible. When crystals that had been annealed at ca. 60 °C were cooled to room temperature and resubjected to DSC, no phase transition at 54 °C was observed, but melting still occurred at 70 °C. When saturated solutions of **1** were seeded with annealed material, needle-shaped crystals were obtained instead of clear plates; the needles and the annealed samples were identical in all respects (DSC, FTIR, CPMAS ^{13}C NMR, powder pattern) and were clearly different from the plates.

The existence of conformational polymorphism in the plate and needle modifications of compound **1** was confirmed by X-ray crystallography.[5] Stereodiagrams showing the molecular conformations are given in Figure 1. The plates are characterized by a rectangular [3,10,3,10] conformation similar to the [3,5,3,5] conformation adopted by the 16-membered ring diketone.[3] In contrast, the molecules in the needle dimorph have what might be termed a zigzag conformation in which indentations in the methylene chain along one side of the long molecular axis are matched by extrusions on the other.

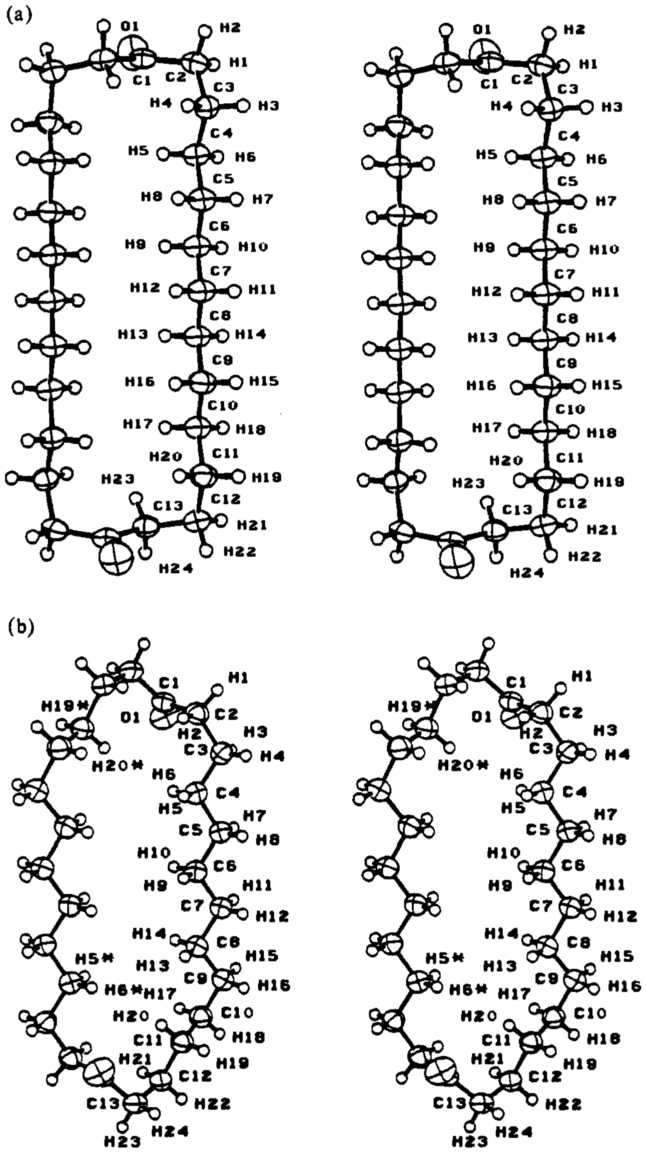
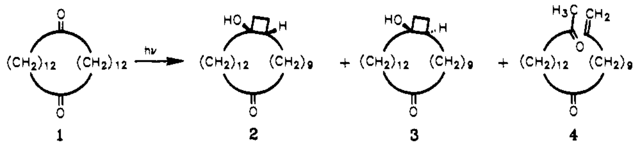


Figure 1. (a) Stereodiagram of the molecular conformation of the $P2_1/n$ (plate) dimorph of diketone **1** and (b) molecular conformation stereodiagram of $P2_1/c$ (needle) dimorph. Owing to a molecular center of symmetry in each case, only half the atoms are numbered.

