# Nanotube Formation between Cyclodextrins and 1,6-Diphenyl-1,3,5-hexatriene

**G. Pistolis and Angelos Malliaris***

*N.R.C. "Demokritos", Athens 153 10, Greece*

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Adduct formation between α-, *β*-, *γ*-, and (permethyl)*γ*-cyclodextrins (CDs) on the one hand and 1,6-diphenyl-1,3,5-hexatriene (DPH) on the other was studied by fluorescence spectroscopy in a DMF/water mixed solvent. The four complexes, CD−DPH, were found to exhibit remarkable differences in their structures. Thus, while the α- and *β*-homologues form 1/1 complexes with DPH, *γ*-homologue forms nanotubes involving ca. 30 cyclodextrin units and an unknown number of DPH molecules. If, however, the hydrogens of all the OH groups in the *γ*-cyclodextrin are replaced by $CH_3$ groups, nanotubes do not form. Also, when the alkalinity of an aqueous solution, in which *γ*-CD and DPH have formed nanotubes, is increased above pH = 12, the nanotubes break down. Moreover, nanotube formation does not occur also when DPH is replaced by certain of its derivatives, very similar to it in structure and rodlike in shape.

## I. Introduction

The homologous cycloamylose series of cyclic oligomers which consist of six to nine α-1,4-linked D-glucopyranosyl residues constitute a class of very important chemical compounds. In particular the six-, seven-, and eight-membered homologues, commonly named α-, *β*-, and *γ*-cyclodextrins (α-CD, *β*-CD, *γ*-CD), are molecules that have been the focus of great efforts, both in pure and applied research.[1,2] Their inexpensive methods of preparation by enzymatic degradation of starch,[3] the low toxicity and biodegradability that characterize them, and their outstanding physicochemical properties have aroused considerable interest for these compounds.[2] Adduct formation with guest molecules in aqueous solutions is one of the most remarkable properties of cyclodextrins. In particular, inclusion compounds are easily formed provided the guest molecule can fit, at least partially, into the 5−8 Å cavity of the α-, *β*-, or *γ*-CD host molecule. Furthermore, depending on the relative sizes of guest and cyclodextrin molecules, more than one guest can be accommodated in the cavity,[4,5] whereas if the guest molecule is long enough, one or two cyclodextrins may be threaded along its length.[6] These structures are most often formed in solution, and therefore their characterization by high-resolution spectroscopic methods is feasible. Under appropriate conditions, supramolecular assemblies such as catenanes,[7] rotaxanes,[8] and polyrotaxanes,[9] nanotubular structures[10] or threaded cyclodextrins[11] that do not involve any covalent bonding between the CD and the other molecule, can be obtained. In the present work our original objective was to study adduct formation between α-, *β*-, *γ*-CD and 1,6-diphenyl-1,3,5-hexatriene (DPH) in pure water. In particular the *β*- and *γ*-CD were reported to form nanotubular structures a few hundred angstroms long, in the presence of DPH.[10] We found however that DPH does not form proper solutions in water; for this reason we have used as solvent the mixture DMF/$H_2O$ (25/75 by volume). To supplement our findings with respect to the nanotube formation of the *γ*-CD homologue, we have also made measurements with the permethylated *γ*-CD (PM*γ*-CD) in which all the hydrogens of the primary and secondary hydroxyl groups have been replaced by methyl groups.

## II. Experimental Section

α-CD, *β*-CD, *γ*-CD, and PM*γ*-CD were purchased from Cyclolab and DPH from Fluka. The two DPH derivatives DPH-$N(CH_3)_2$ and DPH-$NO_2$, in which the substituents $N(CH_3)_2$ and $NO_2$ are attached at the para position of one of the benzene rings of DPH replacing one hydrogen atom, were obtained from Lambda Fluoreszenztechnologie. All chemicals were used as received. Emission spectra and fluorescence anisotropies ($r = (I_p - I_v)/(I_p + 2I_v)$, where $I_p$ and $I_v$ stand for the fluorescence intensities with the polarizers mutually parallel and perpendicular respectively, were recorded on a Perkin-Elmer LS50-B fluorometer equipped with filter polarizers. For absorption spectra the Lambda-16 spectrophotometer of Perkin-Elmer was used. Fluorescence spectra were obtained by excitation at 356 nm where, as we have found from absorption measurements, the absorption coefficient $\epsilon_{356}$ of DPH does not change when the probe is free or complexed with the dextrins studied here. Excitation spectra were recorded by monitoring the emission at 440 nm. In samples with very weak emission, the uncertainty in the numerical values of the anisotropy, *r*, was as high as 0.01 units; in all other samples the errors were considerably lower.

With respect to this work DPH and its derivatives present two very serious experimental problems. The first is the well-known photoisomerization that all polyene molecules undergo when exposed to light.[12] To cope with this difficulty, all the solutions were kept in the dark during preparation and storage. The second problem arises from the fact that DPH does not form proper solutions in water. Instead, small aggregates are formed, as evidenced by the very strong scattering observed in the absorption spectra of aqueous "solutions" of DPH (see Figure 1). However, on top of the scattering background of the spectrum, some very small absorption is discernible, indicating that a very slight amount of DPH, ca. $10^{-9}$ M, is properly, i.e. molecularly, dispersed in water.

