

A Novel Antenna Cyclodextrin: Synthesis and Photosensitized Reaction of an Included Guest

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Abstract: A novel water-soluble photochemical microreactor has been prepared. A perbutylated cyclodextrin bearing seven naphthalenesulfonate antenna chromophores (Bu-CD-N₇) displays improved solubilization of hydrophobic guests in comparison with the unbutylated material (CD-N₇). The photophysical properties of Bu-CD-N₇ are similar to those of the CD-N₇. The naphthyl chromophores of Bu-CD-N₇ were used to sensitize the photolysis of 9-anthrylmethyl pivalate (AP). Inclusion of AP in the cyclodextrin leads to the selective formation of one of the two possible coupling products.

Introduction

In this laboratory there has been an ongoing interest in the antenna effect.^{1–3} This has led to the development of a number of water-soluble antenna polymers which have been shown to act as photocatalysts.^{4–9} With the desire to improve the substrate selectivity of the photocatalysts, two antenna systems which include a group capable of forming host–guest complexes have been developed. In one of these systems, calix[4]arene groups were incorporated into a water-soluble polymer.¹⁰ Naphthalenesulfonate groups acted as the antenna chromophores as well as imparting water solubility.

The second approach, of which this paper is an extension, employs a β -cyclodextrin as the host group. In a previous paper, the synthesis and photophysical properties of a derivatized β -cyclodextrin displaying the antenna effect were presented.¹¹ Cyclodextrin was chosen because of its ability to (1) form inclusion complexes with a variety of guest molecules¹² and (2) influence the outcome of photochemical reactions.¹³ Several other photoactive cyclodextrins^{14–17} were known but none that utilized the antenna effect to enhance photoreactions of included

guests.¹⁸ The antenna cyclodextrin bearing naphthalenesulfonate groups on C6 of each of the seven sugar units possessed several important features: (1) water solubility, (2) absorption in the UV spectral region, (3) energy migration between the antenna naphthyl groups, (4) binding of hydrophobic guests, and (5) energy donation to molecules included in the cyclodextrin cavity. Energy transfer is efficient because excimer formation between antenna chromophores, an energy wasting process, is disfavored by the mutual repulsion of the naphthalenesulfonate groups.

Subsequently, a very similar antenna system in which β -cyclodextrin is labeled with seven naphthalenecarboxylate groups was developed.^{18,19} This system was found to form quite stable 1:1 complexes ($K = 1.2 \times 10^5 \text{ M}^{-1}$ in 5% ethanol) with 4-(dicyanomethylene)-2-methyl-6-(4-(bis(hydroxyethyl)amino)-styryl)-4H-pyran), a derivative of DCM, a merocyanine laser dye. The strong complexation was thought to be due to a good match between the size of the guest and the dimensions of the cavity. Highly efficient energy transfer (efficiency = 1) from the naphthoate groups to the guest was observed.

In order to use the antenna cyclodextrins as photochemical microreactors, high association constants are required. Unfortunately, the association constants for many cyclodextrin–guest complexes are fairly low (typically $K \leq 10^3 \text{ M}^{-1}$).^{12,20} If high concentrations of cyclodextrin are used to ensure that all guest molecules are complexed, most of the light will be absorbed by unoccupied cyclodextrins and the photochemical efficiency will be low. On the other hand, if a high guest concentration is used to ensure that all cyclodextrin molecules are occupied, photochemical reactions of free guest molecules may dominate. For this reason it is desirable to improve the binding of hydrophobic guests by increasing the hydrophobicity of the

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cyclodextrin. This paper describes the synthesis and properties of a butylated cyclodextrin which bears seven naphthalene-sulfonate groups as antenna chromophores. This system displays improved binding of a hydrophobic guest and sensitizes the selective photochemical reaction of the included guest.

Experimental Details

General. ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 200 MHz spectrometer. IR spectra were recorded on a Nicolet 8210E FT-IR. UV-vis absorption spectra were measured with a Hewlett-Packard 8451A diode-array spectrophotometer. Steady state fluorescence spectra (uncorrected) were measured at room temperature with an SLM 4800S spectrofluorometer. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, Canada). GC-MS analyses were performed with a Hewlett-Packard 5890 GC and a VG Analytical 70-250S mass spectrometer. Electrospray ionization mass spectroscopy was performed at the Biological Mass Spectroscopy Laboratory at the University of Waterloo (Waterloo, Canada).

