Photodimerization of acenaphthylene within a nanocapsule: excited state lifetime dependent dimer selectivity†

Lakshmi S. Kaanumalle and V. Ramamurthy*

Received (in Cambridge, UK) 2nd November 2006, Accepted 23rd November 2006
First published as an Advance Article on the web 14th December 2006
DOI: 10.1039/b615937k

Direct excitation of acenaphthylene molecules included in a *syn* fashion within the octa acid nanocapsule dimerizes quantitatively to a *syn* dimer, and upon triplet sensitization, yields both *syn* and *anti* dimers probably by reacting within and outside the capsule.

Recently we established that the water-soluble octa acid (OA), an extended cavitand with dimensions of 10 × 10 Å, can include two aromatic molecules such as naphthalene and anthracene in the configuration shown in Fig. 1.[1] Contrary to their behavior in organic solvents such included aromatics show strong excimer emission rather than photodimerization. For example, anthracene dimerizing with high quantum yield and lacking excimer emission in organic solvents upon inclusion within the capsule of OA shows the reverse behavior. We attributed the lack of dimerization to the dimer of anthracene being too large to fit within the capsule. This observation suggested the possibility of selective photoreaction within the capsule. With this in mind we have explored the photodimerization of acenaphthylene, that yields two dimers, *syn* and *anti* of different dimensions (Scheme 1).[2,3] Based on the dimensions it is evident that only the 7.2 × 6.6 Å *syn* dimer would fit within the capsule while the 6.8 × 11.8 Å *anti* dimer would be too large. In this report we present results of our studies on the direct and triplet sensitized photodimerization of OA encapsulated acenaphthylene in water. Results indicate product control to be a function of the dynamics of the capsule. They suggest the possibility of superb product control in the nanosecond time scale when the capsule is static, while the control decreases with a more dynamic capsule at the longer microsecond timescale.

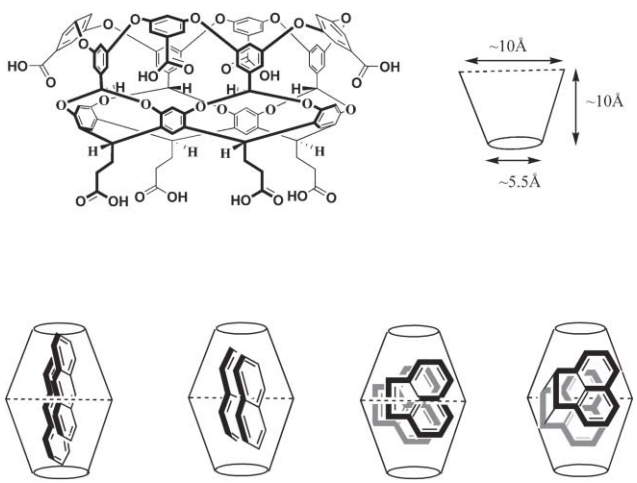
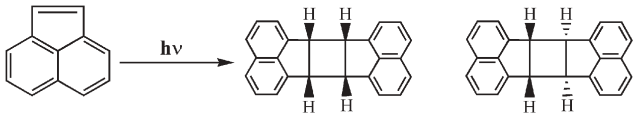


Fig. 1 Top: Structure of octa acid and its dimensions. Bottom: Structures of aromatics within the capsule of octa acid.



Medium	% *Syn* dimer	% *Anti* dimer
Water-direct excitation	40	60
Water-Eosin Y sensitized	51	49
Octa acid-direct excitation	>99	--
Octa acid-Eosin Y sensitized	60	40

Scheme 1 Photodimerization of acenapthylene and the ratio of the dimers in various media.

