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BIS-(POLYETHER)AZOBENZENES: THEIR UTILITY AS PHOTORESPONSIVE COMPLEXING AGENTS FOR THE ALKALI METALS

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Bis-(Polyether)Azobenzenes: Their Utility as Photoresponsive Complexing Agents for the Alkali Metals.

by

Thomas Patrick Rizzo

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1987

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Abstract

Bis-(Polyether)Azobenzenes: Their Utility as Photoresponsive Complexing Agents for the Alkali Metals.

by
Thomas Patrick Rizzo

Adviser: Professor Paul Haberfield

In this work four bis(polyether) azobenzenes:

(1) bis-4,4'-[2-(methoxyethoxy)acetamido]azobenzene (Cm-1);
(2) bis-4,4'-[2-(2-methoxyphenoxy)acetamido]azobenzene (Cm-2);
(3) bis-4,4'-[2-(1,3-dimethoxy-2-propoxy)acetamido]azobenzene (Cm-3);
(4) bis-4,4'-[2-[2-(2-methoxyethoxy)ethoxy]acetamido]azobenzene (Cm-4)

were synthesized and characterized. The trans isomers of the bis(polyether)-azobenzenes were photoisomerized to the cis isomers. Solvent and structural effects were observed on the photostationary state and thermal cis-trans isomerization rates. The partition coefficients for the bis(polyether)azobenzenes between water and various organic solvents were determined. The utility of these compounds as photoresponsive complexing agents for the alkali metals was investigated via a sensitive extraction technique. The extraction involved the use of sodium 5-(4'-N,N-dimethylaminophenylazo)-8-nitro-2-naphthalenesulfonate as a dye, which was synthesized for this purpose. The extraction technique was used to obtain equilibrium constants for dibenzo-18-crown-6 with the alkali metals for comparison with the bis(polyether)azobenzenes.

To Nina, whose undying love, patience and support made it possible to complete this worthwhile endeavor.

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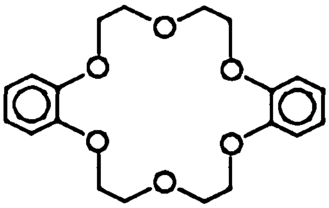
Introduction

Photoresponsive Complexing Agents employ light to affect the stability of a complex. Light energy can then be used to perturb processes which normally operate under thermodynamic control. For instance, such systems could be employed to transport a complex against a concentration gradient. This project investigates the utility of azobenzene as the light sensitive "switch" to regulate complexation of cations by crown ether-like compounds. A short discussion of crown ether complexation and azobenzene isomerization and stability will follow. Also, the recent advances in Photoresponsive Complexing Agents will be discussed.

Crown Ethers

Cyclic polyethers were first synthesized by Luttringhaus and Zeigler in 1937[1]. However, it was not until 1967 that Pedersen observed[2] that these compounds formed complexes with a variety of cations. The first "crown ether" prepared by Pedersen was dibenzo-18-crown-6, shown in Figure 1.

Figure 1



Dibenzo-18-crown-6

It was prepared as a by-product in the synthesis of bis-2-(*o*-hydroxyphenoxy)ethyl ether. When trying to characterize this by-product, Pedersen noted that it was not soluble in methanol but would dissolve in the presence of sodium salts.

This observation led to the birth of crown ether chemistry. In the intervening years, there has been a wealth of imaginative and useful ideas concerning crown ethers[3-14].

Pedersen realized that the crown was complexing the cation in a Lewis acid-base fashion. The ether oxygens of the crown were acting as the base in donating their electron density to the cation. This type of complexation was not new, having been observed in biological systems with antibiotics such as X-537A[15], rifamycin[16], monensin[17], and others. Realizing the importance of these complexes, Pedersen synthesized many more of these crowns varying their sizes. He then complexed each of them with alkali and alkaline earth metals to find which cations fit best in each crown. For example, the potassium ion fit best into 18-crown-6, followed by the sodium ion, while the rubidium ion did not complex. Most of the complexes were found to be 1:1 crown to cation. However, there have been cases of 2:1 and even 3:2 "sandwich" complexes[3].

One use of the crown ethers that was immediately apparent was the solvation of salts in nonpolar organic liquids. Bartsch and his collaborators[18] examined the effects of crown ether complexation in numerous nucleophilic and β-elimination reactions. Pedersen[19,20] saponified esters with stoichiometric amounts of preformed crown-hydroxide complexes. Since then, there have been many other synthetic preparations in which anions were activated through complexation of the cation[6]. The many other uses of crown ethers include cation transport carriers in hydrophobic liquid membrane systems[21-23], study of ion pair structure[24] and optical resolution of racemic mixtures[4, 8, 22].

Azobenzene Isomerization

The cis-trans stereoisomerism of azo compounds has been known for many years and is fairly well understood[25]. The trans-to-cis isomerization is light induced. However, since the trans isomer is more stable, the cis-to-trans isomerization can be thermal or light induced. Photoisomerization of the trans-azo compound does not result in 100 percent conversion to the cis isomer. However, significant conversions have been routinely observed. On the other hand, 100 percent solutions of the trans isomer can be obtained through the thermal process in the dark.

Trans-azobenzene and nearly all of its substituted derivatives have their principal absorption bands (π-π^*) in the ultraviolet region of the spectrum at approximately 330 nm. They also have a weaker band (η-π^*) in the visible region at approximately 450 nm. Upon conversion to the cis isomer, the π-π^* band moves to shorter wavelengths and there is a strengthening of the η-π^* absorption. Consequently, the cis isomer appears darker in color than the trans. The η-π^* band is more affected by substituents on the benzene rings than is the π-π^* band. Electron donating groups pull the η-π^* band further into the visible. This is especially true for amino substituents. This is important because it has been proposed that the η-π^* transition is involved in the trans-to-cis isomerization. For the purpose of the present work, it would be desirable to design compounds whose η-π^* absorption band is near the most intense wavelength of sunlight, which is at 470 nm[26]. This should be feasible by the introduction of the appropriate substituents on the benzene ring of an azobenzene system.

There is some controversy concerning the mechanism of the thermal cis-to-trans isomerization process[27]. One possibility is the Inversion Mechanism in which the azobenzene system remains approximately planar[28-31]. In the Rotation Mechanism, the central π bond is broken, rotation about the N-N bond occurs and the π bond is reformed to give the trans isomer[32,33].

The rate of the isomerization depends on the substituents on the benzene ring, on the polarity of the solvent, and the pH of the system. It is particularly fast in the case of ortho or para hydroxy and amino azobenzenes. The activation energies for the thermal isomerization range from 10 kcal/mol for *o*-hydroxyazobenzenes to 12-16 kcal/mol for *o*-aminoazobenzenes to 20-25 kcal/mol for other substituents, such as alkyl, alkoxy, halogen or nitro[25].

Photoresponsive Complexing Agents

When using crown ethers as liquid-liquid phase transfer catalysts, the highest attainable concentrations are equilibrium mixtures. To circumvent this limitation, a number of different photosensitive complexing agents have been developed[34]. Desvergne and co-workers[35,36] utilized the photo-dimerization of anthracene to design a "switched" crown ether. Yamashita and co-workers[37] also utilized the photo-dimerization of anthracene. Polyethers were attached to the two anthracene units in such a way that upon photo-dimerization a crown ether ring formed. The success of these methods was hindered by the energy necessary to photo-dimerize anthracene.

Ueno and co-workers[38,39] synthesized azobenzene capped β-cyclodextrin to regulate the binding ability of β-cyclodextrin. The complexation of guest molecules was regulated by the azobenzene moiety. However the effects were generally small due to the powerful nature of the β-cyclodextrin as a complexing agent.

Beyond the field of polyether complexing agents, Blank, Soo, Wasserman and Erlanger[40] described the use of 4,4'-bis(α-iminodiacetic acid)azotoluene in the complexation of zinc (II) cations. The cis isomer of the azotoluene mimicked the structure of ethylenediaminetetracetic acid (EDTA) and complexed the zinc cations. The trans azotoluene was incapable of complexation because the diacetic acid groups were to far away from each other.

Shinkai and co-workers[41-49] have synthesized many different crown ethers incorporating the azobenzene moiety. They first synthesized azobenzene bridged crown ethers[41, 43, 45, 49]. The azobenzene bridge could be made to undergo cis-trans isomerization through the use of the appropriate light and heat conditions. This was expected to cause changes in the shape of the crown, which Shinkai hoped would destabilize the complex so that the cation would be released. There was limited success with this method. There was destabilization of the complex but there was only partial release of the cation.

Shinkai and co-workers[42, 44, 46, 47] also synthesized many azobis(benzocrown ether)s. These compounds contain the azobenzene moiety in which the benzene rings are fused to small crown ethers with four to six oxygens. It was hoped that the cis form would "sandwich" a cation to form a complex and the trans form would not be able to form such a complex. However, since there are two crown ether rings in the trans form of the molecule, there was still complexation of cations.

More recently, Shinkai and co-workers[48] synthesized azobenzenophane-type crown ethers. In this molecule the two ends of a polyether are connected to the para position of azobenzene. In the cis form the compounds were expected to mimic a crown ether, while the trans isomer were expected to mimic a straight chain polyether. They did have some success with this molecule. Actually, our initial design for a Photoresponsive Complexing Agent was identical to that of Shinkai's azobenzenophane-type. Therefore, we modified our system by splitting the ring into two polyether chains. The present work describes this system.

Methodology

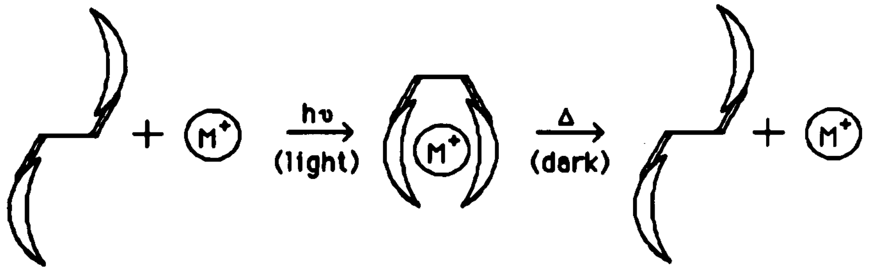
Objective

The aim of this project was to synthesize, characterize and assess the utility of a new class of compounds known as "Photoresponsive Polyethers". These substances would be able to complex with metal ions when irradiated by light and would revert slowly to the inactive (non-complexing) form in the dark. By solubilizing metal ions, crown ethers are capable of transporting a salt into a nonpolar medium or across a membrane until thermodynamic equilibrium is established. Unlike the crown ethers, the photoresponsive polyethers should be able to engage in light energy pumped processes, such as membrane transport against a concentration gradient.

Selection of Photoresponsive Polyether Complexing Agents.

The light sensitive polyethers to be synthesized should be able to form a complex with metal ions or other cations when irradiated with light and revert to the inactive form in the dark, as shown in Figure 2.

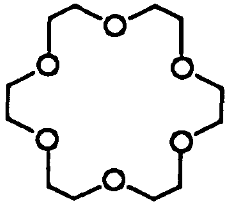
Figure 2



The complexing portion of this proposed molecule consists of two polyether chains, or analogous structures, whose shape would mimic the shape of a crown ether when irradiated. In the dark the proposed molecule should revert to a structure resembling that of an open chain polyether.

The first choice for the light sensitive central part of the molecule was the azo-group. As described above, this functional group is fairly stable, and its chemistry, spectroscopy, and stereoisomerization have been subjected to thorough study and are fairly well understood. Consequently, the first class of compounds to be synthesized were substituted azobenzenes which were expected to mimic the structure of 18-crown-6, shown in Figure 3.