Scheme I



Compound **1** was photolyzed at room temperature through Pyrex in both of its dimorphic crystal modifications as well as in hexane solution.[6] Fascinatingly, widely divergent results were

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[1] Bernstein, J. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; Chapter 13, pp 471–518.

[2] The only other example of a study of this type of which we are aware is that reported: Evans, S. V.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1986**, *27*, 1419.

[3] Lewis, T. J.; Rettig, S. J.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1990**, *112*, 3679.

[4] Prepared according to the procedure: Blomquist, A. T.; Prager, J.; Wolinsky, J. *J. Am. Chem. Soc.* **1955**, *77*, 1804. Compound **1** was first prepared: Ruzicka, L.; Stoll, M.; Huyser, H. W.; Boekenoogen, H. A. *Helv. Chim. Acta* **1930**, *13*, 1152.

[5] Plates: $P2_1/n$; $a = 5.541$ (2) Å, $b = 28.327$ (2) Å, $c = 8.005$ (2) Å; $\beta = 98.89$ (3)°; $Z = 2$; $R = 3.5\%$. Needles: $P2_1/c$; $a = 8.107$ (2) Å, $b = 5.526$ (1) Å, $c = 28.274$ (3) Å; $\beta = 97.98$ (1)°; $Z = 2$; $R = 3.7\%$. Full details will be published separately.

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obtained in each case. In solution, the Norrish type II[7a] cleavage product **4** (Scheme I) predominated, accompanied by lesser amounts of the type II cyclobutanols **2** (cis) and **3** (trans).[7b] In a typical low conversion run, the **2**:**3**:**4** ratio was 1.5:3.5:5. In contrast, the photoreaction of the platelike crystals was essentially completely stereoselective for *cis*-cyclobutanol **2** (>95% by gas chromatography), and the needlelike crystals, whether prepared by annealing or recrystallization, afforded the *trans*-cyclobutanol derivative **3** with greater than 90% stereoselectivity; in neither solid-state photoreaction was there any evidence for the formation of cleavage product.[4] Control experiments showed that as little as 1% of this material could have been detected readily.

The photoproducts were isolated by silica gel column chromatography and identified on the basis of their spectroscopic properties.[8] Particularly informative were the ^{13}C NMR spectra, in which the ring junction C–H carbon of the *cis*-cyclobutanol **2** (easily identified by the attached proton test[9]) appears at 50.08 ppm, whereas the analogous signal for the *trans*-cyclobutanol **3** occurs at 43.71 ppm. This large chemical shift difference has been observed in nine other cis/trans pairs analogous to **2**/**3** and appears to be general;[3,10] in four of the ten cases (but not in the case of compounds **2** and **3**), the stereochemical assignments were verified by X-ray crystallography.

Inspection of the conformational stereodiagrams reveals that, in the case of the plate dimorph (Figure 1a), there are two nonequivalent γ-hydrogen atoms, H5 and H20, whose abstraction must be considered in analyzing the solid-state photoreactivity; H5 lies 3.3 Å from O1 and H20 is situated 2.8 Å from O1′. Previous work from our laboratory has established an upper limit of ca. 3 Å for d, the $C{=}O{\cdots}H_\gamma$ distance,[11] and this makes it likely that H20 is the hydrogen atom that is abstracted in the solid state.[12] Also important in determining hydrogen abstractability is the angular relationship between the abstracting and abstracted atoms.[11,13] Owing to the involvement of the oxygen atom n-orbital in the γ-hydrogen abstraction process,[14] the angle τ, defined as the degree to which the γ-hydrogen atom deviates from the mean plane of the carbonyl group, should be as close to 0° as possible, and the $C{=}O{\cdots}H$ angle Δ should ideally lie in the range 90–120°. The values of τ for H5 and H20 are identical (52°), and the values of Δ are 53 and 82°, slightly favoring abstraction of H20. Regardless of which hydrogen atom is abstracted, however, formation of *cis*-cyclobutanol is predicted to be preferred. This follows from the fact that the abstracting oxygen atom and the nonabstracted γ-hydrogen (H19 or H6) bear a syn relationship to each other in the plate dimorph, and assuming a least-motion solid-state process involving retention of configuration at both centers, these atoms will end up cis to one another in the photoproduct. This is precisely the experimentally observed result.