To avoid the problem of the solubility of DPH in pure water, we have used as solvent a mixture of DMF/$H_2O$, 25/75 by volume, in which DPH was found to form proper solutions. Figure 1 shows the absorption spectra of DPH in pure water and in the 25/75 DMF/water mixed solvent obtained with a 10 cm cell. The spectrum of DPH in the mixed solvent does not show any evidence of scattering, as we have confirmed by the validity of Beer's law, but the absorption is still very low,

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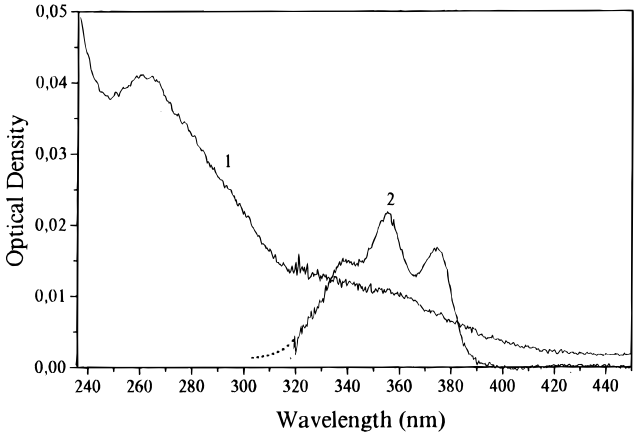


**Figure 1.** Absorption spectra of DPH in water (1) and water/DMF 75/25 (v/v) (2), in a 10 cm cell. DMF absorbs strongly below ca. 320 nm.

corresponding to solubility less than $6 \times 10^{-8}$ M. For this reason the concentration of DPH was kept low, at $4 \times 10^{-8}$ M, in order to combine good solubility with a reasonable fluorescence signal. The CD−DPH complexes in DMF/$H_2O$ were prepared by evaporating in a flask the calculated volume of a solution of DPH in hexane, then adding the required volume of the particular cyclodextrin dissolved in DMF/$H_2O$ mixture, and stirring. The process was facilitated by sonication. In the concentrations employed here, viz., [DPH] = $4 \times 10^{-8}$ M and [CD] = $10^{-4}$−$10^{-2}$ M, all the solutions were optically clear. Finally it is worth mentioning here that the fluorescence and excitation spectra of the CD−DPH complexes were identical in both solvents, viz., in the pure water and in the mixture DMF/water.

## III Results and Discusssion

In a recent publication[10] qualitative evidence was presented indicating that when DPH is added to aqueous solutions of $\beta$-CD and $\gamma$-CD, nanotubes are formed containing as many as 20 and 30 CD units, respectively. According to the same report, this interesting effect was not observed when DPH was added to aqueous solutions of the smaller homologue, α-CD. In our attempt to study the quantitative aspects of this effect we found that DPH does not form proper molecular solutions in pure water. As we mentioned in the previous section, apart from a slight amount of molecularly dissolved DPH, microaggregates of DPH are formed when this compound is dispersed in water. Nevertheless, we have confirmed the formation of nanotubes in pure water from the $\beta$-CD and $\gamma$-CD but not from the α-CD, exactly as reported,[10] despite the fact that these systems, viz. CD+DPH+water, are not homogeneous. The explanation is that when a microdispersion of DPH in water is mixed with an aqueous solution of cyclodextrin, the very small amount of DPH that is molecularly dispersed in water forms complexes with the CDs, thus causing more DPH molecules to go from the microaggregate phase into the solution and to interact with other free CD molecules, until all present DPH has reacted with the added cyclodextrin. Therefore, the final result is the same as if DPH were molecularly dissolved in water from the beginning. However, such inhomogeneous systems of DPH and cyclodextrins in water are not appropriate for quantitative studies. In this work we have studied the interaction of DPH with the CDs making use of three fluorescence parameters of DPH, viz., its excitation spectra, its fluorescence intensity, and its fluorescence anisotropy. For this reason, first we will discuss briefly some relevant spectroscopic properties of DPH.

**Spectroscopic Aspects of DPH.** In Figure 2a the excitation and fluorescence spectra of DPH dissolved in four different solvents, viz., hexane, ethanol, benzene, and DMF/$H_2O$ (25/75), are shown. It is clear from this figure that the excitation spectra of DPH undergo considerable shifts according to the nature of the solvent. The property of the solvent that determines the spectral shift of the excitation is the polarizability which is a function of the refractive index of the solvent. Thus, hexane and benzene, with very similar dielectric constants but different polarizabilities, give rise to excitation spectra of DPH that are red shifted, the latter with respect to the former, by more than 800 $cm^{-1}$. On the other hand, the excitation spectra of DPH in hexane and ethanol, two solvents with similar polarizabilities but different dielectric constants, are nearly identical. Other parameters of the excitation spectra change as the solvent changes; for example, the ratios of the intensities of the vibrational peaks change as the polarizability of the solvent changes, but we will not make use of such differentiations. Similarly, the fluorescence spectra, although they do not demonstrate substantial shifts in energy as the solvent changes, show nevertheless some dependence of their spectral pattern on the solvent (Figure 2b). All these conclusions have been discussed at length in many places in the literature.[13] Furthermore, as shown in Figure 2b, the excitation and fluorescence spectra of DPH complexed with cyclodextrins, CD−DPH, demonstrate the same behavior as the corresponding spectra obtained from pure solvents. Other DPH fluorescence parameters that are very sensitive to the binding of DPH to CDs are the intensity and the anisotropy of the fluorescence. This is clearly shown in Figure 3b, where the total intensity of the fluorescence $F_t$, i.e. the fluorescence emanating both free DPH and CD-bound DPH, emitted from a solution containing $4 \times 10^{-8}$ M DPH in DMF/water, is plotted vs the concentration of added cyclodextrin [CD]. Figure 3a shows a similar increase of the fluorescence anisotropy, $r$, with increasing [CD]. Note, however, that the dependence of the fluorescence intensity and anisotropy of DPH on [CD] is very different between the $\gamma$-CD and the other three other cyclodextrins, as is seen in Figure 3. Thus the intensity of the fluorescence of $\gamma$-CD-associated DPH rises very steeply as the concentration of the cyclodextrin increases, indicating very strong association between the reactants. A similar sudden increase in observed in the values of $r$, indicating that the size of the $\gamma$-CD−DPH complex increases rapidly, reaching its maximum value 0.34 at relatively low $\gamma$-CD concentrations, ca. $(2-3) \times 10^{-3}$ M. In the three other complexes, however, the fluorescence intensity rises much slower than in $\gamma$-CD−DPH, and the same is true for $r$; thus it maximum values, $r_{max}$, are much lower than in $\gamma$-CD−DPH, viz., $r_{max} = 0.07$ in α-CD−DPH, $r_{max} = 0.115$ in $\beta$-CD−DPH, and $r_{max} = 0.155$ in PM$\gamma$-CD−DPH, compared to $r_{max} = 0.34$ in $\gamma$-CD−DPH. The dependence of all three fluorescence parameters of DPH considered here, viz., $F_t$, $r$, and $\upsilon_{ex}$ (the wavenumbers of the lowest energy peak of the excitation spectrum), on the [CD] is very similar for the case of $\gamma$-CD−DPH complex, as is clearly demonstrated in the plots of Figure 4. This dependence will be discussed later.