Materials. The preparation of 6^A,6^B,6^C,6^D,6^E,6^F,6^G-hepta(6-oxy-2-naphthalenesulfonate, sodium salt)- β -cyclodextrin (CD-N₇) has been described.¹¹ 9-Anthrylmethyl pivalate (AP)²¹ and sodium 6-methoxy-2-naphthalenesulfonate (MNSS)¹¹ were prepared as described earlier. 2,2-Di(4-*tert*-octylphenyl)-1-picrylhydrazyl (DPPH; Aldrich) and methylene blue (MB; Aldrich) were used as received. Methanol (Caledon; Spectro Grade) and benzene (Caledon; Spectro Grade) were used without further purification. Deionized water from a Millipore Milli Q water purification system was used to prepare aqueous solutions.

2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G-Tetradecabutyl-6^A,6^B,6^C,6^D,6^E,6^F,6^G-hepta(6-oxy-2-naphthalenesulfonate, sodium salt)- β -cyclodextrin (Bu-CD-N₇). Butylation was performed by a method similar to that used by Brimacombe *et al.*²² A solution of CD-N₇ (3.0 g, 1.1 mmol) in dry dimethylsulfoxide (100 mL) was transferred into a 200 mL flask containing NaH (1.32 g, 55.1 mmol) under a nitrogen atmosphere. The resulting suspension was stirred under nitrogen for 20 min and then cooled in an ice bath before 1-bromobutane (11.5 mL, 107.0 mmol) was added dropwise over 5 min. After 40 min, the nitrogen inlet and cooling bath were removed, and the yellowish, nearly solid suspension was left at room temperature for 40 h. Methanol (12 mL) was added carefully to the suspension with stirring. When effervescence had ceased, the precipitate was filtered. The solvent was removed under vacuum, and the resulting solid was reprecipitated twice from water into methanol and once from water into ethanol. Vacuum drying at 90 °C provided a white powder (1.8 g, 47%).

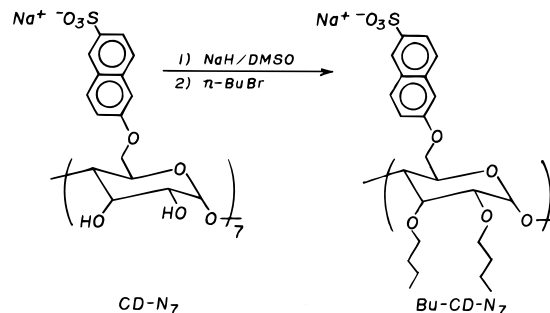
The NMR peaks (both ^{13}C and ^1H) were broad and overlapped. ^{13}C NMR (D₂O, δ): 158.0, 138.5, 135.7, 131.3, 128.2, 126.0, 123.6, 118.6, 107.6, 102.4, 80.8, 73.4, 71.7, 68.6, 32.8, 20.2, 14.6. ^1H NMR (D₂O, δ): 7.9, 7.2, 6.5, 4.8, 3.5, 1.4, 1.0. IR (cm⁻¹): 3444, 2958, 2934, 2873, 1631, 1460, 1265, 1216, 1188, 1129, 1101, 1040. Anal. Calcd for C₁₆₈H₂₁₇O₅₆S₇Na₇: C, 57.36; H, 6.22; S, 6.38 (calcd for C₁₆₈H₂₁₇O₅₆S₇Na₇ + 10 H₂O: C 54.57; H, 6.46; S, 6.07). Found: C, 54.45; H, 6.2; S, 5.76.

Electrospray mass spectra were measured for both the starting material (CD-N₇) and the product (Bu-CD-N₇). Samples were dissolved in 1% CH₃CN or 1% NH₄OH prior to introduction to the mass spectrometer. For CD-N₇ (1% NH₄OH): 2665, 2644, 2622, 2600, 2578, 2476, 2454, 2416, 2398, 2394, 2376, 2354. For Bu-CD-N₇ (1% NH₄OH): 3385, 3363, 3307, 3251, 3195, 3139, 3083.