^{1}H NMR titration studies of acenaphthylene and octa acid in water (borate buffer, pH ~ 9) suggested that they form a 2 : 2 complex similar to those of naphthalene and anthracene. Results of diffusion studies using a PGSE pulse program were also consistent with this conclusion. The signals due to included acenaphthylene were identified by comparing the spectra of perdeuterated acenaphthylene @OA and acenaphthylene@OA (Fig. 2). A comparison of the ^{1}H NMR spectra of acenaphthylene@OA and naphthalene@OA suggested that the two molecules may be oriented in a similar fashion within the capsule (Fig. 2; for details on assignment of signals see ESI†). For example, signals H_2 of naphthalene and acenaphthylene are most upfield shifted within OA suggesting these parts of the molecules to be at the narrow rim of the capsule. The H_1 and H_4 signals of acenaphthylene are relatively less upfield shifted (see ESI†) suggesting them to be located in the mid region of the capsule. The above results and the fact that the signals due to the host OA have similar shifts in acenaphthylene@OA and naphthalene@OA suggest that both naphthalene and acenaphthylene have similar orientation within the capsule (Fig. 1), an orientation that would be expected to yield only the *syn* dimer.

Extensive studies on the photochemistry of acenaphthylene in solution have established that the excited singlet state yields the *syn*

Department of Chemistry, University of Miami, Coral Gables, FL, 33146. E-mail: murthy1@miami.edu; Fax: +1 305 284 4571; Tel: +1 305 284 1534

† Electronic supplementary information (ESI) available: Experimental details, general protocol for binding studies and NMR characterization, inclusion and photolysis, extraction and analysis of photoproducts. See DOI: 10.1039/b615937k

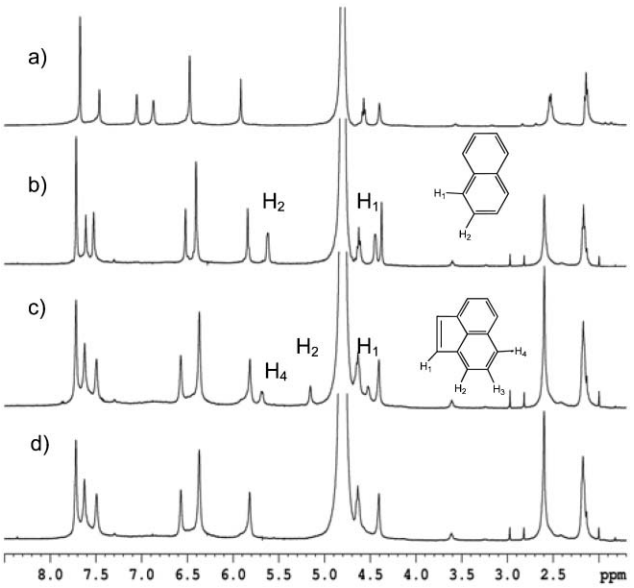
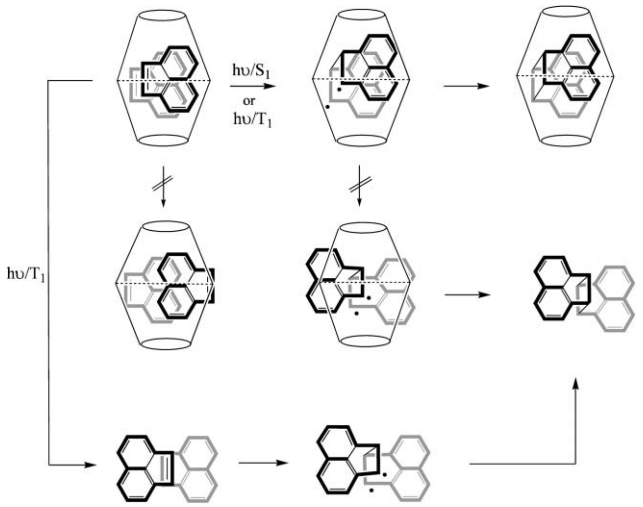


Fig. 2 ^{1}H NMR spectra of (a) octa acid in D_2O (pH = 9); (b) 2 : 2 complex of naphthalene in octa acid; (c) 2 : 2 complex of acenaphthylene in octa acid; (d) 2 : 2 complex of perdeuterated acenaphthylene in octa acid. In all cases the solvent is D_2O with 10 mM borate buffer; [octa acid] = 10^{-3} M; [naphthalene] = 10^{-3} M; [acenaphthylene] = 10^{-3} M. In all spectra, only encapsulated guest protons are labeled, the remainder correspond to host protons.



