Photochemical Dimerization of Acephenanthrylene and the Heavy Atom Effect

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The solution-phase photodimerization of acephenanthrylene (**1**) in cyclohexane, chloroform, dibromomethane, and ethyl iodide with visible light ($\lambda = 419$ nm) occurs to form cis (**2**) and trans (**3**) photodimers in ratios that vary with the solvent and with the presence or absence of oxygen. The photodimerization exhibits a significant heavy atom effect and also is sensitive to selective quenching by dissolved oxygen, in which only cis stereoisomers are produced. Irradiation of the dimers ($\lambda = 254$ nm) shows that the trans dimers cleave more rapidly than the cis dimers. This is attributed to stabilization of the excited state in the cis dimers.

Introduction

There is a continuing interest in the synthesis of compounds with molecular clefts.[1−5] We theorized that the photodimerization of acephenanthrylene (**1**) could form cis dimers that contain a cleft. We also wished to explore how the excited-state behavior of **1** compares to its benzologs acenaphthylene (**4**) and aceanthrylene (**5**), whose excited-state chemistry we[6−17] and others[18−21] had explored. Cowan and Drisko[18] first detailed the unique heavy atom effects (HAE) associated with the photodimerization of **4**. The quantum yields of dimerization of **4** in the presence of solvents containing covalently bound heavy atoms such as bromine or iodine increased

significantly, and the proportion of trans photodimer also increased. The photochemistry of **5**[14−17] proved to be different from **4** in that **5** does not photodimerize in regular solvents but only dimerizes in heavy atom solvents (HAS). These behaviors indicate significant differences between the intersystem crossing rates in **4** and **5** in regular solvents. Hence, we wondered what kind of intersystem crossing behavior **1** exhibits and report here the results of this inquiry.

Results and Discussion

Compound **1** exhibits unique excited state properties. It photodimerizes readily under a variety of conditions to form diastereoisomeric head-to-tail (**ht**) and head-to-head (**hh**) sets **2** and **3**, respectively, upon irradiation with visible light ($\lambda = 419$ nm) into its K-band at 440 nm.[6] When **1** is irradiated in oxygen-saturated cyclohexane and deuteriochloroform only one set of dimers forms. By analogy to the behavior of **4**,[7−13,18−21] from which **1** is formally derived by benzo annelation, we assign cis stereochemistry to this product (vide infra). Both the cis and trans dimers form in degassed cyclohexane, deuteriochloroform, dibromomethane, and ethyl iodide. The isomer ratios and quantum yields are displayed in Table 1.
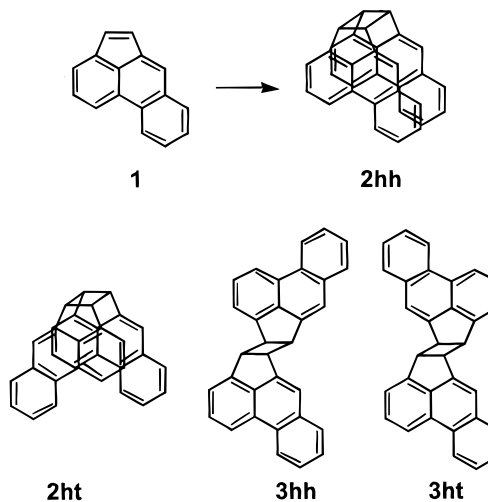
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Table 1. Photodimerization of Acephenanthrylene[a]

solvent	cis/trans ratio	quantum yield
C_6H_{12} (aerated)	100/0	0.039
C_6H_{12} (degassed)	30/70	0.105
CH_2Br_2	33/67	0.306
CH_3CH_2I	29/71	0.312
$CDCl_3$	40/60	*b*
$CDCl_3$ (aerated)	100/0	*b*