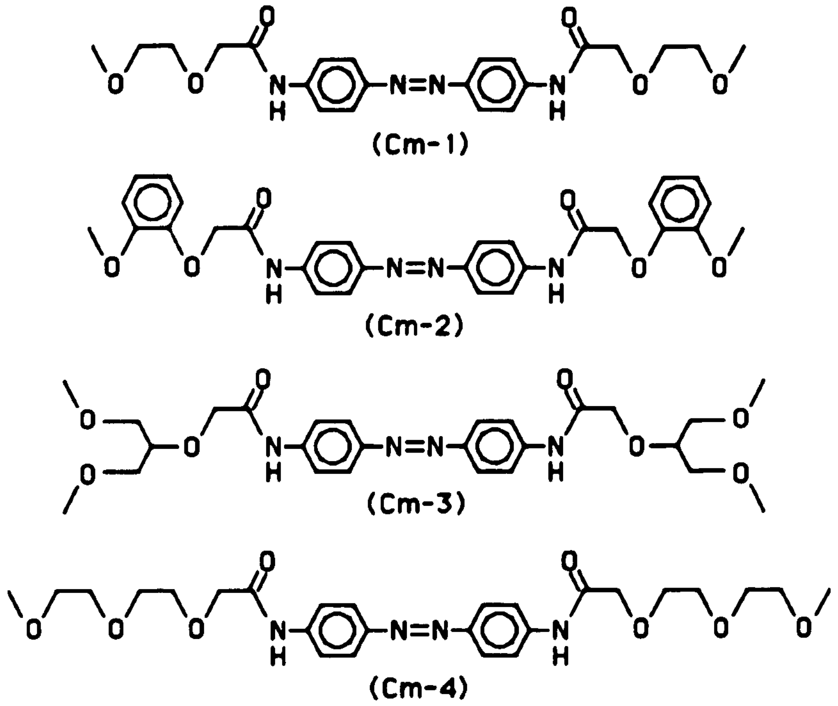
Figure 3



18-crown-6

One requirement for these substituted azobenzenes was that the cis isomer should be able to complex cations while the trans should not. Therefore, the azobenzene moiety would be substituted in the para positions with polyether chains. The requirements for the substituents of the bis-4,4'-disubstituted azobenzenes were that they be relatively short, stable chains containing at least three oxygens. This was half the number of oxygens in 18-crown-6. The oxygens could be part of an ether, alcohol or carbonyl functionality. Four compounds that meet these requirements are shown in Scheme I.

Scheme I



(Cm-1)

(Cm-2)

(Cm-3)

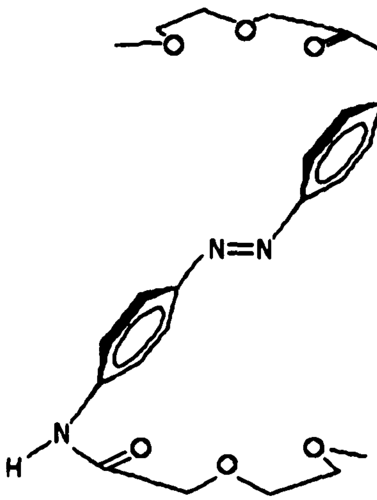
(Cm-4)

It was not obvious from examination of structures, such as those in Scheme I, which of these compounds would best fill the requirements of the photoresponsive polyethers. However, models of all of these compounds were constructed with space filling models which revealed their similarities, or lack thereof, to 18-crown-6.

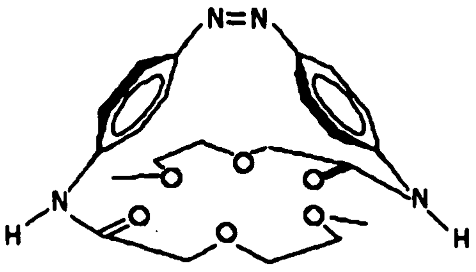
It was noticed, with the aid of the space filling models, that a carbonyl oxygen for the first oxygen in the chain would better form the crown ether-like ring. The amide functionality was employed, since it was the most stable of the carbonyl functions. There was also the possibility that N-H·····O hydrogen bonding might help induce formation of the crown ether-like ring. The ease of formation of the amide linkage made it possible to vary the polyether chain, as seen in Scheme I.

The first complexing agent (Cm-1) had two ether oxygens connected to the azobenzene via the amide linkage. Figure 4 shows how Cm-1 may be able to mimic the structure of 18-crown-6 in the cis and not in the trans form.

Figure 4



(Trans Cm-1)



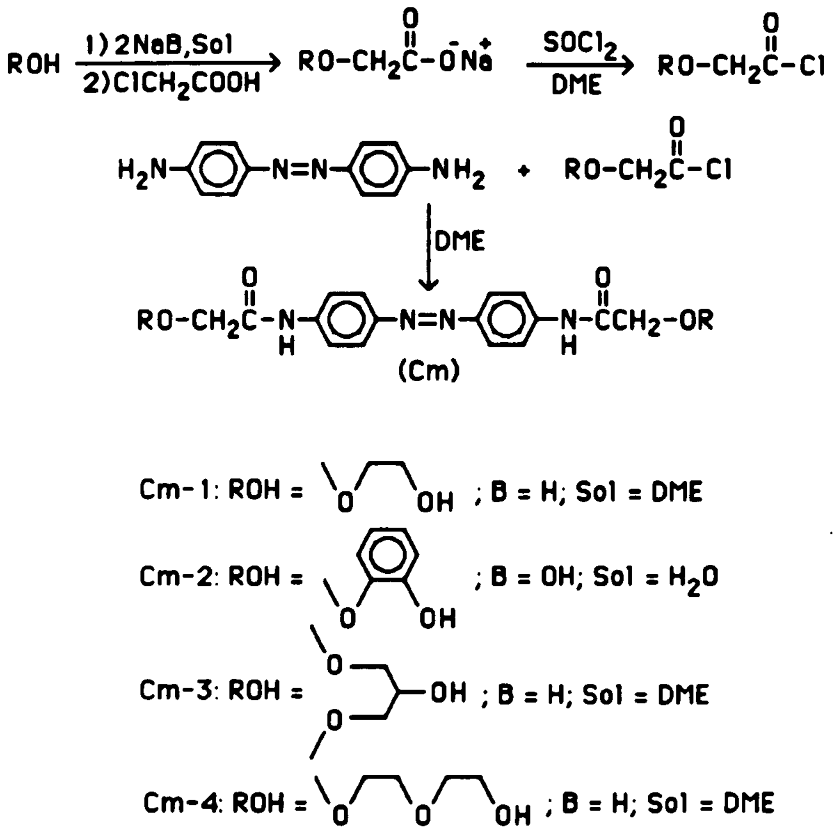
(Cis Cm-1)

The compound Cm-2 had the added rigidity of a benzene ring in the polyether chain. This would keep the ether oxygens in the same plane and reduce the loss of entropy that would accompany complexation. Compound Cm-3 was different in that an extra ether unit was attached forming a branched structure. This branch would help to surround the cation during complexation in a fashion similar to that of Gokel's lariat ethers.[50-51] Compound Cm-4 is an isomer of Cm-3 in which the polyether chain is unbranched. The structure of Cm-4 is similar to that of Cm-1 since it is a straight chain polyether.

Syntheses

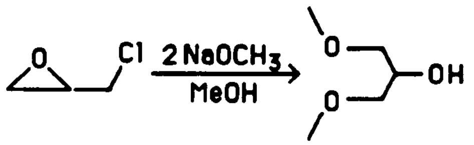
The complexing agents were synthesized according to the method outlined in Scheme II.

Scheme II



The alcohols employed as starting materials for Cm-1, Cm-2 and Cm-4 are commercially available. The alcohol utilized in the synthesis of Cm-3 was prepared by the method outlined in Scheme III.$^{52\text{-}54}$

Scheme III



The commercially available epichlorohydrin was treated with two equivalents of sodium methoxide in methanol. Acidic work-up then afforded the product, 1,3-dimethoxy-2-propanol, in 80% yield.

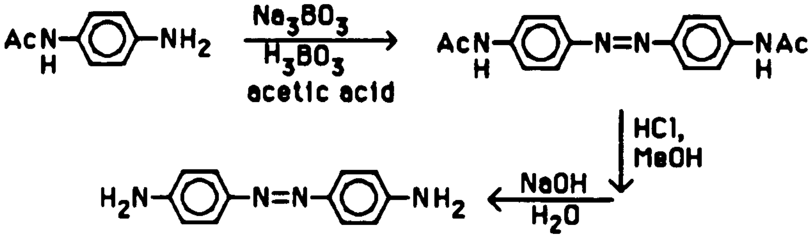
The synthetic route outlined in Scheme II provided ample yields of the complexing agents. The first set of reactions leading to the sodium carboxylate salt for Cm-2 differed from the other complexing agents. The difference was due to the increased acidity of the phenol over that of the alcohols. The deprotonation of guaiacol with sodium hydroxide, followed by the displacement on chloroacetic acid, was accomplished in water.[55-58] The carboxylic acid, 2-(2-methoxyphenoxy)acetic, acid was obtained in 87% yield upon acidic work-up. Standard treatment of the carboxylic acid with thionyl chloride afforded the acid chloride in 65% yield.

Since the formation of the ether linkage was facile in water, it seemed that this type of reaction would work using an alkoxide in an aprotic solvent. For Cm-1, Cm-3 and Cm-4, the alcohol was deprotonated with sodium hydride in dimethoxyethane, followed by treatment with chloroacetic acid. This provided an easy route to the sodium carboxylate salts.

The next logical step in the synthesis was the isolation of the carboxylic acid. However, no easy method for the isolation and purification was found. A literature search showed that Wygant[59] had prepared acid chlorides from carboxylate salts by heating with alkyl polychlorides at high temperatures and pressures. Wygant did not offer a mechanism for the reaction. If the mechanism is nucleophilic, perhaps the use of thionyl chloride under less severe conditions might suffice. The reaction proceeded smoothly with thionyl chloride heated at reflux in dimethoxyethane. For Cm-1, Cm-3 and Cm-4, the percentage yields from the corresponding alcohols were 41%, 52% and 63%, respectively.

As illustrated in Scheme II, the acid chlorides were combined with 4,4'-diaminoazobenzene. The synthetic route to the diamine was shown in Scheme IV.

Scheme IV

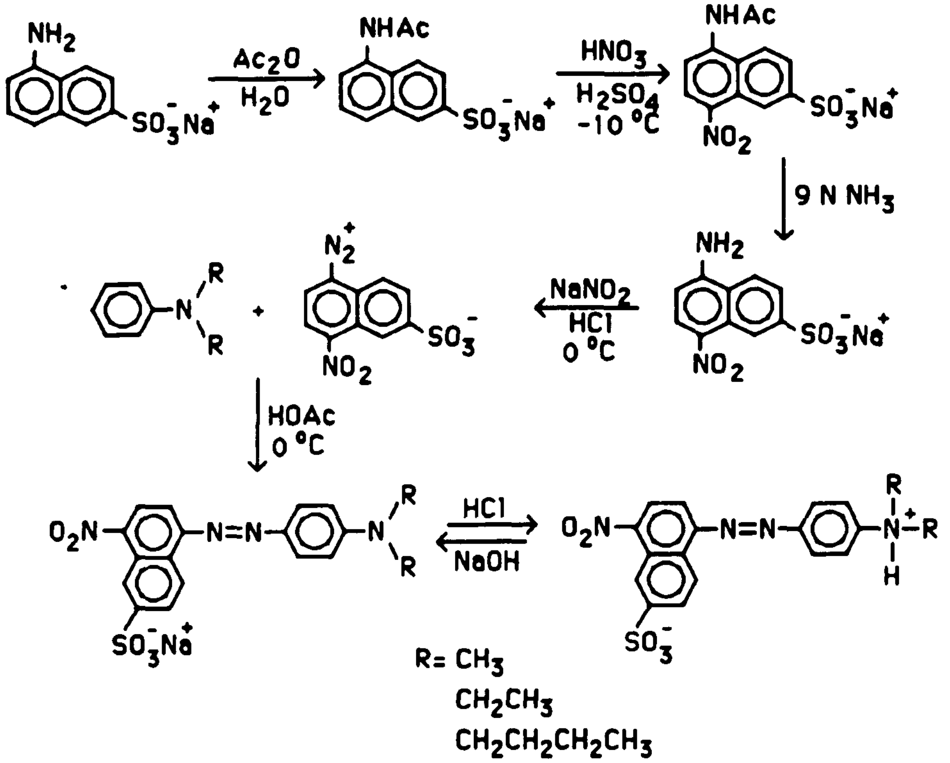


The synthesis of 4,4'-diaminoazobenzene had been accomplished in many different ways.[60-64] However the method chosen was that by Santurri, Robbins and Stubbings.[65] The 4-aminoacetanilide was oxidized with sodium perborate and boric acid in acetic acid.[66] The intermediate, 4,4'-diacetamidoazobenzene, was obtained in 57% yield. The acetamide groups were hydrolyzed in methanolic hydrochloric acid. Neutralizaton with sodium hydroxide provided the product 4,4'-diaminoazobenzene, in 62% yield.

As stated before, the final step in the syntheses of the complexing agents was the formation of the amide bonds as illustrated in Scheme II. The method involved the slow combination of the acid chloride with 4,4'-diaminoazobenzene in the presence of sodium carbonate.[67] The carbonate was present to consume the hydrochloric acid formed during the reaction. The complexing agents were crystalline products that formed orange needles in each case. The percentage yields for Cm-1, Cm-2, Cm-3 and Cm-4 were 69%, 69%, 80% and 69%, respectively.

The syntheses of the dyes employed for the extraction are outlined in Scheme V.