**Complexation of Cyclodextrins with DPH.** The plots in Figure 3b show that the intensity of the fluorescence of DPH increases as its association with the cyclodextrins increases. Therefore this increase can be used to determine the details of the complexation process, viz., the stoichiometry and the equilibrium constant of the complexes between the cyclodextrins and DPH. A simplified, but straightforward, method to obtain such stoichiometries and also a good approximation of the equilibrium constant, without the need to know the fluorescence

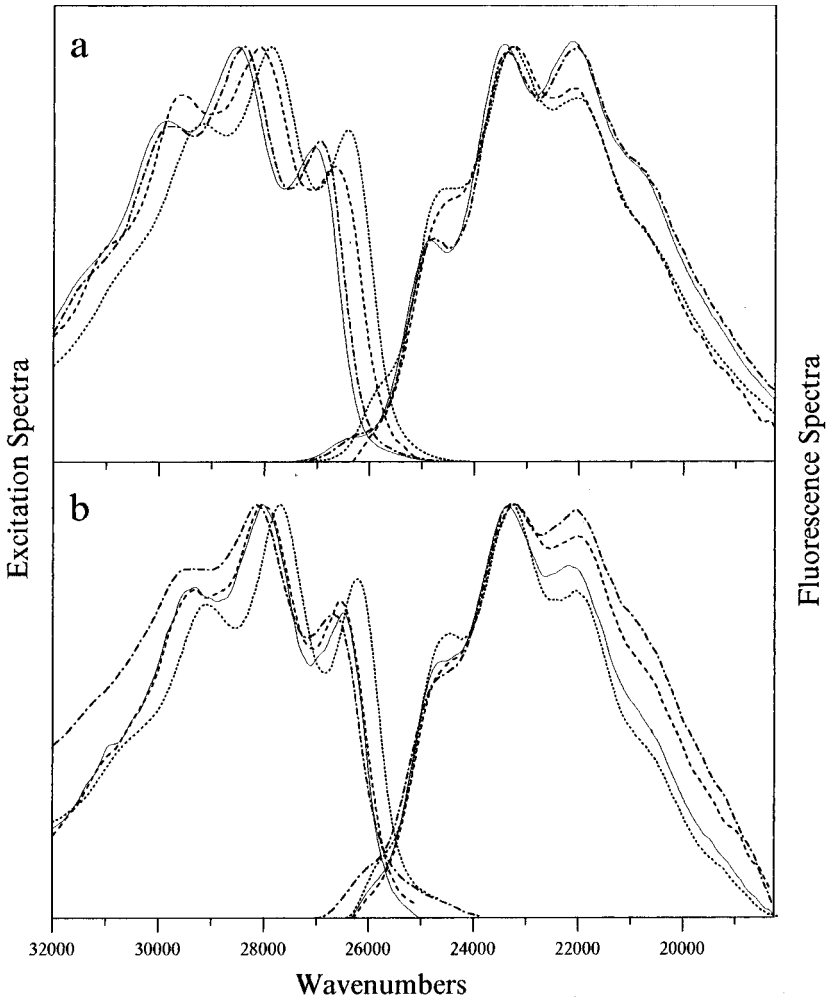


**Figure 2.** Excitation and fluorescence spectra of DPH (a) in various solvents: hexane (continuous line); ethanol (dashed-dotted line); benzene (dotted line); DMF/$H_2O$ (dashed line). (b) In cyclodextrin/DMF/water: α-CD (continuous line); $\beta$-CD (dashed line); $\gamma$-CD (dotted line); PM$\gamma$-CD (dashed-dotted line). Excitation of fluorescence at 356 nm; in excitation spectra the fluorescence intensity was monitored at 440 nm.