[a] Solvents are degassed with an argon stream unless indicated otherwise. Product ratios are obtained from integrated cyclobutyl ^1H NMR signals. [b] Not measured.
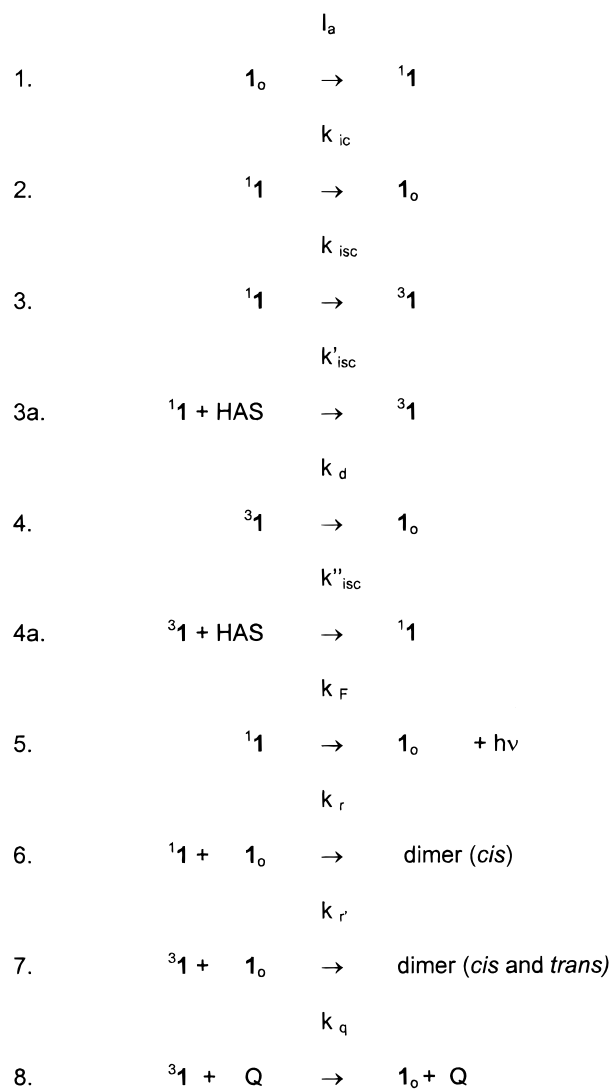
Diastereomeric **2** and **3** are readily separated by TLC in mixtures of ethyl acetate and hexane. Both **2** and **3** fluoresce whereas **1** does not. Pure **2** and **3** were isolated by flash chromatography or by fractional crystallization from 2-butanone in which **3** is less soluble than **2**. This solubility behavior parallels that found for the photo-dimers of **4**, wherein the cis dimer is more soluble in polar solvents than the trans dimer. Parallels are also observed when comparing the melting points of **2** and **3** to the dimers of **4**, where the cis dimers of **1** (mp 204−206 °C) and **4** (lit.[19] mp 231−233.5 °C) are lower than the trans (304 °C dec and 305−307 °C,[19] respectively).

By comparison to the results of the photodimerization of **5**,[14−17] the stereochemistry of each diastereomeric set is readily assigned on the basis of unique ^1H NMR chemical shifts in the cyclobutyl region. The cyclobutyl protons of **2** and **3** appear as multiplets. In the case of the cis dimers **2hh** and **2ht**, their chemical shift is δ 4.8, while in the trans dimers **3hh** and **3ht** the shift is at δ 4.1. Midpoint analysis[22] confirms that **2** and **3** are isomers of each other.

The upfield shift in dimers **3** ($\Delta\delta = 0.7$) is the result of their cyclobutyl protons being shielded by the diamagnetic anisotropic ring current of the neighboring phenanthrene nucleus. Dimers **2** and **3** do not produce evidence in the aromatic region of more than one diastereomer because the perturbation on **hh** and **ht** is too small to entail a significant difference in chemical shifts. However, the ^{13}C chemical shifts do discriminate among some of the carbons whose proton resonances overlap in the ^1H NMR spectra. However, a complete ^{13}C count for all carbons could not discriminate between **hh** and **ht** because of the congruence of some of the chemical shifts in the dimers.

For **5**, a 2D NOESY experiment was successful in establishing the difference between **hh** and **ht** dimers in part due to an enhancement between the cyclobutyl protons and those of the anthracene nucleus.[23] We investigated the possibility of the same type of NOE enhancement existing in **2** and **3**. However, semiempirical AM1 calculations have shown that the vector distances between the cyclobutyl protons and those of the phenanthrene nucleus are too great (>3.0A)[24] for an observable NOE effect.

The AO coefficients of the frontier molecular orbitals of **1**[6] at the cyclopentene bridge differ little in their magnitudes in either the HOMO or LUMO orbitals. Any difference in the proportion of **hh** and **ht** dimers formed is probably determined by factors other than the relative

