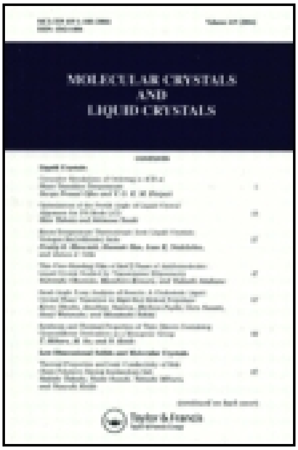

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Environmental Effects on Molecular Properties of Organic Compounds. Part I. The Formation of Inclusion Compounds of β-Cyclodextrin With Salicylideneaniline and Salicylidene-2-Aminophyridine

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To cite this article: E. Hadjoudis , I. Moustakali-mavridis , G. Tsoukaris & F. Villain (1986): Environmental Effects on Molecular Properties of Organic Compounds. Part I. The Formation of Inclusion Compounds of β-Cyclodextrin With Salicylideneaniline and Salicylidene-2-Aminophyridine, Molecular Crystals and Liquid Crystals, 134:1, 255-264

To link to this article: http://dx.doi.org/10.1080/00268948608079589

Mol. Cryst. Liq. Cryst., 1986, Vol. 134, pp. 255-264
0026-8941/86/1344-0255$15.00/0

Printed in the United States of America

ENVIRONMENTAL EFFECTS ON MOLECULAR PROPERTIES OF ORGANIC COMPOUNDS. PART I. THE FORMATION OF INCLUSION COMPOUNDS OF β-CYCLODEXTRIN WITH SALICYLIDENEANILINE AND SALICYLIDENE-2-AMINOPYRIDINE.

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Abstract: β-Cyclodextrin forms inclusion compounds with salicylideneaniline and salicylideneaminopyridine. The formation of the inclusion compounds has been established by i.r. measurements, differential scanning calorimetry and X-rays powder-diffraction. Environmental effects on molecular properties of the guest compounds, such as photochromism and thermochromism have been observed in the solid state.

INTRODUCTION

Alpha, beta and gamma cyclodextrins are macrocyclic carbohydrate molecules which are produced by bacterial degradation of starch. They consist of six, seven, or eight glucose monomers arranged in a torus. The coupling of the glucose moieties gives cyclodextrins a rigid, conical molecular structure[1] with a hollow interior of a specific volume, as shown in Figure 1.

The cavity, shown in Figure 1, is hydrophobic in nature and contains water molecules which is thermodynamically unfavorable because of repulsion effects. Thus, the cyclodextrin will expel the water molecules in order to include less polar species satisfying the size criterion for fitting at least partially into the interior, resulting in an inclusion or "host-guest" complex. Various theories have attempted to explain the favorable thermodynamics associated with this complex formation[2]. However, the complexation is affected also by the size of the guest molecule and the internal diameter of the cyclodextrin (alpha~5Å, beta~8Å and gamma~10Å).

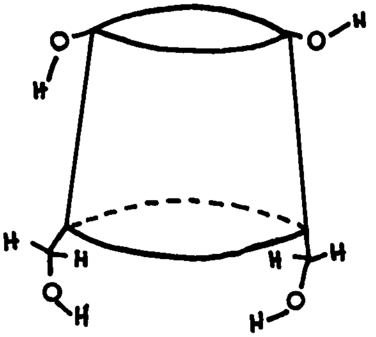

FIGURE 1. Structural representation of the cyclodextrin molecule.

The phenomenon of inclusion complexation between cyclodextrin and a variety of organic molecules has promoted research in various fields. Thus, biochemists have found that the inclusion process is analogous to the binding of enzymes and substrates in the human body, while pharmacologists have used cyclodextrins to stabilize drugs and render them more compatible with body fluids.

Cyclodextrins form complexes in aqueous solutions with azo dyes, nitrophenol, and other substances[3]. The complexes are usually regarded as inclusion compounds in which hydrogen bonding, van der Waals forces, and hydrophobic interactions are the main binding forces. This explains the interest in using cyclodextrins as models for studying the primary step of enzyme or antigen-antibody reactions[4].