<u>Scheme V</u>



The first two reactions in the sequence are modifications of the method used by Ralph.[68] The first step in the synthesis is the acetylation of 5-amino-2-naphthalenesulfonic acid with acetic anhydride in water. The reaction proceeded smoothly with yields of 80% or better of the sodium 5-acetamido-2-naphthalenesulfonate. The nitration of the amide was accomplished at low temperatures, the need for which was demonstrated by the work of Morrison and Lee.[69] The product of the nitration, sodium 5-acetamido-8-nitro-2-naphthalenesulfonate was isolated in 84% yield. However, the proton NMR spectrum showed the presence of some of the hydrolyzed product. This partial hydrolysis could have occurred during the reaction or the basic work-up. The crude product was not purified since it was to be hydrolyzed in the following step. The hydrolysis was achieved using the method of Khorana, Turner and Vizsolyi.[70] The procedure involved dissolving the amide in an aqueous solution of ammonia, and leaving the solution undisturbed for twenty-four hours. The method provided an 85% yield of the product sodium 5-amino-8-nitro-2-naphthalenesulfonate. The method for the final two steps, diazotisation and coupling, were reported by Fieser.[71] The diazotisation was performed by a standard method. However, much of the diazonium salt of sodium 5-amino-8-nitro-2-naphthalenesulfonate precipitated out of solution. The dialkylaniline was mixed with a small amount of acetic acid and poured into the diazonium salt solution. The violet colored dye precipitated immediately. The work-up of each dye was different, and the percentage yields were adequate. As shown in Scheme V, each of the dyes could be converted to the zwitterionic form with concentrated acid. This was useful since the zwitterion provided an easy route to any salt through titration with the corresponding hydroxide. Actually the dimethyl analog was purified by conversion to the tetrabutylammonium salt, which was soluble in organic solvents. This made it possible to use column chromatography for purification. Subsequent conversion back to the zwitterion then allowed a route to pure samples of any salt of the dye.

Isomerization of the Azo Linkage

The photoresponsive polyether complexing agents must be capable of: (1) the light induced conversion of the trans to the cis form; (2) thermal reversion of the cis back to the trans form. Consequently, the first step necessary in the evaluation of these substances was the determination of these two processes. Upon synthesis, the UV-VIS spectrum of each compound was determined both before and after irradiation. The degree of disappearance of the spectrum characteristic of the trans compound after irradiation determined the degree of conversion to the cis isomer.

The rate of reversion of the cis to the trans isomer in the dark was reflected in the UV-VIS spectra, which provided the rate of the thermal isomerization. The derivations of the equations necessary for the calculation of the rates are discussed below.

Derivation of the Thermal Isomerization Equations

The thermal isomerization is described by the forward process of equation 1.

$$Cm_{C,org} \underset{h\upsilon}{\overset{\Delta}{\rightleftarrows}} Cm_{T,org} \qquad \text{(eq 1)}$$

Since this is a unimolecular process, the differential equation 2 may be integrated to give equation 3.

$$\frac{\delta\,[Cm_{C,org}]}{\delta\,t} = k\,[Cm_{C,org}] \qquad \text{(eq 2)}$$

$$\ln\left[\frac{[Cm_{C,org}]_o}{[Cm_{C,org}]_t}\right] = k\,t + b \qquad \text{(eq 3)}$$

In equation 3, '$[Cm_{C,org}]_o$' is the initial concentration of the cis isomer of Cm; '$[Cm_{C,org}]_t$' is the concentration of cis isomer of Cm at time 't'; 'k' is the rate constant; 't' is the time as measured from when the irradiation was discontinued; 'b' is the integration constant.

Equation 3 is linear and yields a straight line if the logarithmic term is plotted against time. The slope of the line is the rate constant and the intercept is b.

In order to simplify the calculation of the logarithmic term, it was assumed that there was a 100% conversion from the trans to the cis isomer during the photochemical isomerization (i.e. $[Cm_{C,org}]_o = [Cm_{T,org}]_{st}$), where '$[Cm_{T,org}]_{st}$' is the stoichiometric concentration of Cm in the organic solution. This assumption would not effect the slope of the line. However, it would be proven true or false by the y-intercept of the plot. If there was 100% photochemical isomerization then

$[Cm_{C,org}]_t$ at t=0 would equal $[Cm_{T,org}]_{st}$. Since the logarithmic term at t=0 would be equal to zero (ln(1) = 0), then the intercept (b) must be zero also. If the conversion in the photochemical process were not complete then the ratio of $[Cm_{T,org}]_{st}/[Cm_{C,org}]_t$ would be greater than one, and the logarithm would be some positive number related to the true photostationary state. During this experiment we observed the reappearance of the absorbance spectrum of the trans isomer. When the time of the reaction approached infinity ($t=\infty$) there was no cis isomer present and the spectrum was due to the stoichiometric concentration of the trans isomer. Therefore the absorbance at $t=\infty$ (A_∞) was proportional to the initial concentration of the cis isomer of Cm. The term $[Cm_{C,org}]_t$ was given by the difference between the stoichiometric concentration of trans isomer and the observed concentration at time t.

$$[Cm_{C,org}]_t = [Cm_{T,org}]_{st} - [Cm_{T,org}]_t \propto A_\infty - A_t \qquad \text{(eq 4)}$$

Therefore the logarithmic term was defined as 'Y' and was expressed as equation 5 following the substitution with equation 4.

$$Y \equiv \ln\left[\frac{[Cm_{C,org}]_o}{[Cm_{C,org}]_t}\right] = \ln\left[\frac{A_\infty}{A_\infty - A_t}\right] = k\,t + b \qquad \text{(eq 5)}$$

Equation 5 made the further assumption that the absorbance spectra of the trans and cis isomers do not overlap at the observed wavelength. There was some overlap, however, this was a small error which can be neglected. Therefore, a plot of $\ln\{A_\infty/(A_\infty - A_t)\}$ vs time results in a straight line whose slope was the rate of the thermal isomerization. From the intercept we could calculate the percent conversion during the photochemical isomerization. The value was given by equation 6.

$$\% \text{ conversion} = \frac{100\,[\mathrm{Cm}_{C,org}]_{t=0}}{[\mathrm{Cm}_{T,org}]_{st}} = \frac{100}{e^{b}} \qquad \text{(eq 6)}$$

The term '$[\mathrm{Cm}_{C,org}]_{t=0}$' was the concentration of Cm_C at time t=0.

An equation for the half life ($t_{1/2}$) of the thermal isomerization could also be derived. The first half life was defined as the time for one half of the starting material to go to product. However, the initial concentration of the cis isomer of Cm was dependent on the effectiveness of the photochemical isomerization. Also, it must be remembered that the experiment involves following the trans isomer of Cm. Therefore, it was necessary to calculate the concentration of Cm_T at $t_{1/2}$. This concentration should be equal to one half the difference between the final and initial concentrations of Cm_T added to the initial concentration of Cm_T, as represented in the following equation.

$$[\mathrm{Cm}_{T,org}]_{t1/2} = [\mathrm{Cm}_{T,org}]_{t=0} + ([\mathrm{Cm}_{T,org}]_{st} - [\mathrm{Cm}_{T,org}]_{t=0})/2 \qquad \text{(eq 7)}$$

Where '$[\mathrm{Cm}_{T,org}]_{t1/2}$' was the concentration of Cm_T at $t_{1/2}$; '$[\mathrm{Cm}_{T,org}]_{t=0}$' was the concentration of Cm_T at t=0; '$[\mathrm{Cm}_{T,org}]_{st}$' was the stoichiometric concentration of Cm_T.

The concentration of the trans isomer is proportional to the absorbance at any time. Therefore, equation 7 is proportional to equation 8.

$$A_{t1/2} = A_0 + (A_\infty - A_0)/2 \qquad \text{(eq 8)}$$

The term '$A_{t1/2}$' was the absorbance of Cm_T at the half life; 'A_0' was the absorbance of Cm_T at the time t=0; 'A_∞' was the absorbance of Cm_T at time t=∞.

The value of the A_0 could be obtained from the intercept of the plot described above. Equation 5 reduces to equation 9 when t=0.

$$b = \ln \left[\frac{A_\infty}{A_\infty - A_0} \right] \qquad \text{(eq 9)}$$

Equation 9 rearranges to:

$$A_0 = A_\infty - \frac{A_\infty}{e^b} \qquad \text{(eq 10)}$$

Substitution of equation 10 into equation 8 reduces to the following, after rearrangement .

$$A_{t1/2} = A_\infty - \frac{A_\infty}{2\,e^b} \qquad \text{(eq 11)}$$

Equation 11 represents the absorbance of Cm_T at $t_{1/2}$. The substitution of $A_{t1/2}$ into equation 5 allows the calculation of the half life($t_{1/2}$). After rearrangement, equation 5 reduces to equation 12.

$$t_{1/2} = \frac{\ln(2)}{k} \qquad \text{(eq 12)}$$

Measurement of Complexation Constants

The capacity of the photoresponsive polyethers for extracting salts into nonpolar media was tested by measuring the partition coefficients of metal salts in the presence of the complexing agent (Cm). The extraction equilibrium constants were obtained by shaking an aqueous solution of a metal dye salt with an organic solution of Cm followed by the spectrophotometric analysis of the two phases. The derivation of the equations necessary for the calculation of the equilibrium constants are discussed below.

Derivation of the Extraction Equations

The following equilibrium expressions describe the extraction process, if the assumption of a 1:1 complex between Cm and M^+ was maintained.

$$Cm_{org} \underset{\longleftarrow}{\xrightarrow{K_1}} Cm_{aq} \qquad \text{(eq 13)}$$

$$Cm_{aq} + M^+_{aq} \underset{\longleftarrow}{\xrightarrow{K_2}} Cm\text{-}M^+_{aq} \qquad \text{(eq 14)}$$

$$Cm\text{-}M^+_{aq} + D^-_{aq} \underset{\longleftarrow}{\xrightarrow{K_3}} Cm\text{-}M^+\text{-}D^-_{org} \qquad \text{(eq 15)}$$

Equation 13 represents the partition of the complexing agent (Cm) between the aqueous and organic phases. The constant K_1 is the partition coefficient for this process. In equation 14, Cm complexes with the cation (M^+) in the aqueous phase to form the complex ($Cm\text{-}M^+_{aq}$). The constant K_2 is the stability constant of $Cm\text{-}M^+_{aq}$. Equation 15 represents the association of $Cm\text{-}M^+$ with the aqueous anion (D^-), followed by the transport of this cation-anion complex ($Cm\text{-}M^+\text{-}D^-$) into the organic phase. Therefore the constant K_3 represents the partition coefficient of the cation-anion complex ($Cm\text{-}M^+\text{-}D^-$).

The following equilibrium expressions were derived from equations 13, 14 and 15.

$$K_1 = \frac{[Cm_{aq}]}{[Cm_{org}]} \qquad \text{(eq 16)}$$

$$K_2 = \frac{[Cm\text{-}M^+_{aq}]}{[Cm_{aq}]\,[M^+_{aq}]} \qquad \text{(eq 17)}$$

$$K_3 = \frac{[Cm\text{-}M^+\text{-}D^-_{org}]}{[Cm\text{-}M^+_{aq}]\,[D^-_{aq}]} \qquad \text{(eq 18)}$$

The above equilibrium assumed that there was only one type of Cm present during the extraction. However, when we extract with the "cis" Cm form, there was not pure cis isomer present. First of all, the photoisomerization from trans to cis isomers was on the order of a 90% conversion. Also, as soon as the light source was extinguished the cis isomer began to thermally revert back to the trans isomer. Therefore the "cis" solution was actually a mixture of cis and trans isomers and must be reflected in the equilibrium equations.

In the case where no dye or salt were present during the extraction, then only equation 13 was involved. For the trans case the following equation was derived for the partition coefficient ($K_{1,T}$) by substitution of Cm_T for Cm in equation 16.

$$K_{1,T} = \frac{[Cm_{T,aq}]}{[Cm_{T,org}]} \qquad \text{(eq 19)}$$

However, for the cis case we must remember that the organic phase was a mixture. The total amount of Cm that was observed ($[Cm_{tot,aq}]_{obs}$) in the aqueous phase after equilibrium had been established was represented by :

$$[Cm_{tot,aq}]_{obs} = [Cm_{T,aq}] + [Cm_{C,aq}] \qquad \text{(eq 20)}$$

Substitution using equation 16 for both the cis and trans isomers afforded the following equation.

$$[Cm_{tot,aq}]_{obs} = K_{1,T}\,[Cm_{T,org}] + K_{1,C}\,[Cm_{C,org}] \qquad \text{(eq 21)}$$

Equation 21 then rearranged to:

$$K_{1,C} = \frac{[Cm_{tot,aq}]_{obs}}{[Cm_{C,org}]} - \frac{K_{1,T}\,[Cm_{T,org}]}{[Cm_{C,org}]} \qquad \text{(eq 22)}$$

Equation 22 represents the partition coefficient of the cis isomer. The second term in equation 22, represents the contribution due to the trans isomer and must be subtracted from the total.