Solubility of Anthrylmethyl Pivalate in Aqueous Solutions. Aqueous solutions were saturated with AP by making four injections (2.5–12.5 μL each) of an AP solution (0.0513 M in ethanol) into 5.0 mL of water or aqueous cyclodextrin solution. The solutions were vigorously shaken after each addition of AP and then left to stand for 3 days in the dark. The solutions were passed through a syringe filter (Whatman GF/F glass microfiber filter) to remove any fine particles of undissolved AP. The aqueous AP solutions were analyzed by UV-vis and fluorescence spectroscopies.

Photolysis. AP solutions were irradiated in quartz tubes with a Rayonet RPR-100 photochemical reactor equipped with 16 300 nm

Scheme 1



lamps (RPR-3000). Quantitative and qualitative analyses of photolyzed solutions were conducted with a Hewlett-Packard 5890 gas chromatograph equipped with an FID and a J&W Scientific DB-1 capillary column (30 m \times 0.25 mm (i.d.) \times 0.25 μm (film thickness)). The photoproducts were identified by GC-MS and/or NMR analysis. Prior to NMR analysis the photoproducts were separated from the reactant by preparative TLC (silica, heptane/benzene (1:1)). The photoproducts consisted of 9-methylanthracene (mass spectrum (EI): 192 (M⁺). ^1H NMR (CDCl₃, δ): 3.11 (s, 3H, CH₃), 7.2–8.4 (m, ArH)), 9-neopentylanthracene (mass spectrum (EI): 248 (M⁺). ^1H NMR (CDCl₃, δ): 0.98 (s, 9H, *t*-Bu), 3.68 (s, 2H, CH₂), 7.2–8.4 (m, ArH)), and 9-*t*-butyl-10-methylanthracene (mass spectrum (EI): 248 (M⁺). ^1H NMR (CDCl₃, δ): 1.54 (s, 9H, *t*-Bu), 3.38 (s, 3H, CH₃), 7.2–8.4 (m, ArH)).

Results and Discussion

Characterization of Bu-CD-N₇. Bu-CD-N₇ was prepared by the butylation of CD-N₇ (Scheme 1). The FT-IR spectrum contains absorptions for CH₃ stretching and bending vibrations (2958, 2871, and 1463 cm⁻¹) and CH₂ stretching vibrations (2933 cm⁻¹) which reveals the presence of butyl groups in Bu-CD-N₇. Similarly, ^{13}C NMR signals at 14.6, 20.2, and 32.8 ppm and ^1H NMR signals at 1.0 and 1.4 ppm can be attributed to the butyl groups. The NMR signals were broad, and it was not possible to accurately quantify the degree of butylation of the cyclodextrin. We believe that this is due to the presence of a mixture of butylated isomers/homologues (*vide infra*) and slow tumbling of the large molecule in D₂O. The elemental analysis revealed lower than expected carbon and sulfur levels; however, it is common for both cyclodextrins and sulfonate salts to include water in their crystalline forms. It appears that the cyclodextrin contains about 10 waters of crystallization.

Electrospray ionization mass spectroscopy (ES-MS) is a "gentle" mass spectral technique applicable to high molecular weight molecules.²³ It has been used to characterize cyclodextrin compounds^{24–26} and inclusion complexes,^{23,27–33} although there is some doubt that it is inclusion complexes that are

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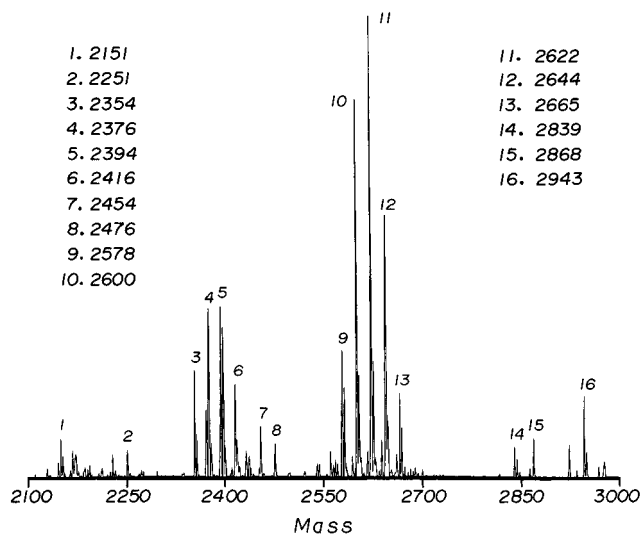


Figure 1. Electrospray mass spectrum of CD-N₇ in 1% NH₄OH.