quantum yields of all the emitting species, viz. free and CD-bound DPH, is the widely used technique of the double-reciprocal plot.[14] Thus, if the complexation reaction follows eq 1,

$$\mathrm{DPH} + \mathrm{CD} \overset{K_1}{\rightleftharpoons} \mathrm{DPH{-}CD} \tag{1}$$

the equilibrium constant is expressed as $K_1 = [\mathrm{DPH{-}CD}]/[\mathrm{DPH}][\mathrm{CD}]$. On the other hand, the total fluorescence intensity $F_t$ of a solution containing DPH and CD will be

$$F_t = a_f F_f + a_b F_b \tag{2}$$

where $F_f$ is the fluorescence intensity when the entire amount of DPH is free, i.e. at the very beginning of the experiment before any CD is added, while $F_b$ corresponds to the case when all DPH is bound to cyclodextrins. The molar fractions $a_f$ and $a_b$, of the free and the CD-bound DPH, are defined by eqs 3:

$$a_f = [\mathrm{DPH}]_f/[\mathrm{DPH}]_0;\ a_b = [\mathrm{DPH{-}CD}]/[\mathrm{DPH}]_0;$$
$$a_f + a_b = 1 \tag{3}$$

Note that $[\mathrm{DPH}]_0$, which is the concentration of the initially added DPH, is kept constant in all experiments and is equal to $4 \times 10^{-8}$ M, while the cyclodextrins are added continuously in a titrational fashion. Note also that $[\mathrm{DPH}]_0 = [\mathrm{DPH}] + [\mathrm{DPH{-}CD}]$, where [DPH] and [DPH−CD] are the concentrations appearing in eq 1. Finally, when eq 2 is transformed to its double-reciprocal counterpart, eq 4 is obtained.

$$1/(F_t - F_f) = 1/\{K_1[\mathrm{CD}](F_b - F_f)\} + 1/(F_b - F_f) \tag{4}$$

In this equation [CD] stands for the total added cyclodextrin at any time of the titration. If the complex really has a 1/1 stoichiometry, then according to eq 4, a plot of the experimental data in the form $1/(F_t - F_f)$ vs 1/[CD] will produce a straight line, the intercept of which with the $1/(F_t - F_f)$ axis will be $1/(F_b - F_f)$ and its slope will be $1/k_1(F_b - F_f)$, whereas the equilibrium constant $K_1$ will be equal to the ratio intercept/slope.

If on the other hand, the stoichiometry is 2/1, which is not unusual in cyclodextrin adduct formation,[15] then there will be two equations, (5) and (6), describing the complexation process, viz.,

$$\mathrm{DPH} + \mathrm{CD} \overset{K_1}{\rightleftharpoons} \mathrm{DPH{-}CD} \tag{5}$$

$$\mathrm{DPH{-}CD} + \mathrm{CD} \overset{K_2}{\rightleftharpoons} \mathrm{CD{-}DPH{-}CD} \tag{6}$$

In this case, to obtain simple expressions for $a_f$ and $a_b$, the assumption must be made that the concentration of the 2/1 complex is much higher than the concentration of the 1/1 complex, i.e.[CD/DPH/CD] ≫ [CD/DPH]. The linear equation thus obtained is eq 7, where $K = K_1K_2$ is the overall equilibrium

$$1/(F_t - F_f) = 1/\{K[\mathrm{CD}]^2(F_b - F_f)\} + 1/(F_b - F_f) \tag{7}$$

constant, whereas the experimental data must be introduced in

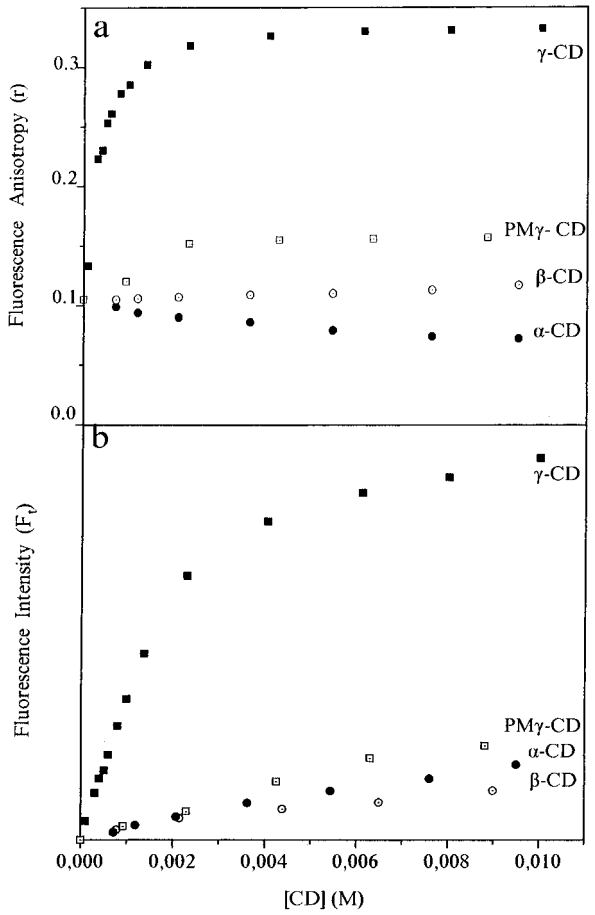


**Figure 3.** Experimental values of (a) fluorescence anisotropy ($r$) and (b) total fluorescence intensity ($F_t$) of $4 \times 10^{-8}$ M DPH complexed with the indicated CD, in a DMF/water (25/75) solvent. The horizontal axis shows the total added concentration of CD.