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Scheme 1

$$I_a$$

1.		1_o	$\rightarrow$	$^1\mathbf{1}$
	k_{ic}			
2.		$^1\mathbf{1}$	$\rightarrow$	1_o
	k_{isc}			
3.		$^1\mathbf{1}$	$\rightarrow$	$^3\mathbf{1}$
	k'_{isc}			
3a.	$^1\mathbf{1}$ + HAS		$\rightarrow$	$^3\mathbf{1}$
	k_d			
4.		$^3\mathbf{1}$	$\rightarrow$	1_o
	k''_{isc}			
4a.	$^3\mathbf{1}$ + HAS		$\rightarrow$	$^1\mathbf{1}$
	k_F			
5.		$^1\mathbf{1}$	$\rightarrow$	1_o + hν
	k_r			
6.	$^1\mathbf{1}$ + 1_o		$\rightarrow$	dimer (*cis*)
	$k_{r'}$			
7.	$^3\mathbf{1}$ + 1_o		$\rightarrow$	dimer (*cis* and *trans*)
	k_q			
8.	$^3\mathbf{1}$ + Q		$\rightarrow$	1_o + Q

excited-state electron distribution. We hypothesized that if one set of dimers (**hh** or **ht**) was formed preferentially the cyclobutyl ^1H NMR signals could be simulated by a standard calculation. Dimers **2hh**, **3hh**, and **3ht** are an AA′BB′ spin system, whereas **2ht** is an A_2B_2 spin system. The cyclobutyl signals for **2** were modeled as an A_2B_2 system using the NMR spin simulation program, employing the LAOCOON algorithm,[25] with the assumption that **ht** dimers are formed exclusively. Simulations used chemical shift differences and coupling constants (J_{AB}) within the range observed previously in cyclobutane rings.[26] All combinations of $\Delta\delta_{AB}$ and J_{AB} failed to give a calculated spectrum matching the experimental result. No correct simulated spectrum was obtained for **2** using the spin system AA′BB′ for the **hh** dimers. These simulation studies in conjunction with the ^{13}C carbon resonances suggest that inseparable mixtures of **hh** and **ht** dimers are being formed. Attempts to separate the **hh** and **ht** dimers by HPLC were unsuccessful under a variety of solvent and flow conditions.

Scheme 1 represents the various rate processes that can occur during excitation of **1** where I_a is the number

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of photons incident on the sample; k_{ic} = rate constant for internal conversion; k_{isc} = rate constant for intersystem crossing to the triplet state; k'_{isc} = rate constant for intersystem crossing in the presence of the HAS; k_d = rate constant for intersystem crossing to the ground state; k''_{isc} = rate constant for intersystem crossing to the ground state in the presence of the HAS; k_F = rate constant for fluorescence emission; k_r = singlet dimerization rate constant; K_r = triplet dimerization rate constant; k_q = rate constant for triplet quenching by quencher (Q).

The fluorescence quantum yield of **1** ($\Phi_F = 3.5 \times 10^{-3}$ at 540 nm)[6] (step 5) represents a trivial loss from the excited-state population of **1**. The oxygen quenching results (step 8) indicate that **1** dimerizes from its excited singlet state (step 6) preferentially to form cis dimers. The exclusive formation of the cis dimers in aerated solvents suggests that an excimer state may intervene, similar to the behavior found for the dimerization of **4**.[27]

In degassed solutions, both cis and trans dimers are formed readily, which suggests that intersystem crossing (step 3) occurs with some efficiency and that the triplet state dimerizes to form both cis and trans dimers. It is notable that the cis/trans ratio in degassed cyclohexane varies only slightly from that obtained in HAS. This is quite different from the photochemical behavior exhibited by **4** wherein the HAE enhances significantly the formation of trans product.[21] While the product ratio for **1** remains relatively invariant in degassed light and heavy atom solvents, the quantum yield increases dramatically relative to degassed cyclohexane. This is characteristic of the HAE in which spin–orbital coupling between solvent and solute enhances the rate of intersystem crossing (step 3a) to increase the number of viable excited triplet states.[20] Their bimolecular reactions with ground state molecules typically produce an increase in trans isomers in similar systems but the behavior of ³**1** is atypical. The fact that the quantum yield increases without a disproportionate increase in trans dimers suggests that the fraction of triplet states that produce cis dimers remains unaffected by the HAE. The HAE enhances k'_{isc} but does not change the cis/trans dimer ratio. A solvent dielectric effect on the cis/trans ratio appears to be small and within experimental error.

Irradiation in parallel of separate solutions of **2** and **3** ($\lambda = 254$ nm), while monitoring the increase of **1** at 410 nm, clearly shows that the trans dimers cleave at twice the rate of the cis dimers over the same time period. Similar selective cleavage behavior was reported for the photodimers of **4**.[28] This result was rationalized by assuming that the cis dimers form a through-space charge-transfer state (excimer-like) that stabilizes the excited molecule, while the trans dimers rapidly cleave back to monomer through a biradicaloid intermediate.[29] Future studies will report on the crossed cycloadditions of **1** to a variety of substrates.