The aim of this work is to show that cyclodextrins can form inclusion compounds with various substrates of interest in non-aqueous solutions and, if possible, to characterize the mechanism of complex formation. This is very important since a great number of organic compounds which are interesting as guest moieties are easily hydrolized. Thus, in the present work we used as guest molecules the photochromic salicylideneaniline and the thermochromic salicylidene-2-aminopyridine. Both compounds are easily hydrolized and inclusion complexation with cyclodextrins in water is impossible.

EXPERIMENTAL

α- and β-Cyclodextrins were obtained from Janssen Chimica. Salicylideneaniline and salicylidene-2-aminopyridine were synthesized from salicylaldehyde and aniline or aminopyridine respectively. Their purity was verified by m.p., i.r., and stoichiometric analysis.

U.V. spectra were taken on a Cary-17 spectrometer and i.r. measurements were performed on a Perkin-Elmer 397 in KBr pellets.

Powder X-ray photographs were taken on a Debye-Scherer camera with Cu-kα radiation unless otherwise stated.

A Du-Pont differential scanning calorimeter has been used to study the thermal behaviour of solids during controlled heating scans.

THE PREPARATION OF INCLUSION COMPLEXES

After many trials DMF was found to be a good solvent for both the host and the guest molecules. Molar ratios of host to guest 1:1, 1:2 and 1:4 were tried. A typical run (e.g. for the case 1:2) is as follows:

2g of cyclodextrin are dissolved in 5ml distilled DMF. To this solution 0.7g of salicylideneaniline were added at room temperature under stirring. The solution is then heated to 75°C in an oil bath. The temperature is kept at 75°C until precipitation occurs. The precipitate is filtered and dried in a desiccator under vacuum.

RESULTS AND DISCUSSION

The precipitates were examined for complexation both in solution and in the solid state. Thus in solution we examined the changes induced in the UV absorption spectrum of the substrates by the addition of α- or β-cyclodextrin. In these solutions we also performed fluorescence measurements.

In the solid state we used the DSC, i.r. measurements and X-ray powder diffraction. The fluorescence in the solid state was observed under a UV-lamp.

UV ABSORPTION SPECTRA

The changes induced in the UV-absorption spectrum of the salicylidene-2-aminopyridine by the addition of various quantities of β-cyclodextrin is shown in Figure 2.

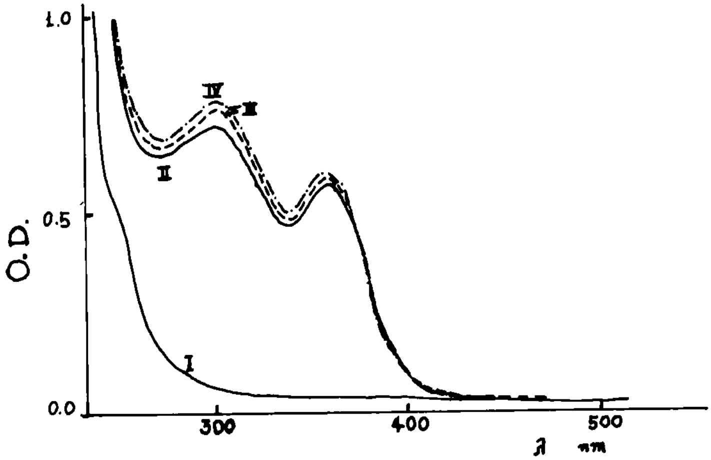

FIGURE 2. UV-absorption spectra of β-cyclodextrin (I), salicylidene-2-aminopyridine (II) with various quantities of β-cyclodextrin (III, IV) in DMF.

We observe that the changes in the UV-absorption spectra are small and evaluation of association constants is difficult, However, there are indications of existing isosbestic points which suggest that complexation was effective.

The results with salicylideneaniline and β-cyclodextrin were more or less the same.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC is used to measure heat flow into or out of a material and can also measure both temperatures and heats of transitions or reaction.

The following conditions were employed:

heating: 30°C to 350°C at 10°C per minute.