The extraction which employed both the dye and salt in the aqueous phase would allow us to calculate the combined constant (K_{123T}), which was defined as the product of the constants $K_{1,T}$, $K_{2,T}$ and $K_{3,T}$. This extraction incorporated the equilibrium equations 13, 14 and 15. The following equation represents the associated cation-anion complex of the trans isomer (Cm_TMD_{org}) in the organic phase, which was derived after combination and rearrangement of equations 16, 17 and 18.

$$[Cm_TMD_{org}] = K_{1,T}\, K_{2,T}\, K_{3,T}\, [Cm_{T,org}]\, [M^+_{aq}]\, [D^-_{aq}] \qquad \text{(eq 23)}$$

Substitution and rearrangement then provided the following equation.

$$K_{123T} = \frac{[Cm_TMD_{org}]}{[Cm_{T,org}]\, [M^+_{aq}]\, [D^-_{aq}]} \qquad \text{(eq 24)}$$

In a similar extraction with the "cis" solution, we would have to account for the fact that the solution was a mixture. At equilibrium, the total amount of the associated complex in the organic phase($[CmMD_{tot,org}]$) could be represented by the following equation.

$$[CmMD_{tot,org}] = [Cm_TMD_{org}] + [Cm_CMD_{org}] \qquad \text{(eq 25)}$$

Substitution with equation 23 for both the cis and trans isomers afforded:

$$[CmMD_{tot,org}] = K_{123T}\, [Cm_{T,org}]\, [M^+_{aq}]\, [D^-_{aq}] + K_{123C}\, [Cm_{C,org}]\, [M^+_{aq}]\, [D^-_{aq}] \qquad \text{(eq 26)}$$

Equation 26 rearranged to the following equation:

$$K_{123C} = \frac{[CmMD_{tot,org}]}{[Cm_{C,org}]\,[M^{+}_{aq}]\,[D^{-}_{aq}]} - \frac{K_{123T}\,[Cm_{T,org}]}{[Cm_{C,org}]} \qquad \text{(eq 27)}$$

The equations 24 and 27 allowed the calculation of the combined constants K_{123T} and K_{123C} for the trans and cis isomers, respectively. However, we would like to compare the stability constants (K_2) with those of other complexing agents. The partition coefficient K_1 was much more sensitive to small structural changes in Cm than the partition coefficient K_3. The ionic nature of the complex ($[Cm_TMD_{org}]$) should be responsible for the insensitivity of K_3. Therefore, the division of equations 24 and 27 by $K_{1,T}$ and $K_{1,C}$, respectively, provided the following equations.

$$K_{2,T}K_{3,T} = \frac{[Cm_TMD_{org}]}{K_{1,T}\,[Cm_{T,org}]\,[M^{+}_{aq}]\,[D^{-}_{aq}]} \qquad \text{(eq 28)}$$

$$K_{2,C}K_{3,C} = \frac{[CmMD_{tot,org}]}{K_{1,C}[Cm_{C,org}]\,[M^{+}_{aq}]\,[D^{-}_{aq}]} - \frac{K_{1,T}\,K_{2,T}K_{3,T}\,[Cm_{T,org}]}{K_{1,C}\,[Cm_{C,org}]} \qquad \text{(eq 29)}$$

The term K_2K_3 was employed for comparison among different complexing agents and salts.

The extra information necessary in the "cis" case was the ratio of the trans to cis isomers at the start and finish of the extraction. This information was obtained by following the thermal cis to trans isomerization. Once the rate of thermal isomerization and the original cis concentration were known, the ratio of the trans to cis isomers during extraction was easily calculated.

The above derivation hinged upon the assumption that there was a 1:1 complex between Cm and M^{+}. If there was a 2:1 complex of Cm with M^{+}, then the equilibrium equations 30, 31 and 32 would be employed in the derivation of the equilibrium constants.

$$Cm_{org} \overset{\longrightarrow}{\underset{\longleftarrow}{K_1}} Cm_{aq} \qquad \text{(eq 30)}$$

$$2\,Cm_{aq} + M^+_{aq} \overset{\longrightarrow}{\underset{\longleftarrow}{K_2}} Cm_2M^+_{aq} \qquad \text{(eq 31)}$$

$$Cm_2M^+_{aq} + D^-_{aq} \overset{\longrightarrow}{\underset{\longleftarrow}{K_3}} Cm_2M^+D^-_{org} \qquad \text{(eq 32)}$$

The partition coefficients $K_{1,T}$ and $K_{1,C}$ would be evaluated as with the simple 1:1 complex by equations 19 and 22, respectively. However the evaluation of the equilibrium constants K_2K_3 would differ. A similar derivation of the K_2K_3 expressions, as described above, provided equations 33 and 34.

$$K_{2,T}K_{3,T} = \frac{[(Cm_T)_2MD_{org}]}{K_{1,T}^2[Cm_{T,org}]^2[M^+_{aq}][D^-_{aq}]} \qquad \text{(eq33)}$$

$$K_{2,C}K_{3,C} = \frac{[Cm_2MD_{org}]}{K_{1,C}^2[Cm_{C,org}]^2[M^+_{aq}][D^-_{aq}]} - \frac{K_{1,T}^2K_{2,T}K_{3,T}[Cm_{T,org}]^2}{K_{1,C}^2[Cm_{C,org}]^2} \qquad \text{(eq 34)}$$

Equations 33 and 34 illustrated that for the 2:1 complex the terms $[Cm_{C,org}]$, $[Cm_{T,org}]$, $K_{1,C}$ and $K_{1,T}$ were squared and in the case of the 1:1 complex these terms were <u>not</u> squared. Therefore varying the concentration of Cm in the organic phase should distinguish between the 1:1 and 2:1 complexes.

The possibility of a 1:2 complex between Cm and M^+ was also considered. The equilibrium expressions were illustrated in the equations 35, 36 and 37 below.

$$Cm_{org} \overset{\longrightarrow}{\underset{\longleftarrow}{K_1}} Cm_{aq} \qquad \text{(eq 35)}$$

$$Cm_{aq} + 2\,M^+_{aq} \overset{\longrightarrow}{\underset{\longleftarrow}{K_2}} CmM_2{}^+{}_{,aq} \qquad \text{(eq 36)}$$

$$CmM_2{}^+{}_{,aq} + 2\,D^-{}_{aq} \underset{\longleftarrow}{\overset{\longrightarrow}{K_3}} CmM_2{}^+D_2{}^-{}_{,org} \qquad \text{(eq 37)}$$

Again the constants $K_{1,T}$ and $K_{1,C}$ could be evaluated with equations 19 and 22, resectively. The equilibrium constants K_2K_3 were expressed by the following equations 38 and 39.

$$K_{2,T}K_{3,T} = \frac{[Cm_TM_2D_{2,org}]}{K_{1,T}\,[Cm_{T,org}]\,[M^+{}_{aq}]^2\,[D^-{}_{aq}]^2} \qquad \text{(eq 38)}$$

$$K_{2,C}K_{3,C} = \frac{[CmM_2D_{2,org}]}{K_{1,C}\,[Cm_{C,org}]\,[M^+{}_{aq}]^2\,[D^-{}_{aq}]^2} - \frac{K_{1,T}K_{2,T}K_{3,T}\,[Cm_{T,org}]}{K_{1,C}[Cm_{C,org}]} \qquad \text{(eq 39)}$$

In equations 38 and 39, the terms $[M^+{}_{aq}]$ and $[D^-{}_{aq}]$ were squared and with the simple 1:1 complex these terms were not squared. Therefore varying either the salt or dye concentrations would distinguish between the 1:1 complex and the 1:2 complex.

Results

Selection of Extraction Solvent

The selection of an organic solvent, to be employed in the extraction experiment, met with some difficulty. The solvent had to meet the following requirements: (1) reasonable solubility of complexing agents; (2) could not be miscible with water; and (3) large difference in density from that of water. The last requirement was necessary to keep the time required for separation of phases after extraction at a minimum. The first choice for the class of solvent was the chlorinated hydrocarbons. Shinkai had illustrated that alkyl chlorides react with azobenzenes during the photoisomerization[41]. This restricted the choice to aryl chlorides, *o*-dichlorobenzene met all the requirements. The complexing agents Cm-1, Cm-3, and Cm-4 were soluble in *o*-dichlorobenzene. However, Cm-2 had limited solubility in *o*-dichlorobenzene. This solvent had a low solubility in water and a large difference in density with that of water.

The choice of *o*-dichlorobenzene as solvent was tested by preliminary extractions (employing dibenzo-18-crown-6 as the complexing agent with various dyes). The results showed the solvent *o*-dichlorobenzene to be deficient. The complex (CmM^+D^-) was not appreciably extracted into the organic phase. In order to increase the solubility of the complex in *o*-dichlorobenzene, it was decided that an alcohol be added to the solvent. Shinkai had also employed an alcohol in his system[46]. Cyclohexanol was chosen for the additive because of its low solubility in water and high solubility in *o*-dichlorobenzene. The addition of 1.00 percent cyclohexanol by weight in *o*-dichlorobenzene provided the increase in solubility of the complex that was desired. For future reference the index of refraction for the 1.000% and 2.000% by weight cyclohexanol in *o*-dichlorobenzene were recorded as $n_D^{25} = 1.5480$ and 1.5465, respectively.

Selection of Light Source and Determination of Extinction Coefficients of Complexing Agents

In order to obtain thermal cis-trans isomerization rates, the extinction coefficients (ε) were obtained in a variety of solvents.

The extinction coefficients listed in Table I correspond to the absorption maxima for the trans isomers of each of the complexing agents at 367 nm (λ_{max}). The absorption spectra of the complexing agents were very similar, since they all contained the identical chromophore (see Appendix I). The extinction coefficients of the complexing agents at the λ_{max} were in the vicinity of 3.5 x 10^4 L $mol^{-1}cm^{-1}$, as shown in Table I. The complexing agents had two other absorption bands. The band at 245 nm had an extinction coefficient that ranged about half that of the value for the λ_{max}. The values of the extinction coefficients obtained for Cm-1 and Cm-4 at 245 nm in methanol were 1.60±0.07 x 10^4 and 1.62±0.01 x 10^4 L $mol^{-1}cm^{-1}$, respectively. The band at 450 nm was a shoulder with an extinction coefficient less than one tenth that of the value for the λ_{max}. The values of the extinction coefficients obtained for Cm-1 and Cm-4 at 450 nm in methanol were 2.59±0.07 x 10^3 and 2.49±0.06 x 10^3 L $mol^{-1}cm^{-1}$, respectively.

An efficient way to photoisomerize the trans isomer into the cis had to be found before we could observe the thermal cis-trans isomerization. A number of light sources were tried and the results are listed in Table II.

Table I

Extinction Coefficients of Trans Isomers of Complexing Agents in Various Solvents at 25 °C and 367 nm (λ_{max}).

Solvent	Cm-1 $\varepsilon \times 10^{-4}$ [a,b]	Cm-2 $\varepsilon \times 10^{-4}$ [a,b]	Cm-3 $\varepsilon \times 10^{-4}$ [a,b]	Cm-4 $\varepsilon \times 10^{-4}$ [a,b]
o-dichlorobenzene*	3.39 ±0.09	3.60 ±0.08	3.51 ±0.08	3.17 ±0.03
water	3.58 ±0.04	3.73 ±0.06	3.68 ±0.05	3.47 ±0.03
methanol	3.64 ±0.09		3.62 ±0.03	3.52 ±0.02
octanol	3.19 ±0.08			
o-dichlorobenzene	3.40 ±0.06			
chlorobenzene	3.56 ±0.08			
toluene	3.65 ±0.11			
benzene	3.76 ±0.10			

*) Contains 1.00% by weight cyclohexanol.

a) Calculated from ε= absorbance/(conc. x path length), all absorbances were 0.8 or larger. Units were (L $mol^{-1}cm^{-1}$).

b) Average of minimum of four trials with standard deviation shown.

Table II

Photostationary States of Cm-1 Listed as Percent Conversion Trans-Cis,
in *o*-Dichlorobenzene* at Ambient Temperature,
Irradiation with Various Light Sources for 15 min.