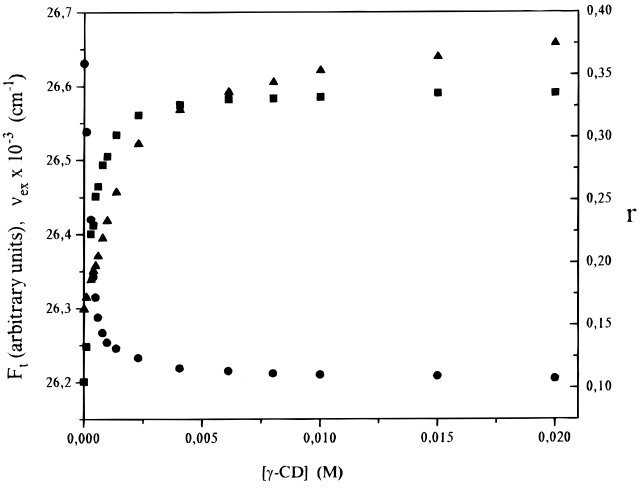


**Figure 4.** Plots of the total fluorescence intensity $F_t$ (tringles); the fluorescence anisotropy $r$ (squares); and the position of the first maximum of the excitation spectrum $\upsilon_{ex}$ (circles), vs [$\gamma$-CD]. All experimental data refer to the $\gamma$-CD−DPH nanotubes formed in a solvent made of 25% DMF and 75% water.

the form $1/(F_t - F_f)$ vs $1/[CD]^2$ in eq 7. $K$ will be equal to the ratio intercept/slope, as in eq 4 for the 1/1 complex.

By plotting the data according to eqs 4 and 7, the stoichiometry can be determined, depending on which plot produces a straight line. Such plots are shown in Figure 5 for the experimental data for α-, $\beta$-, and PM$\gamma$-CD. It is quite clear that in the cases of α- and $\beta$-CD the data form straight lines

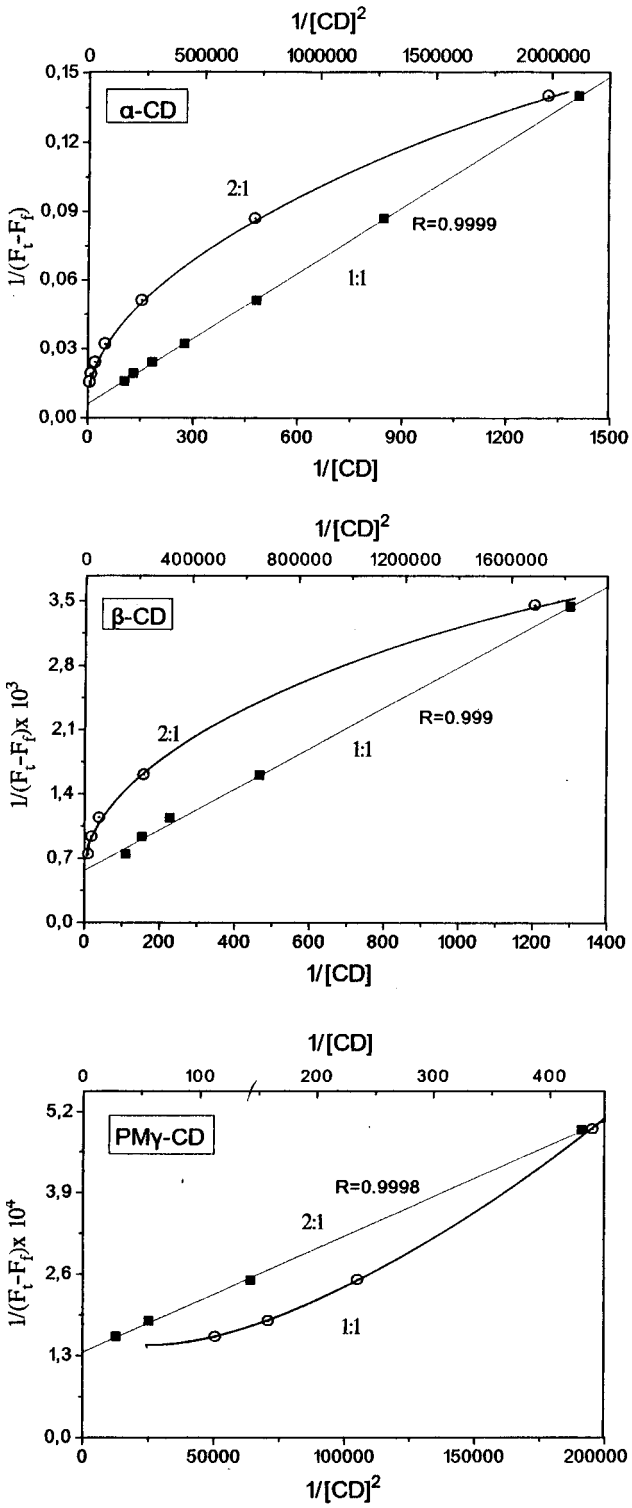


**Figure 5.** Double-reciprocal plots for 1/1 and 2/1 reaction models. $F_t$ is the total fluorescence intensity, and $F_f$ is the fluorescence intensity of the free DPH before any CD is added. Linear least squares fits (filled squares); manual drawing of the curve (open circles).