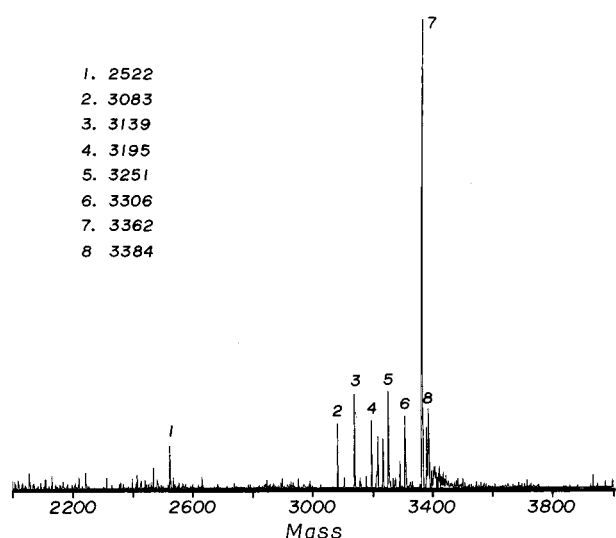
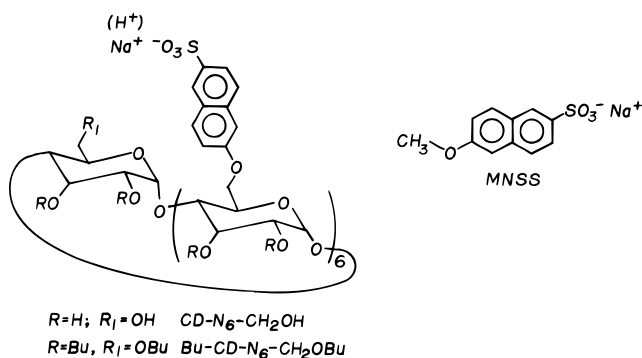


Figure 2. Electrospray mass spectrum of Bu-CD-N₇ in 1% NH₄OH.

Scheme 2



detected.³⁴ ES-MS was used to study CD-N₇ (Figure 1) and Bu-CD-N₇ (Figure 2). The spectrum of CD-N₇ consists of a set of peaks, centered at 2622 g/mol due to β -cyclodextrin bearing seven naphthalenesulfonates (CD-N₇), and a smaller set, centered at 2394 g/mol arising from β -cyclodextrin bearing six naphthalenesulfonates (see for example CD-N₆-CH₂OH, Scheme 2). Within each set, many of the peaks arise from cyclodextrins in which some of the sodium sulfonates have been converted to sulfonic acids during the electrospray experiment. For example, the peak at 2622 g/mol is for a β -cyclodextrin with

two naphthalenesulfonates in the sodium salt form and five in the acid form and that at 2578 g/mol is for the cyclodextrin bearing seven naphthalenesulfonic acid groups. It should be emphasized that the naphthalenesulfonic acid is formed by the vaporization and ionization processes during the ES-MS experiment with the cyclodextrin/1% NH₄OH solution and does not reflect the concentration of this species in aqueous solution. In aqueous solution, the naphthalenesulfonate groups of CD-N₇ exist as the sodium salt.