Source	% Conversion Trans-Cis[a]
Tungsten 150 W	18
Florescent Cool White 20 W	18
Florescent Black 20 W	47
Mercury Arc 1000 W	33
Mercury Arc 1000 W, BP 520[b]	17
Mercury Arc 1000 W, BP 355[c]	89

*) Contains 1.00% by weight cyclohexanol.

a) Data calculated by method described on page 73: Experiment and Calculation of the Rate of the Thermal Isomerization.

b) BP 520 was a band pass filter centered at 520 nm.

c) BP 355 was a band pass filter centered at 355 nm.

The most convenient sources were chosen first, namely the 150 watt tungsten bulb and the 20 watt cool white fluorescent bulb. They both provided a photostationary state of 18% for the trans-cis isomerization. Although these results were poor, it was obvious that the photoisomerization was facile. Also, the handling of the trans isomer would have to be carried out in the dark. The use of the 20 watt black fluorescent bulb, which had an emission maximum near 357 nm, provided a 47% photoisomerization. This was encouraging, but the goal was to attain higher percent conversions. Therefore, a 1000 watt mercury arc lamp was employed, but only a 33% photoismerization resulted. This was surprising in light of the results obtained from the 20 watt black fluorescent lamp. These results suggested that not only the intensity but the wavelength of light was important to effect the photoisomerization. Band pass filters were employed, which would allow windows of light 50-100 nm wide to pass to the sample. In conjunction with the 1000 watt mercury arc lamp, the 520 nm band pass filter (which would irradiate the shoulder centered at 450 nm, and not the λ_{max} at 367 nm) provided a 17% conversion. The use of the 355 nm band pass filter (which would irradiate the main band of the trans isomer only) provided an 89% conversion. With the use of any of the light sources, the final photoisomeric equilibrium was always independent of the isomeric composition before irradiation. This had been observed by Fisher, Frankel, and Wolovsky[72] on various azo compounds.

The idea suggested for the use of photoresponsive complexing agents was to induce complexation by irradiation and decomplexation by the thermal cis-trans isomerization in the dark. However, a facile decomplexaton may be attained by switching the wavelength of irradiation especially if the thermal isomerization is slow.

Thermal Isomerizations Results

A number of thermal isomerization experiments on the complexing agents were accomplished once the irradiation technique had been perfected. The thermal isomerization rates, half-lives, and photostationary states of the complexing agents are listed in Table III.

Table III

Thermal Cis-Trans Isomerization Rates, Half-Lives and
Photostationary States of Complexing Agents in *o*-Dichlorobenzene* at 25 °C.

Compound	$k \times 10^5 (sec^{-1})^{a,b}$	$t_{1/2}(min)^{a,b}$	% Conversion Trans-Cis^{a,b}
Cm-1	3.71 ±0.35	314 ±28	89.8 ±1.5
Cm-2	3.04 ±0.42	379 ±29	56.0 ±2.3
Cm-3	3.81 ±0.19	304 ±16	90.0 ±0.9
Cm-4	2.91 ±0.05	398 ±7	88.3 ±1.8

*) Contains 1.00% by weight cyclohexanol.

a) Average of a minimum of four trials with standard deviations shown.

b) Data calculated by method described on page 73 : Experiment and Calculation of the Rate of the Thermal Isomerization.

As illustrated by Table III the rates of the thermal isomerizations are slow for each of the complexing agents in the extraction solvent. This was exemplified by the half-lives which range from five to six hours. Also listed in Table III are the average photostationary states for the complexing agents. For Cm-2 the photoisomeric percent conversion was low as compared with the other complexing agents. Cm-2 was the only complexing agent with benzene rings in the polyether chains. The presence of the benzene rings must have adversely affected the photostationary state.

The complexing agent Cm-1 was photoisomerized in a number of different solvents, as shown in Table IV.

Table IV

Thermal Cis-Trans Isomerization Rates, Half-lives and Photostationary States of Cm-1 in Various Solvents at 25 °C.

Solvent	k x $10^5(sec^{-1})^a$	$t_{1/2}(min)^a$	% Conversion Trans-Cis^a
o-dichlorobenzene*	3.71 ±0.35	314 ±28	89.8 ±1.5
o-dichlorobenzene	3.73 ±0.05	309 ±5	87.9 ±3.5
octanol	3.35 ±0.06	345 ±4	87.6 ±2.0
chlorobenzene	3.28 ±0.07	352 ±7	91.9 ±9.0
toluene	3.19 ±0.04	362 ±4	94.0 ±7.9
benzene	2.96 ±0.02	390 ±3	95.7 ±3.7
water	43.9 ±0.1	26.3 ±0.1	90.7 ±1.1
0.01 N LiCl(aq)	42.9 ±0.3	26.9 ±0.2	83.4 ±1.6
0.01 N NaCl(aq)	40.5 ±0.1	28.6 ±0.1	87.9 ±0.6
0.01 N KCl(aq)	38.3 ±0.2	30.2 ±0.1	88.9 ±1.2
0.01 N CsCl(aq)	38.7 ±0.2	29.9 ±0.1	94.5 ±2.3

*) Contains 1.00% by weight cyclohexanol.

a) Data calculated by method described on page 73 :Experiment and Calculation of the Rate of the Thermal Isomerization.

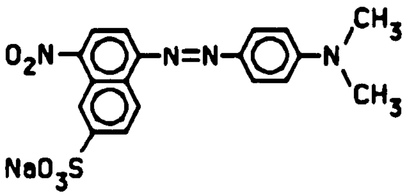
Inspection of the organic solvents employed suggests that the rate of thermal isomerization increases and the percent photoisomeric conversion decreases, with increasing polarity. The effect of solvent on the thermal isomerization of azo compounds had been previously investigated[25-33]. In the aqueous system there was a tenfold increase in the rate of thermal isomerization over that in the organic media. The effect of salt in the aqueous system slightly decreased the thermal isomerization rate. It was curious that the trend of the decrease in rate seemed to reflect the order of complexation of the alkali metals with Cm-1. The results also illustrated a trend, in the photostationary state, of a slight steady increase along the alkali metals. The cesium solution had the highest percent conversion.

Selection of Dye

The extraction experiment measured the ability of a complexing agent to extract a cation into the organic phase. An anion was extracted also, to observe electronic neutrality in the organic phase. The requirements for the anion were as follows: (1) to be lipophilic; (2) to have a single negative charge; (3) not to complex with cations; and (4) to have an absorption spectrum that was sufficiently different from the complexing agents. The fourth requirement suggested that the anion have an absorption band in the visible region at wavelengths longer than 500 nm. (The absorption spectra of the complexing agents Cm-1, Cm-2, Cm-3, and Cm-4 tailed to 500 nm in the visible region, as shown in the UV spectra found in Appendix I.)

The dye literature was reviewed for a dye that would meet all the above requirements, but to no avail. It was realized that the synthesis of a dye was necessary. A number of dyes were designed and synthesized, as described above. The dyes synthesized are homologues of sodium 5-(4'-N,N-dialkylaminophenylazo)-8-nitro-2-naphthalenesulfonate. The size of the alkyl group (e.g. dimethyl, diethyl or dibutyl) greatly influenced the solubility of the dye in organic solvents. In fact the dibutyl homologue is extracted from water into toluene without the aid of a phase transfer catalyst. Conversely, the dimethyl homologue can only be extracted from water into an organic solvent in the presence of a phase transfer catalyst. Therefore, the dye selected for the extraction was sodium 5-(4'-N,N-dimethylaminophenylazo)-8-nitro-2-naphthalenesulfonate (D1) shown in Figure 5.

Figure 5



(D1)

Table V

Extinction Coefficients[a] of Dye (D1) in Various Solvents at λ_{max} and 25 °C

Solvent	$\varepsilon \times 10^{-4}$ (L mol^{-1}cm^{-1})[b]
H_2O[c]	2.89
0.01N LiCl(aq)[c]	2.84
0.01N NaCl(aq)[c]	2.75
0.01N KCl(aq)[c]	2.76
0.01N CsCl(aq)[c]	2.71
o-dichlorobenzene*[d]	2.74

*) Contains 1.00% by weight cyclohexanol.

a) Calculated from ε= absorbance/(conc. x path length), all absorbances were 0.8 or larger.

b) Average of minimum of four trials with standard deviation of 0.02 or better.

c) Employed the lithium salt of dye (D1).

d) Found using 10^{-3} M organic solution of dibenzo-18-crown-6 with 3×10^{-5} M potassium salt of dye (D1).

The λ_{max} of the dye (D1) was at 520 nm in the visible region. The extinction coefficients of the dye (D1) in various solvents are listed in Table V. There seems to be little variation in the extinction coefficients as we proceed through the aqueous salt solutions including the organic extraction solvent (1.00% by weight cyclohexanol in *o*-dichlorobenzene).

Extraction of Alkali Metals with Dibenzo-18-crown-6

To test the selection of the extraction solvent and dye, extractions of the alkali metals with dibenzo-18-crown-6 were undertaken. The results of these extractions are listed in Table VI.

Table VI

Extraction Equilibrium Constants K_{123} for Dibenzo-18-crown-6 with Alkali metals at 25 °C between Water and *o*-Dichlorobenzene*, Compared with Extraction Constants (K_{ex}) between Water and Benzene.[73]

Salt	K_{123} x 10^{-3}(L^2mol^{-2})^a	K_{ex} x 10^{-2} (L^2mol^{-2})^b
LiCl	2.49 ±0.07	--
NaCl	20.2 ±0.3	1.6
KCl	1700 ±50	450
CsCl	114 ±3	12

*) Contained 1.00% by weigth cyclohexanol.

a) The data is found in Appendix V Table A. The methods of analyses are described on pages 84, 96: (1) Extraction Method #4; (2) Calculation of K_{123} for Dibenzo-18-crown-6. Each value is the average of six trials.

b) Data obtained from A. Sadakane, T. Iwachido and K. Toei by the extraction of alkali metal picrates with Dibenzo-18-crown -6.[73]

The values of K_{123} obtained for dibenzo-18-crown-6 in these experiments illustrated the same tendencies as found by Sadakane and coworkers[73], in the water-benzene system. The differences in order of magnitude of the constants K_{123} and K_{ex} are explained by the use of the more polar organic solvent (o-dichlorobenzene compared with benzene) and the more lipophilic anion (dye D1 compared with picrate). These changes greatly increased the values of K_1 and K_3 in the present case.

The values of K_1 and K_3 for the dibenzo-18-crown-6 system were difficult to obtain separately since the absorption spectrum of the complexing agent was masked by the solvent *o*-dichlorobenzene. Therefore, the stability constants (K_2) were not obtained separately for comparison with the literature. The variance illustrated in Table VI for K_{123} should be a reflection of K_2. The values of the partition coefficients K_1 and K_3 should be affected little by varying the alkali metal salt. As can be seen from Table VI, the data reflects the variance in the stability constants for dibenzo-18-crown-6 with the alkali metals from the literature[5,74-76].

Partition Coefficients (K_1) of Complexing Agents

The values of the partition coefficients (K_1) between water and the organic extraction solvent for complexing agents Cm-1, Cm-2, Cm-3, and Cm-4 are listed in Table VII.

Table VII

Partition Coefficients (K_1) for Complexing Agents
between Water and *o*-Dichlorobenzene* at 25 °C.

Compound	$K_1 \times 10^4$ [a]		$K_{1,C}/K_{1,T}$ [a]
Cm_T-1	1.41	±0.15	33.2
Cm_C-1	46.8	±5.6	
Cm_T-2	0.177	±0.019	3.06
Cm_C-2	0.543	±0.065	
Cm_T-3	0.407	±0.043	3.31
Cm_C-3	1.35	±0.16	
Cm_T-4	11.5	±1.2	10.4
Cm_C-4	121	±14	

*) Contains 1.00% by weight cyclohexanol.

a) The data is found in Appendix V Table B. The methods of analyses are described on pages 78,84 & 86 :(1) Extraction Method #1; (2) Calculation of Partition Coefficient $K_{1,T}$; (3) Calculation of Partition Coefficient $K_{1,C}$.

It should be realized that because of the way K_1 was expressed (equations 19 and 22) all of the complexing agents, both cis and trans, overwhelmingly favor the organic phase. Inspection of Table VII illustrates some interesting points concerning the relation of structure and solubility. One would expect that the solubility of Cm-2 would be decreased in water, with respect to Cm-1, due to the addition of two aromatic rings to the structure, as was observed. One might expect that the addition of two ethylene oxide units to the structure of Cm-1 would increase the solubility in water. The results seemed to depend on the point of attachment of the ethylene oxide units. The complexing agents Cm-3 and Cm-4 were structural isomers, both had two ethylene oxide units more than Cm-1. The straight chain isomer, Cm-4 had a partition coefficient for the trans isomer that was 8.2 times that of Cm-1. The branched chain isomer Cm-3, had a partition coefficient for the trans isomer that was 3.5 times smaller than that of Cm-1. The same general trend appeared for the cis isomers.