only when plotted according to the 1/1 model, and not the 2/1 model. On the contrary the data from PM$\gamma$-CD form a straight line only when plotted according to the 2/1 model. The equilibrium constants estimated from these plots are $69 \pm 3$ $M^{-1}$ for the α-CD, $258 \pm 10$ $M^{-1}$ for the $\beta$-CD, and $7 \times 10^4 \pm 1 \times 10^3$ $M^{-2}$ for the PM$\gamma$-CD. In the last case the equilibrium constant is the overall constant of eqs 6 and 7 corresponding to the 2/1 model. At this point we should mention an important difference we have observed between the

complexation of $\beta$-CD with DPH in pure water and in DMF/water solutions. This difference is that in pure water $\beta$-CD behaves like $\gamma$-CD and forms nanotubes[10] in the presence of DPH, while in DMF/water with complexation leads to simple 1/1 $\beta$-CD−DPH adducts. The case of the complexation of the $\gamma$-CD with DPH is quite different because this cyclodextrin in the presence of DPH forms nanotubes, as concluded from the sharp increase of the fluorescence anisotropy in Figure 3a. Since there are many steps in the nanotube formation, the double-reciprocal plot approximation cannot be applied in this case. This complex will be discussed below, in terms of its $r$ values.

**Relative Sizes of the CD−DPH Complexes.** If it is assumed that when DPH forms complexes with the various CDs, its fluorescence lifetime does not change from one CD to the other and that the macroscopic viscosity is the same in all the solutions containing CDs and DPH, then any observed changes in the fluorescence anisotropy $r$ can be attributed to differences in the effective volume $V$ of the CD−DPH complexes. In this way the relative sizes of the CD−DPH complexes can be approximated by means of their corresponding $r$ values. Equation 8 is derived from the combination of the Perrin and Einstein equations and on the above mentioned two assumptions.

$$r_2(r_0 - r_1)/r_1(r_0 - r_2) = V_2/V_1 \qquad (8)$$

In this equation $r_0$ is the maximum value that $r$ can take for the particular probe (for DPH and its two derivatives we have found $r_0 = 0.38$ in vitrified solutions of glycerol and EPA), and $r_1$ and $r_2$ are the values of $r$ measured in two different systems 1 and 2, whereas $V_1$ and $V_2$ stand for the effective volumes of these two systems. However, the ratio $V_1/V_2$ can be approximated by the ratio of the molecular weights of the appropriate CD−DPH complexes, viz., $MW_1/MW_2$. Note that the contribution of DPH to the effective volume is not taken into account since it is assumed that this rodlike molecule goes inside the cavity of the dextrin and it does not contribute considerably to the volume of the complex.

The relationship of eq 8 can be used to compare the maxima of the $r$ values for α-CD−DPH and PM$\gamma$-CD−DPH obtained from Figure 3a. Thus introducing, in the right-hand part of eq 8, the numerical values found in this study, viz., $r_0 = 0.38$, $r_{\alpha\text{-CD-DPH}} = 0.07$, and $r_{PM\gamma\text{-CD-DPH}} = 0.155$, we find that the right-hand ratio of eq 8 takes up the value 3.05, whereas the right-hand ratio is the ratio of the molecular weights of PM$\gamma$-CD and α-CD. We know however from the data of the previous section that the complex PM$\gamma$-CD−DPH has stoichiometry [DPH]/[PM$\gamma$-CD] = 2/1, while in the α-CD−DPH the stoichiometry is 1/1, therefore the ratio $V_2/V_1$ of the left-hand side of eq 8 is $2 \times MW_{PM\gamma\text{-CD}}/MW_{\alpha\text{-CD}} = 3.36$, in very good agreement with the number 3.05 obtained from the right-hand ratio of eq 8, the difference being less than 10%. Furthermore, if $r$ values and molecular weights are compared in a similar way between the α-CD−DPH and the $\gamma$-CD−DPH complexes, we find that the $\gamma$-CD−DPH complex must contain 28 $\gamma$-CD units at the highest CD concentration, [$\gamma$-CD] = 0.01 M. If the same calculation is repeated with respect to PM$\gamma$-CD−DPH, the corresponding number of CD units in the $\gamma$-CD−DPH complex turns out to be 31, in excellent agreement with the previous calculation. These good agreements suggest that the aforementioned assumptions about lifetimes and viscosities are reasonable. In fact, by measuring the macroscopic viscosity, we have confirmed that this parameter increases by a more 5% from the pure 75/25 water/DMF solvent to a $10^{-2}$ M $\gamma$-CD−4 $\times$ $10^{-8}$ M DPH solution in water/DMF. Extending this approximate calculation for the entire range of the experimental values of $r$, obtained from the data of Figure 3a, we have produced the graph of Figure 6, which shows the average growth of the $\gamma$-CD−DPH nanotubes vs the $\gamma$-CD concentration.

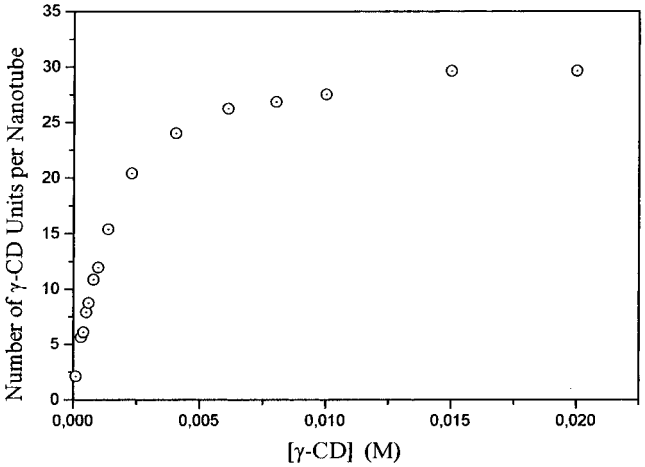


**Figure 6.** Average number of $\gamma$-CD units per nanotube vs $\gamma$-CD concentration, calculated from the fluorescence anisotropy data of Figure 3a (see text).