The portion of the mass spectrum due to cyclodextrin with six naphthalenesulfonates indicates that several species are present. It appears that C6 of the unsubstituted sugar unit may exist as a CH₃ (peaks at 2354, 2376, and 2398 g/mol), CH₂OH (2372, 2394, and 2416 g/mol), or CH₂Br (2454 and 2476 g/mol) group. Both the CH₃ and CH₂Br groups are remnants of earlier steps in the synthesis of CD-N₇.¹¹ In addition, the small peak at 2151 g/mol is consistent with β -cyclodextrin bearing five naphthalenesulfonates (acid form) with the two unlabeled C6 positions in the form of a CH₃ and CH₂OH. The peak at 2943 g/mol is consistent with a γ -cyclodextrin bearing eight naphthalenesulfonic acids, where the γ -cyclodextrin occurred as a minor impurity in the β -cyclodextrin starting material. The results for CD-N₇ illustrate the great utility of ES-MS for the characterization of cyclodextrin compounds.

The spectrum of Bu-CD-N₇ measured for a sample dissolved in 1% CH₃CN was rather complex, since the peaks due to cyclodextrins of differing degrees of butylation were further split by the conversion of some naphthalenesulfonates from the salt to the acid form during vaporization and ionization. In 1% NH₄OH, the conversion of the sodium sulfonates to sulfonic acid groups is more complete, and the spectrum (Figure 2) is considerably simplified. The peaks at 3363 and 3385 g/mol are from the fully butylated β -cyclodextrin bearing seven naphthyl groups, Bu-CD-N₇ (Scheme 1). The peaks at 3307, 3251, 3195, and 3139, and 3083 g/mol are for this cyclodextrin substituted with 13, 12, 11, 10, and 9 butyl groups, respectively. From the intensity of these peaks it can be estimated that, on average, 12.6 of the 14 possible OH groups have been butylated. Thus, butylation has been extensive but not complete, which is not surprising since alkylation of cyclodextrins are often incomplete.²⁶ The mass spectrum also contains several smaller peaks at about 3155, 3177, 3215, and 3234 g/mol, which are consistent with Bu-CD-N₆-CH₂OBU (Scheme II) bearing 14 and 15 butyl groups. Thus, with the aid of ES-MS it is possible to conclude that the antenna cyclodextrin denoted as Bu-CD-N₇ is composed of β -cyclodextrin bearing seven naphthalenesulfonates (as the sodium salt) on the primary rim and, on average, 12.6 butyl groups on the secondary rim.

Inclusion of AP. UV-vis and fluorescence spectroscopies revealed that 9-anthrylmethyl pivalate (AP) is sparingly soluble (9×10^{-7} M) in water containing 1% ethanol, but that the solubility increases considerably in an aqueous solution of Bu-CD-N₇. As displayed in Figure 3, the emission spectrum of AP solubilized in aqueous Bu-CD-N₇ is about 10 times more intense than that from water. In addition, the AP spectrum is broadened and shifted toward longer wavelengths in Bu-CD-N₇. The enhanced solubility and the changes in the fluorescence spectrum are presumably due to inclusion of AP into the hydrophobic Bu-CD-N₇. The association constant ($K = [AP \cdots Bu-CD-N_7]/([AP][Bu-CD-N_7])$) for AP in Bu-CD-N₇ in 1% ethanol/water was determined to be 7.8×10^4 ($\log K = 4.9$). This is at least 35 times higher than that observed for AP in CD-N₇ or β -cyclodextrin or for anthracene in β -cyclodextrin (Table 1).²⁰

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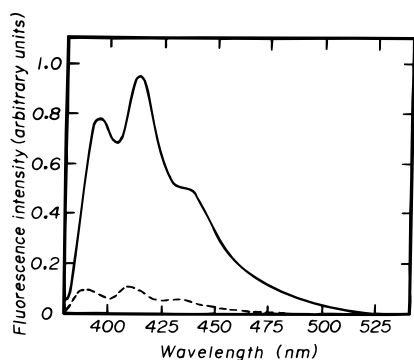


Figure 3. Steady state fluorescence spectra of saturated solutions of AP dissolved in (—) aqueous Bu-CD-N₇ (2.8×10^{-4} M) and (---) water ($\lambda_{\text{ex}} = 363$ nm).

Table 1. Association Constants (K) for Complexes of Cyclodextrin with Anthryl Compounds

cyclodextrin	compound	K (M ⁻¹)
Bu-CD-N ₇	AP ^a	78000
CD-N ₇	AP	2200
β -cyclodextrin	AP	80
β -cyclodextrin	anthracene	2060 ^b

^a AP = 9-anthrylmethyl pivalate. ^b Reference 20.