For all cases, the cis isomers are more soluble in water than are the corresponding trans isomers. However, there was considerable variance in the ratios of $K_{1,C}$: $K_{1,T}$ among the complexing agents, as shown in Table VII. If the increase in solubility in water of the cis isomer is purely due to the polarity increase of the cis isomer over the trans, then the ratios of $K_{1,C}$: $K_{1,T}$ would be constant for all the complexing agents. The variance in the ratios could be explained by the solvation of the polyether chains being adversely affected by steric bulk.

The solvent effects on the partition coefficient (K_1) were studied for Cm-1. The K_1 values are listed in Table VIII, for Cm-1 between water and various organic solvents.

Table VIII

Partition Coefficients (K_1) for Cm-1 between Water and
Various Organic Solvents at 25 °C.

Solvent	$K_{1,T}$ x10^4 ^{a}	$K_{1,C}$ x10^4 ^{a}	$K_{1,C}/K_{1,T}$
o-dichlorobenzene*	1.33 ±0.13	44.2 ±5.3	33.2
o-dichlorobenzene	1.16 ±0.12	23.4 ±2.8	20.2
octanol	4.16 ±0.42	77.3 ±9.3	18.6
chlorobenzene	2.97 ±0.30	33.5 ±4.0	11.3
toluene	10.9 ±1.1	34.0 ±4.0	3.11
benzene	8.33 ±0.83	45.4 ±5.4	5.44

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table C. The methods of analyses are described on pages 78, 84 & 86: (1) Extraction Method #1; (2) Calculation of Partition Coefficient $K_{1,T}$; (3) Calculation of Partition Coefficient $K_{1,C}$.

The magnitude of the partition coefficients ($K_{1,T}$) for the trans isomer increased when the polarity of the organic solvent decreased. The partition coefficients ($K_{1,C}$) for the cis isomer remained unchanged. The net result was a lowering of the $K_{1,C}$: $K_{1,T}$ ratio for Cm-1.

Determination of the Stoichiometry of the Complex Cm-M^+

The ratio of Cm:M^+ in the complex Cm-M^+ had to be determined in order to utilize the proper extraction equilibrium equations. As explained earlier, at least three ratios of Cm:M^+ (1:1, 2:1 and 1:2) might be formed. The concentrations of Cm and M^+ were varied and the possible "constants" K_2K_3 for the trans and cis isomers were evaluated with equations 28, 29, 33, 34, 38 and 39. Tables IX, X and XI illustrate the results for the extraction of potassium chloride with complexing agents Cm-1, Cm-3 and Cm-4, respectively.

For each table, the concentration of Cm in trial 2 was reduced to 1/3 of the value in trial 1, and the concentrations of the $[D^-aq]$ and $[M^+]$ remained essentially unchanged. Similarly, the concentration of M^+ in trial 3 was 1/3 the value in trial 1, and the concentrations of the $[D^-aq]$ and [Cm] remained essentially unchanged. The experimentally determined data were used to evaluate the "constants" K_2K_3 for each of the Cases I(1:1), II(2:1) and III(1:2). The equations that provided "true" constants would yield values that remained unchanged for each trial. As can be seen from Tables IX, X and XI, the values for the Case I (1:1) remained unchanged over these concentrations. These facts suggest that the simple 1:1 ratio for the complex Cm-M^+ was the correct one in these cases.

Table IX

Determination of Stoichiometry of Complexes for Cm-1 with Alkali Metals. Extraction Data for Cm-1 in *o*-Diclorobenzene* with Aqueous KCl at 25 °C.

Species (mol/L)	Trial 1[a,c]		Trial 2[b,c]		Trial 3[b,c]	
	Trans	Cis	Trans	Cis	Trans	Cis
$[M^+_{aq}] \times 10^2$	1.00	1.00	1.00	1.00	0.334	0.334
$[Cm_{T,org}] \times 10^3$	6.96	1.76	2.21	0.740	6.58	3.13
$[Cm_{C,org}] \times 10^3$	-	5.20	-	1.45	-	3.45
$[CmMD_{org}] \times 10^7$	3.67	5.92	0.814	1.36	0.836	1.13
$[D^-_{aq}] \times 10^4$	1.31	1.28	0.966	1.03	0.935	0.853
Calc Case I (1:1) K_2K_3 (L^2mol^{-2})						
$K_{2T}K_{3T} \times 10^{-5}$	2.85		2.71		2.89	
$K_{2C}K_{3C} \times 10^{-4}$		1.61		1.53		1.67
Calc Case II (2:1) K_2K_3 (L^3mol^{-3})						
$K_{2T}K_{3T} \times 10^{-11}$	2.91		8.72		3.12	
$K_{2C}K_{3C} \times 10^{-9}$		0.751		2.67		1.29
Calc Case III (1:2) K_2K_3 (L^4mol^{-4})						
$K_{2T}K_{3T} \times 10^{-11}$	2.18		2.81		9.27	
$K_{2C}K_{3C} \times 10^{-10}$		1.26		1.46		6.11

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table G.

b) The data can be found in Appendix V Table D.

c) The methods of analyses are described on pages 82, 91, 91 & 93 :(1) Extraction Method #3; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #3; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

Table X

Determination of Stoichiometry of Complexes for Cm-3 with Alkali Metals. Extraction Data for Cm-3 in *o*-Diclorobenzene* with Aqueous KCl at 25 °C.

Species (mol/L)	Trial $1^{a,c}$		Trial $2^{b,c}$		Trial $3^{b,c}$	
	Trans	Cis	Trans	Cis	Trans	Cis
$[M^+_{aq}] \times 10^2$	1.00	1.00	1.00	1.00	0.334	0.334
$[Cm_{T,org}] \times 10^3$	6.35	1.60	2.21	0.476	5.68	2.65
$[Cm_{C,org}] \times 10^3$	-	4.74	-	1.73	-	3.03
$[CmMD_{org}] \times 10^7$	1.12	7.39	0.317	2.26	0.261	1.27
$[D^-_{aq}] \times 10^4$	1.25	1.24	0.986	1.03	0.995	0.947
Calc Case I (1:1) K_2K_3 (L^2mol^{-2})						
$K_{2T}K_{3T} \times 10^{-5}$	3.47		3.58		3.44	
$K_{2C}K_{3C} \times 10^{-5}$		8.96		9.11		8.88
Calc Case II (2:1) K_2K_3 (L^3mol^{-3})						
$K_{2T}K_{3T} \times 10^{-12}$	1.34		3.99		1.50	
$K_{2C}K_{3C} \times 10^{-12}$		1.44		3.99		2.29
Calc Case III (1:2) K_2K_3 (L^4mol^{-4})						
$K_{2T}K_{3T} \times 10^{-11}$	2.77		3.64		10.4	
$K_{2C}K_{3C} \times 10^{-11}$		7.23		8.84		28.2

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table H.

b) The data can be found in Appendix V Table E.

c) The methods of analyses are described on pages 82, 91, 91 & 93 :(1) Extraction Method #3; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #3; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

Table XI

Determination of Stoichiometry of Complexes for Cm-4 with Alkali Metals. Extraction Data for Cm-4 in *o*-Diclorobenzene* with Aqueous KCl at 25 °C.

Species	Trial $1^{a,c}$		Trial $2^{b,c}$		Trial $3^{b,c}$	
(mol/L)	Trans	Cis	Trans	Cis	Trans	Cis
$[M^+_{aq}] \times 10^2$	1.00	1.00	1.00	1.00	0.334	0.334
$[Cm_{T,org}] \times 10^3$	6.70	0.879	2.21	0.377	6.58	4.02
$[Cm_{C,org}] \times 10^3$	-	5.82	-	1.84	-	2.57
$[CmMD_{org}] \times 10^7$	59.0	57.6	20.8	18.5	19.5	15.3
$[D^-_{aq}] \times 10^4$	0.887	0.931	0.958	0.915	0.884	0.717
Calc Case I (1:1) K_2K_3 (L^2mol^{-2})						
$K_{2T}K_{3T} \times 10^{-5}$	8.63		8.50		8.74	
$K_{2C}K_{3C} \times 10^{-4}$		7.55		7.42		7.63
Calc Case II (2:1) K_2K_3 (L^3mol^{-3})						
$K_{2T}K_{3T} \times 10^{-11}$	1.12		3.33		1.15	
$K_{2C}K_{3C} \times 10^{-9}$		1.22		3.95		4.09
Calc Case III (1:2) K_2K_3 (L^4mol^{-4})						
$K_{2T}K_{3T} \times 10^{-11}$	9.73		8.87		29.6	
$K_{2C}K_{3C} \times 10^{-10}$		8.04		8.19		42.1

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table I.

b) The data can be found in Appendix V Table F.

c) The methods of analyses are described on pages 82, 91, 91 & 93 :(1) Extraction Method #3; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #3; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

Extraction Equilibrium Constants K_2 and K_3 for Complexing Agents

The equilibrium constants of K_2 and K_3 were determined for the complexing agents Cm-1, Cm-3 and Cm-4. The low solubility of Cm-2 in the extraction solvent made it impossible for us to obtain values for the equilibrium constants for Cm-2 via the extraction methods outlined. The results for Cm-1 with the alkali metals are listed in Table XII . The product of the constants K_2 and K_3 are listed in Table XII along with the ratios of K_2K_3 for the trans and cis isomers. The values of K_2K_3 for the cis isomer seem to remain constant among the different alkali metals. However, the values of K_2K_3 for the trans isomer are higher for potassium and sodium. This is also indicated by the ratios for these two cases.

Table XIII and Table XIV similarly represent the results obtained for the other complexing agents, Cm-3 and Cm-4, respectively.

In Table XIV the values of K_2K_3 for Cm-4 reflect similar tendencies to those of Cm-1. The values for potassium and sodium are larger for the trans isomer. The differences between the values for Cm-1 and Cm-4 are that the values for Cm-4 are larger as exemplified by the factor of five in the sodium case. However, the values for K_2K_3 cis for both Cm-1 and Cm-4 were essentially the same. The net result is larger ratios in favor of the trans isomer for Cm-4.

In Table XIII the values of K_2K_3 for the trans isomer of Cm-3 are approximately the same as that of Cm-4 in Table XIV. However, the values of K_2K_3 for the cis isomer of Cm-3 are forty times those of Cm-1 or Cm-4. Correspondingly, the ratios of K_2K_3 for the trans to cis isomers are low, in favor of the cis isomer. For Cm-3 the cis isomer complexes cations better than does the trans isomer. There seems to be little specificity among the different alkali metals.

Table XII

Equilibrium Constants K_2K_3[a] for Cm-1 in *o*-Dichlorobenzene* at 25 °C.

Type Cm, M^+ [b]	$[CmMD_{org}]$ (mol/L)10^7	$[Cm_{T,org}]$ (mol/L)10^3	$[Cm_{C,org}]$ (mol/L)10^3	$[D^-_{aq}]$ (mol/L)10^4	K_2K_3[c] $x10^{-5}$	$\frac{K_2K_{3T}}{K_2K_{3C}}$
Cm_T-1, Li	1.50	7.00	...	1.41	1.08	3.42
Cm_C-1, Li	12.8	1.02	5.98	1.42	0.316	
Cm_T-1, Na	2.02	6.97	...	1.26	1.62	7.71
Cm_C-1, Na	7.14	1.49	5.48	1.24	0.211	
Cm_T-1, K	3.67	6.96	...	1.31	2.84	17.6
Cm_C-1, K	5.92	1.76	5.20	1.28	0.162	
Cm_T-1, Cs	1.04	7.01	...	1.27	0.829	2.00
Cm_C-1, Cs	1.37	1.46	5.55	1.25	0.415	

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table G. The methods of analyses are described on pages 82, 91, 91 & 93 :(1) Extraction Method #3; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #3; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

b) Concentration of alkali metal chloride $[M^+] = 0.0100$ M for all cases.

c) The units of K_2K_3 are L^2mol^{-2}.

Table XIII

Equilibrium Constants K_2K_3[a] for Cm-3 in *o*-Dichlorobenzene* at 25 °C.