From the traces obtained, the positions and magnitudes of thermal transitions could be found. Thus, Figure 3 is a schematic representation of the DSC traces obtained for solid β-cyclodextrin (I), salicylideneaniline (II) and precipitates from solutions of β-cyclodextrin and salicylideneaniline of molar ratio 1:1 (III), 1:2 (IV) and 1:4 (V) respectively. Differences between the pure cyclodextrin and

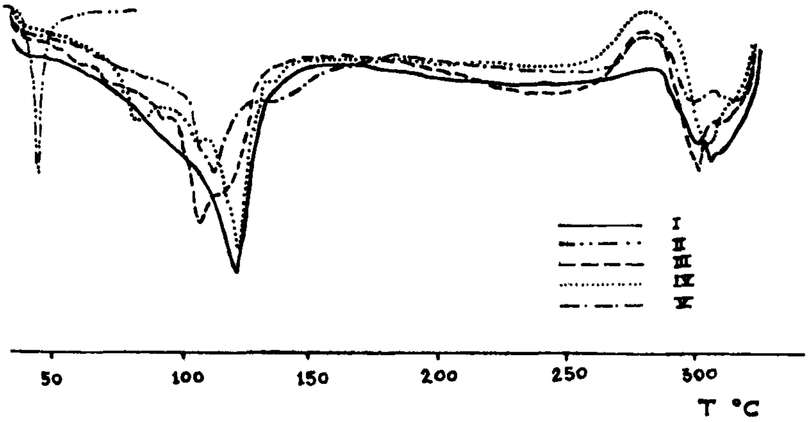

FIGURE 3. Schematic DSC traces for the indicated compounds.

the "complexes" are observed in the region of water evaporation indicating a change in the cavity.

I.R. SPECTRA

The i.r. spectra of the following solid compounds and "complexes" have been measured in KBr pellets. 1) salicylideneaniline 2) salicylidene-2-aminopyridine 3) β-cyclodextrin

4) "complexes" from solutions of host:guest molar ratios 1:1, 1:2 and 1:4. Figure 4 shows the case of salicylideneaniline (I), β-cyclodextrin (II) and the precipitate (III) from their solution of molar ratio 2:1. The behavior of salicylidene-2-aminopyridine is similar.

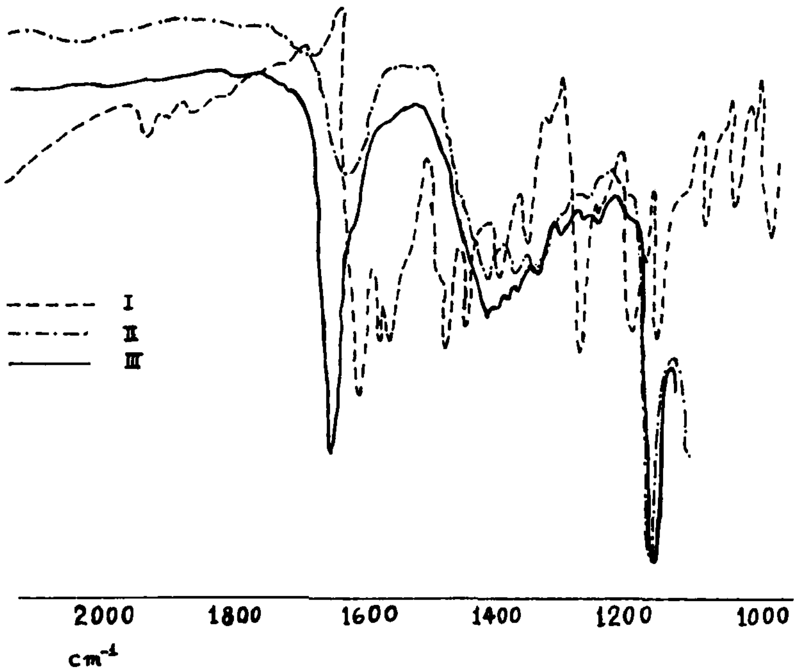

FIGURE 4. I.r. spectra of the indicated compounds.

An observation of the spectra of the "complexed" compounds shows a common feature: a sharp strong band at 1660 cm^{-1}. Salicylideneaniline (and salicylidene-2- aminopyridine) display a sharp strong band at 1600-1620 cm^{-1} due to the C = N band of the bridge while β-cyclodextrin shows a broad weak band around 1620cm^{-1}. Therefore, the new strong sharp band is most probably due to the complexation and may originate from a carbonyl group of the type shown in Figure 5 for

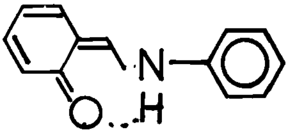

FIGURE 5. Quinoid Salicylideneaniline.

the case of salicylideneaniline. Such a quinoid band, which is formed by the photochromic mechanism of this class of compounds[5] may be formed also by hydrogen bonding in the cavity of **the host molecule of β-cyclodextrin.**

X-RAY POWDER DIFFRACTION

X-ray diffraction photographs of powdered samples were taken on a Debye-Scherrer camera of radius 5.7 cm with Cu-kα radiation at about 8 hrs exposure. This technique was the most successful in showing the complexation between salicylideneaniline, salicylidene-2-aminopyridene and α- and β-cyclodextrins.