ES-MS has proven to be a useful technique for the detection of cyclodextrin-guest complexes,²⁷⁻³³ as well as other host-guest complexes.³⁵⁻³⁹ When an aqueous solution containing AP (2×10^{-5} M) and Bu-CD-N₇ (2.8×10^{-4} M) was analyzed by ES-MS, no evidence for a host-guest complex could be detected. This may indicate that the complex is not stable enough to survive introduction to the gas phase. While anthracene (molecular dimensions 9.2×5.0 Å) appears to fit into the cavity of β -cyclodextrin (diameter 6.0–6.4 Å), the addition of the methyl pivalate ester group to the 9-position of anthracene will certainly rule out complete inclusion of AP in the cyclodextrin cavity. Thus, AP may only be partially included in the cavity or it may be dissolved in the naphthyl or butyl groups of Bu-CD-N₇, and these complexes may dissociate upon introduction to the gas phase. A complex containing a more appropriately shaped guest may exhibit an even higher association constant and be detectable by ES-MS. However, the AP/Bu-CD-N₇ complex displays strong enough binding for efficient solubilization, energy transfer, and a selective photo-reaction (*vide infra*).

Photophysical Properties. The steady state fluorescence spectrum of Bu-CD-N₇ (Figure 4) is dominated by monomer emission ($\lambda_{\text{max}} \approx 355$ nm) from the naphthyl chromophores, and the fraction of excimer emission is nearly identical to that from CD-N₇ (Figure 4). In the presence of AP, the naphthyl emission ($\lambda_{\text{ex}} = 314$ nm) of Bu-CD-N₇ is efficiently quenched and intense AP emission is observed (Figure 5). Since essentially all of the light is absorbed by the naphthyl chromophores, the strong AP fluorescence demonstrates that energy transfer is occurring. The emission spectrum of CD-N₇ containing AP (Figure 5) displays a negligible amount of energy transfer which confirms that the host-guest complex is not formed in high concentrations for the unbutylated antenna cyclodextrin.

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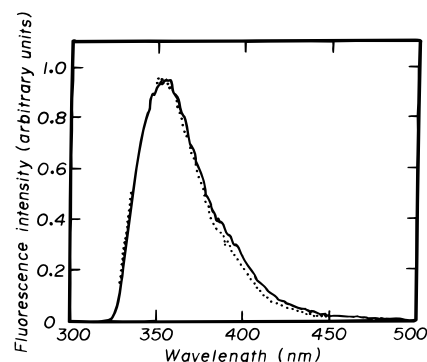


Figure 4. Steady state fluorescence spectra of aqueous solutions of (—) Bu-CD-N₇ (1×10^{-5} M) and (···) CD-N₇ (1×10^{-5} M) ($\lambda_{\text{ex}} = 280$ nm).

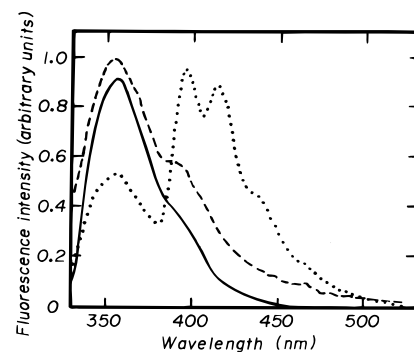


Figure 5. Steady state fluorescence spectra of (—) Bu-CD-N₇ (2.8×10^{-4} M) and saturated solutions of AP in (···) Bu-CD-N₇ (2.8×10^{-4} M) ([AP] $\approx 1.8 \times 10^{-5}$ M) and (---) CD-N₇ (3.5×10^{-4} M) ([AP] $\approx 1 \times 10^{-6}$ M) ($\lambda_{\text{ex}} = 314$ nm, front-face cell).