Type Cm, M^+ [b]	$[CmMD_{org}]$ (mol/L)10^7	$[Cm_{T,org}]$ (mol/L)10^3	$[Cm_{C,org}]$ (mol/L)10^3	$[D^-_{aq}]$ (mol/L)10^4	K_2K_3[c] $x10^{-5}$	$\frac{K_2K_{3T}}{K_2K_{3C}}$
Cm_T-3, Li	1.96	6.57	...	1.32	5.57	0.526
Cm_C-3, Li	10.2	1.61	4.96	1.36	10.6	
Cm_T-3, Na	0.972	6.57	...	1.23	2.96	0.308
Cm_C-3, Na	5.66	3.34	3.22	1.24	9.58	
Cm_T-3, K	1.12	6.35	...	1.25	3.49	0.330
Cm_C-3, K	7.39	1.60	4.74	1.24	8.97	
Cm_T-3, Cs	2.27	6.29	...	1.24	7.17	0.499
Cm_C-3, Cs	9.43	2.22	4.06	1.11	14.3	

*) Contains 1.00% by weight cyclohexanol.

a) The data can be found in Appendix V Table H. The methods of analyses are described on pages 82, 91, 91 & 93 :(1) Extraction Method #3; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #3; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

b) Concentration of alkali metal chloride $[M^+] = 0.0100$ M for all cases.

c) The units of K_2K_3 are L^2mol^{-2}.

Table XIV

Equilibrium Constants K_2K_3[a] for Cm-4 in *o*-Dichlorobenzene* at 25 °C.

Type Cm, M^+ [b]	$[CmMD_{org}]$ (mol/L)10^7	$[Cm_{T,org}]$ (mol/L)10^3	$[Cm_{C,org}]$ (mol/L)10^3	$[D^-_{aq}]$ (mol/L)10^4	K_2K_3[c] $x10^{-5}$	$\frac{K_2K_{3T}}{K_2K_{3C}}$
Cm_T-4, Li	51.4	6.70	...	1.23	5.44	12.8
Cm_C-4, Li	44.9	0.691	6.01	1.28	0.424	
Cm_T-4, Na	47.9	6.70	...	0.803	7.75	22.3
Cm_C-4, Na	35.9	0.680	6.02	1.15	0.347	
Cm_T-4, K	59.0	6.70	...	0.887	8.62	11.4
Cm_C-4, K	57.6	0.879	5.82	0.931	0.754	
Cm_T-4, Cs	43.7	6.70	...	1.18	4.80	9.16
Cm_C-4, Cs	50.2	0.747	5.95	1.20	0.524	

*) Contains 1.00% by weight cyclohexanol.

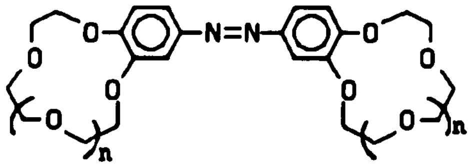
a) The data can be found in Appendix V Table I. The methods of analyses are described on pages 79, 90, 91 & 93 :(1) Extraction Method #2; (2) Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method #2; (3) Calculation of $K_{2,T}K_{3,T}$; (4) Calculation of $K_{2,C}K_{3,C}$.

b) Concentration of alkali metal chloride $[M^+]$ = 0.0100 M for all cases.

c) The units of K_2K_3 are L^2mol^{-2}.

In order to compare the extraction abilities of the complexing agents Cm-1, Cm-3 and Cm-4 with dibenzo-18-crown-6 and the azobis(benzo crown ethers) of Shinkai[45,46], A-4 and A-5 (Figure 6), the values of K_{123} are listed in Table XV. The values of K_{123} were obtained by multipling the corresponding values of K_1 with K_2K_3. Table XV shows that the bis(polyether)azobenzenes are from 2 to 5 orders of magnitude less efficient than dibenzo-18-crown-6 and A-5 in extracting the alkali metals. The K_{123} values obtained for the bis(polyether)azobenzenes are comparable to those obtained for A-4. However, Table XV illustrates that the cis isomer of the bis(polyether)azobenzenes tend to extract more of the salt than the trans isomers. This is especially true for Cm-3, the ratios of $K_{123C}:K_{123T}$ being approximately 10. The ratios for Cm-1 tend to also favor the cis isomers. In the case of Cm-4 the values for the trans isomer are slightly greater than for the cis isomers. These results suggest that for weak complexing agents the stability constants (K_2) and the partition coefficients (K_1) should be considered when designing these compounds. The same conclusions were drawn by Yoshida and Hayano[77] when they studied the relationship between extractability and the rate of transfer of potassium ion by macrocyclic carriers in liquid membrane systems.

<u>Figure 6</u>



Azobis(benzocrown ethers) of Shinkai[45,46].

A-4 : n = 1

A-5 : n = 2

Table XV

Extraction Equilibrium Constants $K_{123}{}^{a}$ for Dibenzo-18-crown-6, Azobis(benzo crown ethers) and Bis(polyether)azobenzenes with the Alkali Metals at 25 °C between water and *o*-Dichlorobenzene*.

		Ratio		Ratio		Ratio		Ratio
Compound	Li	C:T	Na	C:T	K	C:T	Cs	C:T
DB-18-cr-6	24.9		202		17000		1140	
A-$5_T{}^b$	-		1400	0.099	43.9	63.7	1060	1.86
A-$5_C{}^b$	-		139		2800		1990	
A-4_T	-		-		0.740	0.672	0.980	2.30
A-4_C	-		-		0.473		2.25	
Cm_T-1	0.152	9.74	0.229	4.31	0.400	1.89	0.117	16.6
Cm_C-1	1.48		0.986		0.756		1.94	
Cm_T-3	0.226	6.33	0.120	10.8	0.142	8.52	0.292	6.64
Cm_C-3	1.43		1.29		1.21		1.94	
Cm_T-4	6.25	0.819	8.91	0.471	9.91	0.920	5.52	1.15
Cm_C-4	5.12		4.20		9.12		6.34	

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a) The units of the constants K_{123} are L^2mol^{-2} and the constants are multiplied by a factor of 10^{-2}.

b) Extraction constants calculated by method in Appendix VI, from data obtained from Shinkai and coworkers[45,46].

Discussion

The present study focuses on the extraction of alkali metals by photoregulated polyethers. Shinkai and co-workers[45,46] studied a similar system (azobis(benzo crown ethers) shown in Figure 6) that could be compared with the bis(polyether)-azobenzenes. The compounds A-4 and A-5 contain two crown ether rings fused to the azobenzene moiety. The extraction data of Shinkai's work was represented as percent loss of the anionic chromophore (methyl orange) from the aqueous phase, and not expressed as extraction equilibrium constants. However, there was enough information available so that the equilibrium constants (K_{123}) could be calculated as shown in Appendix VI. In Table XV the equilibrium constants are expressed as the product K_{123} for the compounds Dibenzo-18-crown-6, A-4, A-5, Cm-1, Cm-3, and Cm-4. The value of the equilibrium constants for A-5 are of the order of magnitude observed for Dibenzo-18-crown-6. This would be expected with the presence of two 15-crown-5 rings in the compound. The K_{123} cis : K_{123} trans ratio for A-5 was large for potassium only. The large ratio was reflective of the unusually low value obtained for the trans isomer with potassium relative to the other salts. The compound A-4 extraction equilibrium constants are of the same order of magnitude as the bis(polyether)azobenzenes. However, the ratios of K_{123} cis : K_{123} trans are low. The ratios obtained for Cm-1, Cm-3, and Cm-4 suggest that open chain polyethers more effectively differentiate the cis and trans isomers with a given salt.

Although the goal of an "on-off" switch was not reached with the bis(polyether)-azobenzenes studied, Table XV illustrates that an extractability difference between the cis and trans isomers exists. It is important to note that the partition coefficient K_1 (Table VII, p. 36) is a prominent factor determining the relative extractability of cis and trans isomers. Table XV shows that the cis isomer of Cm-1 extracts metals more effectively than the trans, especially for the cesium ion. However, Table XII (p. 44) indicates that the trans isomer of Cm-1 is a more effective complexing agent. The apparent contradiction is due to the $K_{1C} : K_{1T}$ ratio of 33.2, which heavily favors the cis isomer of Cm-1. The complexing agents Cm-3 and Cm-4 similarly have K_{1C} : K_{1T} ratios that favor the cis isomer. For Cm-4 the $K_{1C} : K_{1T}$ ratio is 10.8 and does not overwhelm the K_2K_3 ratios of Table XIV (p. 46) which favor the trans isomer. Therefore the ratios of K_{123} for Cm-4 are near unity but in favor of the trans isomer. For Cm-4 the trans isomers extract salts slightly better than the cis isomers. For Cm-3, the $K_{1C} : K_{1T}$ ratio of 3.3 is modest, but the K_2K_3 ratios of Table XIII (p. 45) also favor the cis isomer. Therefore, the extractability ratios for Cm-3 favor the cis isomer as shown by Table XV.

The data herein illustrate that the trans isomers of the bis(polyether)azobenzenes complex with cations. Since a 1:1 complex has been demonstrated, speculation towards the nature of the complex will be presented. In a 1:1 complex, only one of the polyether chains of the trans isomer can interact with the cation. Since there are too few oxygens in a single polyether chain, the solvent may participate in the complex. The participation of solvent in the coordination may be very effective with the hydroxyl group of the water or cyclohexanol versus the ether group of the straight chain polyether. This could explain the lower K_2K_3 values for the cis isomer of Cm-1 and Cm-4. The proximity of the second polyether chain of the cis isomer may disturb the solvation sphere of the cation and not offer enough stabilization to replace it. The comparison of a branched polyether chain (Cm-3) versus the straight chain (Cm-4) further illustrates the point of steric hindrance. In the trans isomer, the branched chain does not stabilize the cation as well as a straight chain. However, in the cis isomer the proximity of the second branch chain aids the coordination since complexation was poor with the single branched chain in the trans isomer.

When designing new compounds to use as photoregulated polyethers, a few factors should be considered. First, the stability of a complex is reflected in K_2, which is governed by the length and connectivity of the polyether chains. The long straight polyether chains seem to complex cations better than branched polyethers. Second, the partition coefficient ratio (K_{1C}:K_{1T}) for cis and trans isomers will enhance the extractability of the more favored isomer. The magnitude of the K_1 ratio is governed by the polarity difference between the trans and cis isomers. It appears that the shorter less polar polyether chains tend to increase the K_1 ratio in favor of the cis isomer(e.g. compare Cm-1 versus Cm-4). If the K_1 ratio favors the same isomer as the K_2K_3 ratio, then the greatest extractability will be obtained. Third, with the use of the proper wavelengths of light, for the irradiation of photoresponsive systems involving the azobenzene moiety, one could both "switch on" and "switch off" the photoresponsive system. Lastly, the extraction methods outlined could be employed to determine the utility of complexing agents with reasonable reliability. The reliability in this method is a function of the complexing ability of the agent employed.

Experimental

Solvents

Dimethoxyethane (Baker) was purified by drying over potassium hydroxide, followed by distillation from sodium metal in a nitrogen atmosphere, with the radical anion of benzophenone as an indicator, bp 84 °C (lit (78): bp 83.5-84.0 °C). Cyclohexanol (Fisher) was distilled from lithium aluminum hydride in a nitrogen atmosphere, bp 161 °C (lit (79): bp 160.9-161.0 °C). *o*-Dichlorobenzene (Baker Analyzed Reagent) was HPLC grade and no further purification was necessary, n^{20}_D=1.5520 (lit (80): n^{20}_D =1.5555). Water was deionized by a Continental Millipore System. The following solvents were reagent grade and utilized without further purification: acetone; benzene; chlorobenzene; *o*-chlorotoluene; diethyl ether; diisopropyl ether; dimethylsulfoxide; ethanol; methanol; methylene chloride; toluene.

Materials

Dimethylaniline (Baker Analyzed Reagent) was vacuum distilled at 78 °C(8.0 mmHg), bp 194 °C (lit (81): bp 193.5 °C). Guaiacol (Aldrich) was vacuum distilled at 69 °C (5.0 mmHg), bp 203 °C, n^{20}_D=1.5439 (lit (82): bp 202.3 °C, n^{20}_D=1.5429). Thionyl chloride (Fisher) was distilled from safflower oil under a nitrogen atmosphere in an all glass system, bp 79 °C (lit (83): 78.8 °C). The following salts were dried at 100 °C in vacuo for approximately 6 hours: barium chloride (Baker Analyzed Reagent); calcium chloride (Fisher,Anhydrous Reagent Grade); cesium chloride (Alpha); lead chloride (Fisher Certified); lithium chloride (Fisher Reagent Grade); magnesium chloride (Fisher Certified); potassium chloride (Fisher Certified); sodium acetate (Fisher Certified); sodium carbonate (Fisher Certified); sodium chloride (Fisher Certified); sodium nitrite (Fisher Certified); strontium nitrate (Baker Analyzed Reagent). The following materials were reagent grade and used as such: *p*-aminoacetanilide (Cresent); acetic anhydride (Fisher); 5-amino-2-naphthalenesulfonic acid (Kodak); boric acid (Fisher); chloroacetic acid (Aldrich); N,N-dibutylaniline (Kodak); N,N-diethylaniline (Baker); epichlorohydrin (Reidel de

Haan); 2-methoxyethanol (Aldrich); sodium hydride, 57% oil dispersion (Alpha Ventron); sodium perborate tetrahydrate (Cresent); tetrabutylammonium hydroxide, 1.0 M solution in methanol (Aldrich).