Experimental Section

General Methods. NMR spectra were obtained on either 300 or 400 MHz spectrometers using CDCl₃ calibrated against CHCl₃ at δ 7.24 for ¹H and 77.0 for ¹³C. DMSO-d_6 solutions were calibrated against DMSO at δ 39.5. Melting points were determined in a capillary apparatus and are uncorrected. IR spectra were obtained as either KBr pellets or as a CHCl₃ film on NaCl plates using an FT-IR spectrometer. Mass spectrometry was performed by the Laboratory for Biological Mass Spectrometry, Texas A & M University. Irradiations were conducted using argon degassed or aerated solutions in a commercial photochemical reactor that emits a Gaussian distribution of light from 365 to 435 nm centered around 419 nm. All solvents used were analytical grade (Aldrich). Compound **1** was prepared using modifications of the literature procedure.[30] Purified **1** was subjected to vacuum sublimation and then recrystallized from methanol to give yellow plates, mp 140–141 °C (lit.[31] mp 140–142 °C). Pure **4** was obtained by photolysis of its dimers at 300 nm followed by flash chromatography (hexane) and then recrystallization (ethanol) to afford yellow plates, mp 92–93 °C (lit.[32] mp 92–93 °C).

Preparation of 2hh and 2ht. A solution of **1** (20 mg, 0.1 mmol) in cyclohexane (12 mL) was aerated by bubbling a stream of air through the yellow solution for 0.5 h. After irradiation at 410 nm for 21 h, the solution was evaporated under vacuum to give a brown residue (23 mg). This was treated by two successive flash chromatography purifications (5:95 EtOAc/hexane) to give cis photodimer **2hh** and **2ht** as a white solid (13 mg, 64%): mp 204–206 °C; UV λ_{max} (ϵ) (CHCl₃) 355.5 (1900), 338.5 (1400), 309.5 (16 600), 297.0 (14 700), 252.5 (73 400); IR (KBr) v_{max} 3046, 2945, 1626, 1601, 1448, 1460, 1485, 770, 748 cm⁻¹; ¹H NMR (CDCl₃) δ 8.12 (dd, 2H, J = 1.8, 7.0 Hz), 7.81 (d, 2H, J = 8.1 Hz), 7.59 (dd, 2H, J = 2.1, 3 Hz), 7.23 (m, 10H), 4.81 (m, 4H, bridgehead protons); ¹³C NMR (CDCl₃) δ 144.2, 144.0, 143.0, 142.8, 140.3, 133.7, 128.4, 128.3, 128.2, 128.0, 127.3, 126.0, 125.0, 124.9, 122.6, 122.5, 122.3, 122.1, 120.7, 120.3, 118.9, 47.5, 47.4, 46.4, 46.2; HRMS (+EI, M⁺) calcd 404.1566, found 404.1556.

Preparation of 3hh and 3ht. A solution of **1** (20 mg, 0.1 mmol) in cyclohexane (12 mL) in a Pyrex irradiation tube was degassed by purging with argon for 0.5 h and irradiated at 419 nm for 21 h. The white solid (6 mg) that crystallized from the resulting colorless solution was isolated by suction filtration. The irradiation tube was washed several times with hot cyclohexane and combined with the mother liquor and concentrated. Upon cooling, a second crop (2 mg) was isolated. The mother liquor was evaporated to give a brown residue that was submitted to flash chromatography eluting with 5:95 EtOAc/hexane to give a further crop (1 mg). Total yield **3hh** and **3ht** (9 mg, 45%): mp 340 °C dec; UV λ_{max} (ϵ) (CHCl₃) 355.0 (2100), 337.5 (1900), 314.0 (24 000), 301.0 (19 000), 261.0 (67 000); IR (KBr) v_{max} 2959, 2928, 1627, 1598, 1463, 1448, 1409, 804, 747 cm⁻¹; ¹H NMR (CDCl₃) δ 8.67 (dd, 4H, J = 1.8, 8.1 Hz), 8.46 (d, 4H, J = 8.1 Hz), 7.98 (m, 4H), 7.71 (m, 20H), 4.10 (m, 8H, bridgehead protons); ¹³C NMR (CDCl₃) δ 146.9, 145.5, 137.6, 136.0, 134.1, 133.0, 129.7, 129.1, 128.8, 128.7, 128.3, 127.0, 126.0, 123.2, 123.0, 122.0, 121.9, 120.1, 119.6, 119.4, 52.3, 51.7, 51.3, 50.8; HRMS (+EI, M⁺) calcd 404.1566, found 404.1558.

Supporting Information Available: Proton NMR spectra of pure diastereomers **2** and **3**, experimental procedure for determination of quantum yields, and absorbance time data for cleavage of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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