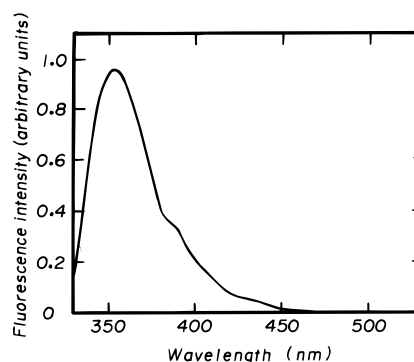


Figure 6. Steady state fluorescence spectrum of 60% methanol solution containing MNSS (2×10^{-3} M) and AP (2.05×10^{-5} M) ($\lambda_{\text{ex}} = 314$ nm, front-face cell).

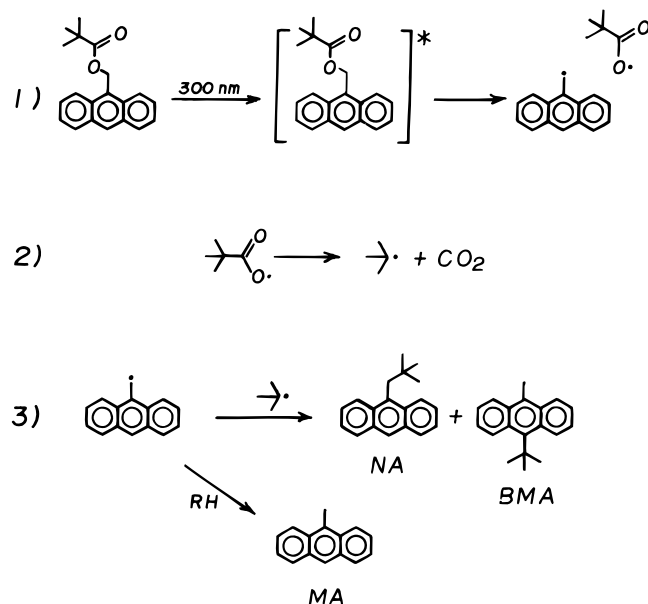
The emission spectrum (Figure 6, $\lambda_{\text{ex}} = 314$ nm) of a 60% methanol solution containing AP and sodium 6-methoxy-2-naphthalenesulfonate (MNSS), a model chromophore for the naphthalenesulfonate groups in Bu-CD-N₇, displays nearly indiscernible AP emission on the tail of the strong naphthyl emission of MNSS. The AP (2.05×10^{-5} M) and MNSS (2×10^{-3} M) concentrations were selected to match those in the AP/Bu-CD-N₇ system. The inefficient energy transfer for AP/MNSS demonstrates that the energy transfer observed for the AP/Bu-CD-N₇ system was not simply the result of energy transfer between two independent species in solution (i.e., collisional quenching).

Photosensitized Reaction of AP Included in the Bu-CD-N₇ Cavity. Upon direct excitation in deoxygenated methanol or benzene, AP produced a mixture of three primary products as determined by GC-MS. One of the products was identified as 9-methylanthracene (MA) with $M^+ = 192$ g/mol. The two

Table 2. Ratio of Products Formed during Irradiation of 9-Anthrylmethyl Pivalate (AP) in Isotropic Media and in Aqueous Solutions of Bu-CD-N₇^{a,b}

system	10 ⁵ [AP] ₀ (M)	product ratio		
		MA	BMA	NA
AP/benzene	1	1	1.9	2.1
AP/MeOH	1	1	1.5	2.7
AP/MNSS/MeOH	1	1	1.4	2.1
AP/MNSS/DPPH/MeOH	1	1	0.3	0.4
AP/Bu-CD-N ₇ /water	1.4	1	0	3.4
AP/Bu-CD-N ₇ /water	5.2	1	0.3	2.6

^a λ_{irr} = 300 nm; irradiation time = 30 min. ^b AP = 9-anthrylmethyl pivalate; MA = 9-methylanthracene; BMA = 9-*tert*-butyl-10-methylanthracene; NA = 9-neopentylanthracene; MNSS = 6-methoxy-2-naphthalenesulfonate, sodium salt; DPPH = 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl.