Scheme 2 A mechanistic scheme for the formation of *syn* and *anti* dimers.

dimer while the triplet state yields both *syn* and *anti* dimers with the latter being the major product. It is well known that in organic solvents the ratio of *syn* to *anti* dimers, apart from the concentration of acenaphthylene, depends on the solvent or the presence of a triplet quencher.[2] In benzene, upon direct excitation, even at concentrations as high as 0.2 M the *anti* dimer was obtained to an extent of ~25%. Direct excitation of a suspension of acenaphthylene in water (due to its insolubility in water) gave two dimers, *syn* and *anti* in the ratio 2 : 3 (Scheme 1). In contrast, after 3 h irradiation of acenaphthylene@OA (10^{-3} M), quantitative conversion to the *syn* dimer was achieved. No dimerization occurred in this time period in benzene solution at the same concentration. The exclusive formation of the *syn* dimer from acenaphthylene@OA (2 : 2 complex) suggests that in the excited singlet state the acenaphthylene pair (arranged as shown in Fig. 1) is quantitatively transformed to the product. ^{1}H NMR spectral analysis of the irradiated sample revealed that the *syn* dimer remained within the OA capsule (for comparison of the ^{1}H NMR spectra of irradiated sample and the *syn* dimer@OA see Fig. S1 in ESI†).

Results presented above established that on the time scale of the S_1 state (0.35 ns)[4] the acenaphthylene molecules pre-arranged in a *syn* fashion do not rearrange to produce the *anti* dimer. Knowledge that the T_1 state of acenaphthylene, with a longer (6 ms)[5] lifetime, yields the *anti* dimer in solution prompted us to examine its photobehavior within the OA capsule. For these experiments water-soluble eosin-Y was used as the triplet sensitizer (E_T = 46.8 kcal mol^{-1}). When an aqueous solution of acenaphthylene@OA and eosin-Y was irradiated (>500 nm), *syn* and *anti* dimers were formed in the ratio 60 : 40. Several observations are noteworthy: (a) even in the absence of direct contact, eosin-Y in solution sensitized the acenaphthylene molecules trapped within the capsule. (b) Although the *syn* dimer remained the major product during triplet sensitization the *anti* dimer is also formed. (c) Unlike the *syn* dimer that was retained within the capsule the *anti* dimer was deposited on the sides of the irradiation tube and could only be identified by GC and NMR (following extraction with chloroform).

Formation of the *anti* dimer from the two acenaphthylene molecules pre-arranged in a *syn* fashion raises interesting questions on the mechanism of its formation. The mechanistic model we visualize illustrated in Scheme 2 assumes a dynamic OA capsule that expands (opens and closes) on the ms time scale. An important point to note is the *anti* dimer, *via* a diradical intermediate (Scheme 2), from the two acenaphthylene molecules prearranged in a *syn* fashion, can only be formed after their reorientation preceding bond formation. Such reorientation is unlikely within the OA capsule. We believe that the longer lifetime (ms) allows the triplet acenaphthylene to escape the capsule as an excimer that reorients and forms the preferred *anti* dimer *via* the diradical B. Admittedly, we currently can not substantiate the proposed model based on the dynamics of the capsule. This interesting observation, that needs further scrutiny, is underway. Clearly, the dynamic nature of most nanocavities need to be taken into account when using them as reactions cavities and especially when long lifetime reactive states and intermediaries are involved.

Previously acenaphthylene photodimerization has been conducted in a number of confined and ordered media such as liquid crystals, micelles, dendrimers, polymers, silica surface, clay, zeolites and Pd-nanocages.[6–22] Selectivity obtained in most media (except the Pd-nanocage) is lower than that observed within the octa acid capsule. Selectivity and enhanced reactivity during direct excitation is attributable to the ability of the nanocapsule to localize, preorient and restrict the mobility of the reactant olefins in the short excited singlet state lifetime. The larger cavity of the Pd-nanocage allows guest reorientation even in the solid state[20] while such a reorientation in the tightly held OA nanocapsule has to occur outside the cage. The fact that OA allows photoreactions to be conducted in water is an added bonus of which we will continue to take advantage.

We thank the National Science Foundation, USA for financial support (CHE-0213042) and B. Gibb and C. Gibb for very useful discussions and interest in the use of OA as a reaction cavity.

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