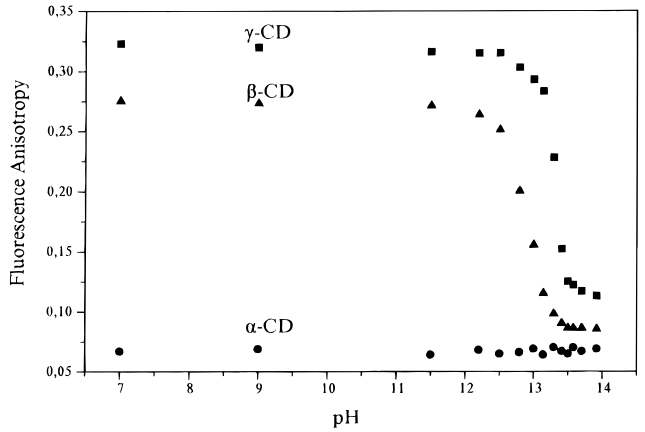


**Figure 7.** Fluorescence anisotropy of CD−DPH complexes in pure water vs pH. [DPH] = $10^{-5}$ M, [α-CD] = [$\beta$-CD] = [$\gamma$-CD] = $10^{-2}$ M.

**Nanotube Formation.** The formation of nanotubes seems to be the result of a very delicate equilibrium among various forces either favoring or opposing this process. There are essentially two main contributions that can conceivably affect the formation of nanotubes in solution, between $\gamma$-CD and DPH. One is the H-bonding interactions between the ring OH groups of different cyclodextrins, and the other is the van der Waals interactions between DPH and the interior of a CD cavity. Some conclusions are immediately evident; thus the fact that cyclodextrins do not form nanotubes in solution unless some DPH is present suggests that that van der Waals interactions play an important role in nanotube formation. On the other hand, the importance of H-bonds is shown by the fact that the PM$\gamma$-CD in which all the hydrogens of the OH groups on both rings of the $\gamma$-CD have been replaced by $CH_3$, thus eliminating the possibility of H-bonding, does not form nanotubes. The delicate equilibrium between H-bonding and van der Waals interactions is also illustrated by the fact that while $\gamma$-CD forms nanotubes in both pure water and DMF/water solution, the $\beta$-CD forms nanotubes only in the former solvent. On the other hand, although DPH favors nanotube formation by both $\beta$- and $\gamma$-CD, when it is replaced by either one of its two derivatives, DPH-$N(CH_3)_2$ or DPH-$NO_2$, which are also rodlike molecules and very similar to their parent molecule, nanotubes no longer form from the $\beta$- or from the $\gamma$-CD. Furthermore, we have found that when the pH of a pure aqueous solution increases beyond