A similar analysis successfully rationalizes the formation of *trans*-cyclobutanol **3** from the needle dimorph of compound **1**. In this case, the γ-hydrogens to consider are H6 (d = 2.7 Å, τ = 49°, Δ = 85°) and H20 (d = 3.3 Å, τ = 57°, Δ = 58°). Abstraction of H6 is clearly preferred, and this leaves H5 and O1 in an anti relationship which becomes trans in the final photoproduct. Using similar reasoning it is apparent that abstraction of H20 should lead to *cis*-cyclobutanol, and 5–10% of this product is formed in the solid-state photolysis of the needle dimorph. It is difficult to say whether this is the result of abstraction of H20 or is due to loss of control of biradical closure following abstraction of H6. In this context, a brief discussion of the solution-phase photochemistry of **1** is in order. As was the case with the 16-, 18-, and 22-membered ring analogues,[3] all selectivity is lost in this medium, a result that can be attributed to reaction from alternate conformers (of which there are many) and/or conformational isomerization of the intermediate 1,4-biradicals prior closure.

In summary, we draw attention to the analogy between our results with the macrocyclic diketones and the classic studies of Schmidt and co-workers on the solid-state [2 + 2] photodimerization of the cinnamic acids.[15] In both cases, distance and geometric requirements for photoreaction have been established, and the structure and stereochemistry of the products are directly and simply related to the molecular and crystal structure of the reactants as shown by the study of polymorphic crystal modifications. Studies from our laboratory of other macrocyclic diketones support the general picture described above, and these results will be published in the near future.

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(6) The Pyrex-filtered output of a 450-W Hanovia medium pressure mercury lamp was the light source in both the solid-state and solution-phase photolyses. At this wavelength only the n,π^* absorption band (λ_{max} 280 nm, ϵ 60 in cyclohexane is excited. Conversions were kept low (2–15%) in order to minimize secondary photoreactions of the products as well as to avoid loss of topochemical control through melting in the solid-state runs. Identical results were obtained with carefully grown single crystals as well as polycrystalline and powdered samples, indicating that defects probably play no role in these reactions.

(7) (a) Review: Wagner, P. J. In *Molecular Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1980; Chapter 20. (b) Cyclobutanol products in type II photochemistry were first reported: Yang, N. C.; Yang, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 2913.

(8) The photoproducts exhibited spectral and analytical data entirely consistent with their assigned structures. Details will be provided in a forthcoming full paper.

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(10) Lewis, T. J.; Scheffer, J. R., unpublished results.

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(12) Burke, S. D.; Silks, III, L. A.; Strickland, S. M. S. *Tetrahedron Lett.* **1988**, *23*, 2761 have shown that relative O···H abstraction distances control regioselectivity in the Barton reaction, a ground-state analogue of the type II process.

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New Mode of Porphyrin Complexation with Nucleobase

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Molecular recognition of nucleobases by artificial receptors is of current interest in artificial receptor chemistry. By analogy with the interactions operating in DNA and/or RNA duplexes, the hydrogen-bond interaction is considered to be the most general and important driving force for molecular recognition of nucleobases.[1] Recently, we reported that nucleobases strongly interact with porphyrin metal complexes through coordination,[2] which suggests the possibility of another type of artificial receptor using a nonbiological recognition mode for nucleobases.[3]

Herein we report a new mode of adenine recognition by a porphyrin zinc complex involving both a hydrogen-bonding and

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