Photographs of the pure components and of the "complexed" compounds at various host/guest ratios were taken. Changes were observed both in spacing and in intensity of the lines which were estimated as strong(s), moderately strong (ms), medium(m), moderately weak(mw), and weak(w). Figure 6 shows the X-rays Debye-Scherrer photographs for the case of salicylideneaniline and β-cyclodextrin for the indicated compositions.

In the photographs below if the diffraction pattern does not correspond to those of the pure components, a true inclusion complex may exist. Indeed differences are observed and the formation of inclusion compounds is shown. Differences were observed in the "complexes" of the same guest molecules (e.g. salicylideneaniline) but of different host/guest ratios. It is not clear whether these are due to differences in the stoichiometry of the components or to differences in occupancy of the guest molecules.

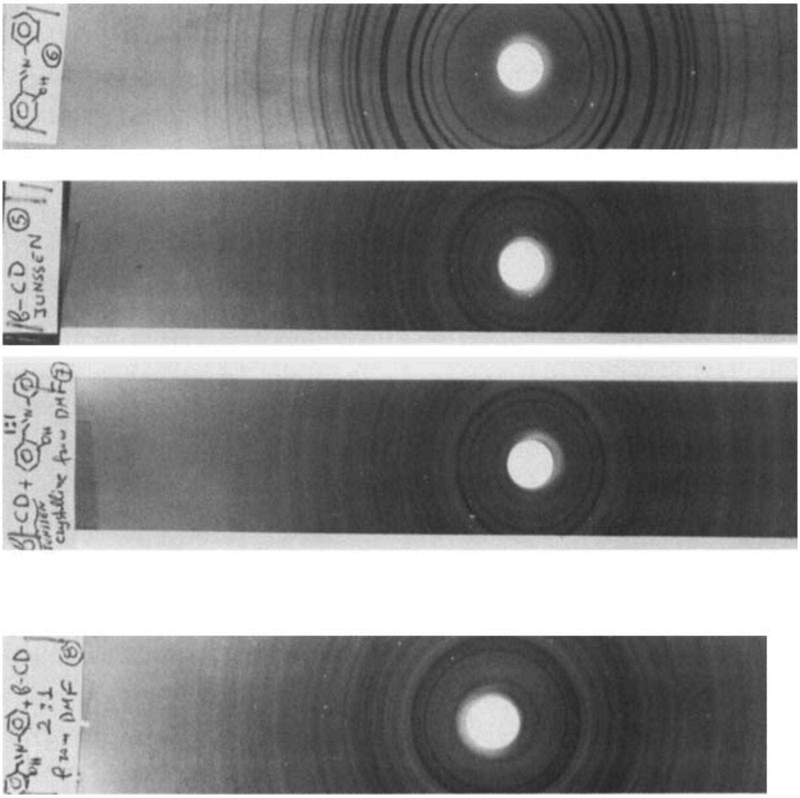

FIGURE 6. X-Ray diffraction Debye-Scherrer photographs.

ENVIRONMENTAL EFFECTS

Spectroscopic investigations of various cyclodextrin inclusion complexes have shown that the cyclodextrin provides a protective, more constrained microenvironment to an electronically excited lumiphor such that the resulting fluorescence is enhanced as, for instance, in the case of 1-anilino-8-naphthalenesulfonate with β- and γ-cyclodextrins which shows a tenfold increase[3].

In the present case, the photochromic guest molecule, namely the salicylideneaniline is not fluorescent in the crystalline state. The resulting inclusion complex, however, is strongly fluorescent. This fluorescence decreases as the red-photoproduct is produced by the UV-irradiation.

ACKNOWLEDGMENT

We would like to thank Mrs. S. Philippakopoulou for valuable technical assistance.

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