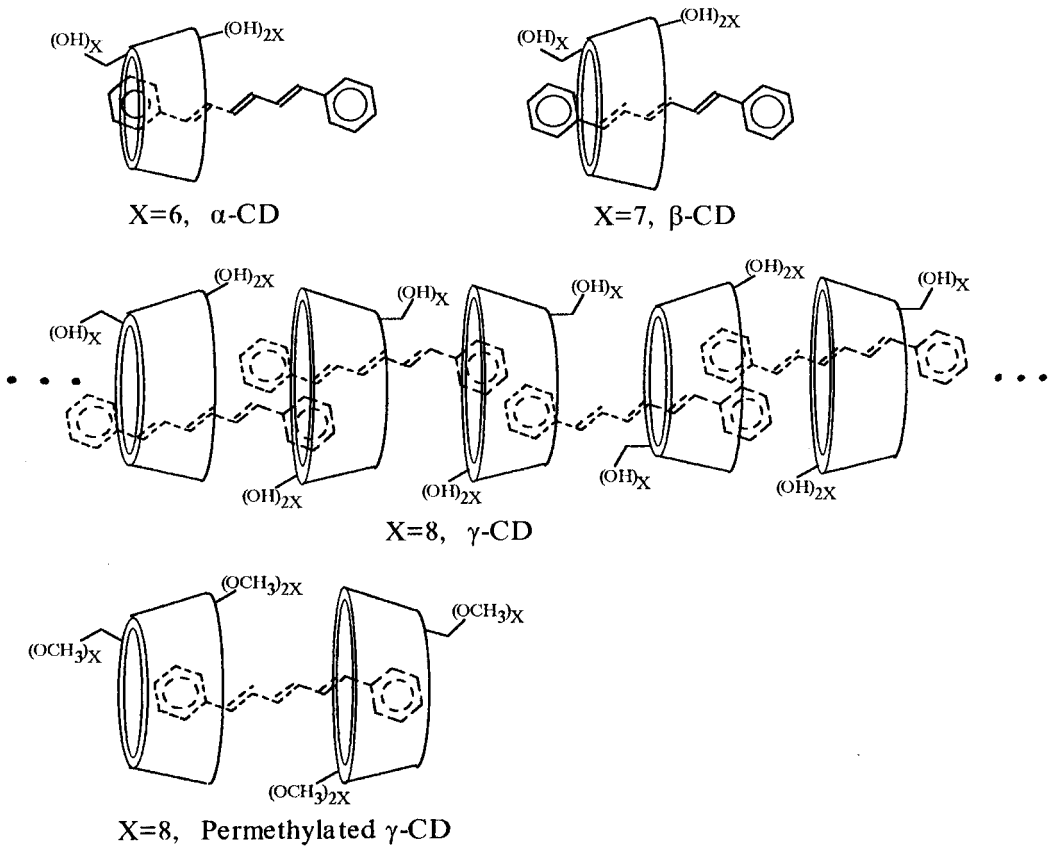


**Figure 8.** Proposed approximate structures of the various CD−DPH complexes studied in the present work.

ca. 12.2, nanotubes do not form at all. This is shown in Figure 7, where the dependence of *r*, which reflects nanotube formation, on the pH is graphically presented. This finding is in very good agreement with the potentiometrically determined acid dissociation constant $pK_\alpha = 12.1$, for the secondary hydroxyl groups of $\gamma$-CD.[16] The experiments at high pH values were conducted only in pure aqueous solutions because DMF decomposes when the alkalinity of the medium is raised.

On the basis of the above results, and additional ones to be described shortly, it is possible to draw approximate schemes depicting the complex and nanotube formation between the CDs and DPH. These proposed schemes are shown in Figure 8. Examining the excitation spectra of the CD−DPH complexes in Figure 2b, it is seen that for the cases of α- and $\beta$-CD the spectra are very nearly the same. This is in agreement with the proposed structure for the CD−DPH complexes of these two cyclodextrins as shown in Figure 8. According to this structure, in both cases the DPH is similarly exposed to the solvent and therefore it is expected to give the very similar excitation spectra shown in Figure 8. The excitation spectra of the PM$\gamma$-CD−DPH and the $\gamma$-CD−DPH complexes, on the other hand, are different from the spectra of the complexes of the two other cyclodextrins. This is also in agreement with the corresponding structures of the complexes shown in Figure 8. Indeed, the exposure of DPH to the solvent is different in PM$\gamma$-CD and $\gamma$-CD than in the α- and $\beta$-CD due to the dimers formed by PM$\gamma$-CD−DPH and the nanotubes formed by $\gamma$-CD, which protect differently DPH from the surrounding solvent. Further evidence that the structures of Figure 8 are correct, at least in principle, is provided by the fact that the excitation spectrum of DPH in $\gamma$-CD, after the pH has been increased above 12 and the nanotubes have been broken, is blue shifted to where the spectra of the other CD−DPH complexes appear. This behavior is rationalized by the fact that when the nanotubes break, the DPH in $\gamma$-CD is no longer protected from the solvent and

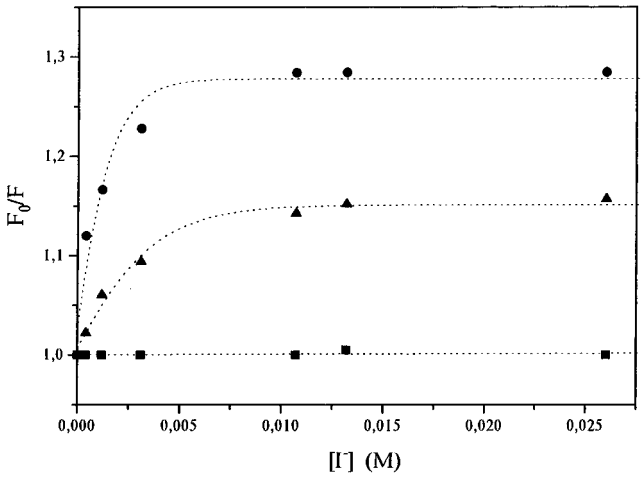


**Figure 9.** Fluorescence quenching by I- of DPH/$H_2O$ (circles); of α-CD−DPH/$H_2O$ (triangles); and $\gamma$-CD−DPH/$H_2O$ (squares).

therefore undergoes shift of its excitation similar to the shift of the other complexes. Finally, quenching of the fluorescence of DPH in α-CD and $\gamma$-CD, in pure water by iodine ions, followed the curves shown in Figure 9. The DPH in $\gamma$-CD was adequately protected by the nanotubes from the solvent and the quencher ions, and therefore the latter could not reach it and quench its emission. In the α-CD the DPH, being exposed to the solvent, was easily approached by the I- and quenched.

## IV. Conclusions

The main conclusions of this study are the following. (i) In a mixture of DMF with water, 25/75 by volume, α-, $\beta$-, and PM$\gamma$-CD form complexes with DPH, having stoichiometries 1/1, 1/1, and 2/1, and overall equilibrium constants $69 \pm 3\ M^{-1}$, $258 \pm 10\ M^{-1}$ and $7 \times 10^4 \pm 1 \times 10^3\ M^{-2}$, respectively. (ii)

Complexation of DPH with $\gamma$-CD produces nanotubes in the DMF/water mixed solvent, as well as in pure water. These nanotubes are made of ca. 30 $\gamma$-CD units. (iii) $\beta$-CD does not form nanotubes in the mixed solvent, but it does in pure water. (iv) If the hydrogens of all OH groups in $\gamma$-CD are replaced by $CH_3$ groups, nanotubes no longer form, either in water or in the mixed solvent. (v) At pH > 12, where H-bonding is ineffective, the nanotubes of $\gamma$-CD in water break down. (vi) When DPH is replaced by either one of its derivatives, DPH-$N(CH_3)_2$ or DPH-$NO_2$, nanotubes no longer form from either $\gamma$-CD or $\beta$-CD, in either water or DMF/water solvent.

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