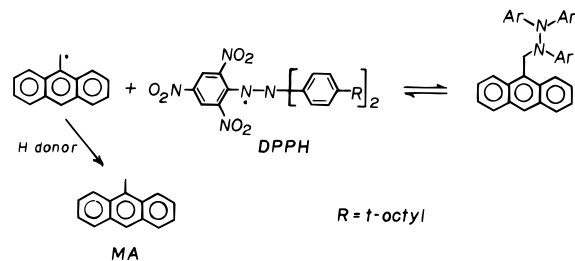
Scheme 3

other products (both with M⁺ = 248 g/mol) were tentatively identified as 9-neopentylanthracene (NA) and 9-*tert*-butyl-10-methylanthracene (BMA). A ¹H NMR spectrum of a mixture of the three photoproducts was consistent with the assigned structures.

When AP was irradiated in methanol, a fourth photoproduct was formed in trace amounts (*ca.* 2%). This product was identified as 9-anthrylmethyl methyl ether (AnCH₂OCH₃) on the basis of GC-MS analysis (222 (M⁺), 191 (M⁺ - OCH₃)). Presumably, heterolytic photolysis producing AnCH₂⁺ is a minor photochemical pathway for AP in methanol.

The product distribution (Table 2) is not particularly dependent on the polarity of the solvent. The triplet state quencher, methylene blue, does not effect the rate of the photoreaction, indicating that reaction occurs from the singlet state of AP. Photolysis sensitized by the model chromophore (MNSS) leads to the same product mixture. The photoreaction of AP can be described by the reaction scheme given in Scheme 3.

In the presence of the free radical scavenger DPPH, the main product of photolysis was MA (Table 2). Following photolytic cleavage, *t*-Bu radicals which escape the solvent cage may be rapidly scavenged by DPPH rather than recombining with the anthrylmethyl radical. Scavenging of the anthrylmethyl radical (AnCH₂^{*}) by DPPH may be much less efficient for both

Scheme 4

thermodynamic and steric factors. It has been shown that the reaction between radical traps (e.g., nitroxides) and carbon-centered resonance-stabilized radicals is reversible even at ambient temperature.⁴⁰ Since the 9-anthrylmethyl radical is among the most stable of all resonance-stabilized radicals,⁴¹⁻⁴³ the AnCH₂^{*}/DPPH adduct may be fairly labile (Scheme 4). Steric interactions between the anthryl group and the three phenyl rings of DPPH may further destabilize the adduct.

When Bu-CD-N₇ (1 × 10⁻³ M) is used to solubilize and sensitize the photolysis of AP ([AP]_{total} = 1 × 10⁻⁵ M), only two major photoproducts are formed: MA and NA. We propose that the NA is formed by the "cage" recombination of the *tert*-butyl radical with the anthrylmethyl radical while it is still in the cyclodextrin cavity. MA is produced by hydrogen abstraction by the anthrylmethyl radical in the event that the *tert*-butyl radical escapes from the immediate vicinity of the cyclodextrin complex. The absence of BMA from the reaction products indicates that the 10-position of AP is protected upon inclusion in Bu-CD-N₇. This is in agreement with the earlier observation that cyclodextrins influence the regiochemistry of the coupling of arylmethyl radicals with other radicals (i.e., the photo-Fries reaction).¹³

Conclusions

A β-cyclodextrin bearing seven naphthalenesulfonate antenna chromophores was made more hydrophobic by butylation of the 2- and 3-OH groups on each sugar unit. Electrospray ionization mass spectroscopy proved to be a powerful technique for the characterization of these cyclodextrin compounds and showed that the butylation was successful. The butylated cyclodextrin Bu-CD-N₇ solubilized AP much more effectively than either the unbutylated material, CD-N₇, or β-cyclodextrin. The naphthyl groups of Bu-CD-N₇ displayed principally monomer emission and efficiently transferred energy to solubilized AP. The naphthyl antenna chromophores of Bu-CD-N₇ were shown to sensitize a selective photoreaction of AP included in the cyclodextrin cavity. Inclusion in Bu-CD-N₇ modifies the photoreactivity of AP, suppressing reaction of the *tert*-butyl radical with the 10-position of the anthryl ring. The preparation of an antenna cyclodextrin which better solubilizes hydrophobic molecules is an important development in the search for an effective photochemical microreactor.

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