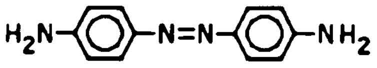
Mico analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Spectra

NMR spectra were obtained on either a Varian Associates model T-60 spectrometer or Bruker model WP 200 SY spectrometer. All chemical shifts were given in terms of the δ scale relative to tetramethylsilane. IR spectra were obtained with a Perkin-Elmer model 267 spectrophotometer. UV spectra were obtained on a Beckman model Acta C III spectrophotometer.

Syntheses

A. Synthesis of 4,4'-diaminoazobenzene



A 1000-mL three-neck round bottom flask was equipped with a mechanical stirrer, reflux condenser, and a thermometer. Into the reaction flask was placed 29.02 g (0.1032 moles) of p-aminoacetanilide(Cresent), 40.00 g (0.2605 moles) of sodium perborate tetrahydrate(Cresent), 10.00 g (0.2352 moles) of boric acid (Fisher) and 500 mL of acetic acid. The mixture was heated to 50-60 °C and stirred at this temperature for 6 hours. The flask was slowly cooled to room temperature with continued stirring. A yellow solid was collected. The 4,4'-diacetamidoazobenzene weighed 16.19 g (0.05463 moles) a 56.56% yield.

The 4,4'-diacetamidoazobenzene was used in the following hydrolysis step without purification. The entire precipitate was placed in a 500-mL one-neck round bottom flask with 300 mL of 1:1 methanol:6.0 N hydrochloric acid. The flask was equipped with a reflux condenser and a magnetic stirrer. The mixture was heated at reflux for 1.5 hours.

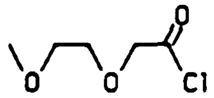
After cooling, the mixture was filtered to yield a violet solid, presumably the hydrochloride of the 4,4'-diaminoazobenzene. The entire violet precipitate plus 100 mL of water were placed in a 1000-mL three-neck round bottom flask. The flask was equipped with a stirrer and a dropping funnel. A 2.5 N sodium hydroxide solution was slowly added through the funnel until the brown solution turned yellow. The yellow product was collected and dried in vacuo at 100 °C. The dried 4,4'-diaminoazobenzene weighed 9.984 g (61.65% yield from 4,4'-diacetamidoazobenzene), mp 221-228 °C. The dried product, after the recrystallization from ethanol-water, weighed 4.314 g (26.64% yield from 4,4'-diacetamidoazobenzene) : mp 239-241 °C (lit (65): mp 238-241 °C);

IR (KBr) 3480(N-H,s), 3380(N-H, s), 3200(N-H, w), 3020(C-H, w), 1619(C-N-H, s), 1589(aromatic skeletal vibration, s), 1247(C-N, s) 832(1,4-disubstituted benzene, s) cm^{-1};

1H NMR (60 MHz, CD_3SOCD_3) δ 7.2 (AB-quartet, 8 H, aromatic), 5.8 (s, 4 H, NH_2).

B. Total Synthesis of bis-4,4'-[2-(methoxyethoxy)acetamido] azobenzene

B1. Synthesis of 2-(2-methoxyethoxy)acetyl chloride



In a 1000-mL three-neck round bottom flask was placed 58.19 g (1.376 moles) of 57% sodium hydride (Alpha Ventron) and 100 mL of dry dimethoxyethane. The flask was equipped with a mechanical stirrer, a reflux condenser with a drying tube attached, and a nitrogen inlet valve. The nitrogen was used to provide an inert atmosphere. The nitrogen valve was removed and replaced with a pressure equalizing dropping funnel, containing 54.86 g (0.7210 moles) of 2-methoxyethanol (Aldrich) in 100 mL of dimethoxyethane. This solution was added dropwise over a period of 20 minutes, while cooling the flask in an ice bath. The dropping funnel was then replaced with one containing 62.00 g (0.6561 moles) of chloroacetic acid (Aldrich) in 100 mL of dimethoxyethane. This solution was added slowly under the same conditions. After the addition was complete, the dropping funnel was removed and replaced with a stopper, the reaction flask was placed on a steam bath and the mixture was heated at reflux for 48 hours.

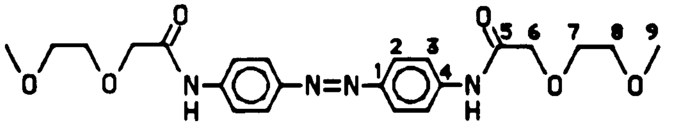
After cooling to room temperature, a solution of 94.35 g (0.7931 moles) of thionyl chloride (Fisher) in 100 mL dimethoxyethane was added dropwise while cooling the flask in an ice bath. The reaction flask was placed back on the steam bath for 24 hours.

Upon cooling to room temperature, the sodium chloride precipitated. The salt was filtered, washed, dried and weighed 79.31 g (98.31% of the theoretical yield). The filtrate was fractionally distilled to remove the dimethoxyethane, excess thionyl chloride, and the by-product 2-chloroethyl methyl ether. Approximately 500 mL of distillate were collected at a temperature range of 84-94 °C. The oil remaining was vacuum distilled to yield 41.51 g of product (41.47% yield): bp 96 °C (35 mmHg);

IR (thin film) 2940(C-H, br), 1800(Cl-C=O, s), 1140(C-O-C, s) cm^{-1};

^1H NMR (60 MHz, $CDCl_3$) δ 4.4 (s, 2 H, $OCH_2C{=}O$), 3.5 (m, 4 H, OCH_2CH_2O), 3.2 (s, 3 H, OCH_3).

B2. Synthesis of bis-4,4'-[2-(methoxyethoxy)acetamido] azobenzene



The reaction flask was a 1000-mL three-neck round bottom flask equipped with a reflux condenser with a drying tube attached, a mechanical stirrer, and a pressure equalizing dropping funnel. Into the flask was placed 8.81 g (0.0415 moles) of 4,4'-diaminoazobenzene, 20.27 g (0.1913 moles) of sodium carbonate (Fisher) and 200 mL of dimethoxyethane. The salt did not dissolve which made it necessary to stir vigorously. After heating the reaction flask to reflux, a solution of 15.46 g (0.1014 moles) of 2-(2-methoxyethoxy)acetyl chloride in 200 mL dimethoxyethane was added dropwise. The color of the reaction flask changed from light brown to blood red. When the addition was complete, the funnel was replaced with a stopper. The flask was then heated on a steam bath for 12 hours at reflux.

The red solution was cooled and filtered. The precipitate was partially dissolved in 300 mL of 1.0 N hydrochloric acid solution. There was a carbon dioxide gas discharge due to the sodium carbonate present. This acid solution turned red, presumably from unreacted starting material. The solution was filtered to afford approximately 2.0 g of a red solid. The filtrate was distilled to yield 12.0 g of the same red solid. These two crops were combined and recrystallized twice from methanol-water using norite. The dried orange crystals weighed 12.66 g (68.64% yield): mp 155-156 °C;

IR (KBr) 3320(N-H, s), 3013(C-H, w), 2930(C-H, m), 1680(C=O amide, s), 1600(aromatic skeletal vibr., s), 1530(C-N-H, s), 1140(C-O-C, s), 1090(C-O-C, s) cm^{-1}(see Appendix II);

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.11(s, 2 H, N*H*), 7.92(d of AB-q, 4 H, J=8.9 Hz, aromatic), 7.76(d of AB-q, 4 H, J=8.9 Hz, aromatic), 4.14(s, 4 H, $OCH_2C{=}O$), 3.72(m, 8 H, $CH_2OCH_2CH_2OCH_3$), 3.50(s, 6 H, OCH_3) (see Appendix III);

^{13}C NMR(50 MHz, $CDCl_3$) δ 168.5(C_5), 149.2(C_1), 139.9(C_4), 123.8(C_3), 119.8(C_2), 71.5(C_7), 71.4(C_8), 70.5(C_6), 59.1(C_9) (see Appendix IV);

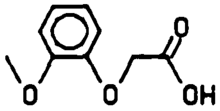
UV (Water) λ_{max} 367 nm (ε 3.58×10^4), (*o*-Dichlorobenzene) λ_{max} 367 nm (ε 3.39×10^4) (see Appendix I).

Anal. Calcd for $C_{22}H_{28}O_6N_4$: C, 59.45; H, 6.35.

Found: C, 59.36; H, 6.22.

C. Total Synthesis of bis-4,4'-[2-(2-methoxyphenoxy)acetamido]azobenzene

C1. Synthesis of 2-(2-methoxyphenoxy)acetic acid



In a 250-mL Erlenmeyer flask, 100.0 g (0.8057 moles) of guaiacol (Aldrich) was dissolved in 100 mL of 8.0 N sodium hydroxide. Also in a 500-mL Erlenmeyer flask, 302.9 g (3.205 moles) of chloroacetic acid (Aldrich) was dissolved in 400 mL of 8.0 N sodium hydroxide. The sodium salt solutions were combined in a 2000-mL two-neck round bottom flask. The reaction flask was equipped with a mechanical stirrer and a reflux condenser, then heated at reflux for 24 hours on a steam bath.

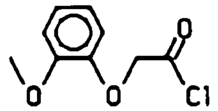
After cooling to room temperature, the reaction flask was partially neutralized with 45 mL (0.810 moles) of concentrated sulfuric acid. The product was filtered, washed with water three times and dried at 100 °C in vacuo. A weight of 99.58 g of product was obtained (67.84% yield). The filtrate was extracted three times with 300 mL of diethyl ether. The ether was distilled to yield a mixture of approximately 2 g of product and 28 g of guaiacol. This accounted for the remainder of the starting material.

The entire crude product was recrystallized from an ethyl acetate-petroleum ether (bp 30-60 °C) mixed solvent. The white needles obtained, in 87% yield from the recrystallization, were dried in vacuo at room temperature for six hours: mp 120.5-121.5 °C (lit (55): mp 122-123 °C);

IR (KBr) 3200-2500(O-H, br), 3010(C-H, w), 2920(C-H, w), 1740(C=O, s), 1250(C-O acid, s), 1125(C=C-O-C, s), 750 (1,2-disubstituted benzene, s) cm^{-1};

^1H NMR (60 MHz, CD_3COCD_3) δ 9.1 (s, 1 H, COO*H*), 6.3 (s, 4 H, aromatic), 4.1 (s, 2 H, OCH_2CO), 3.3 (s, 3 H, OCH_3).

C2. Synthesis of 2-(2-methoxyphenoxy)acetyl chloride



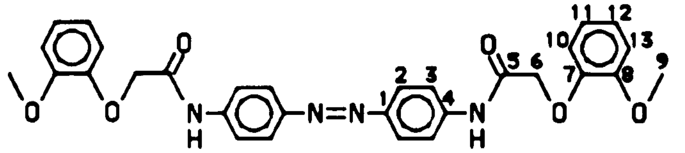
The reaction flask was a 1000-mL three-neck round bottom flask, equipped with a mechanical stirrer, dropping funnel, and reflux condenser with a drying tube attached. Into the flask was place 18.25 g (0.1002 moles) of 2-(2-methoxyphenoxy)-acetic acid in 300 mL of dimethoxyethane. The reaction flask was heated to reflux on a stream bath. Then 29.89g (0.2512 moles) of thionyl chloride in 60 mL of dimethoxyethane was added through the funnel. The flask was heated on the steam bath at reflux for 12 hours.

After cooling, the solvent was removed with a rotary evaporator to yield a yellow oil. The oil was vacuum distilled to yield a clear liquid that weighed 12.96 g (64.51% yield): bp 115 °C (0.3 mmHg), (lit(53): 151 °C(20mmHg));

IR (thin film) 3010(C-H, w), 2930(C-H, w), 1820(C=O, s), 1600(aromatic skeletal vibr., s), 1250(C-O, m), 1125(C=C-O-C, s), 750(1,2-disubstituted benzene, s) cm^{-1};

^1H NMR (60 MHz, $CDCl_3$) δ 7.0(m, 4 H, aromatic), 5.0(s, 2 H, OCH_2COCl), 3.9(s, 3 H, OCH_3).

C3. Synthesis of bis-4,4'-[2-(2-methoxyphenoxy)acetamido]azobenzene



The reaction flask was a 500-mL three-neck round bottom flask, equipped with a mechanical stirrer, dropping funnel and reflux condenser with a drying tube attached. Into the flask was placed 3.197 g (0.01506 moles) of 4,4'-diaminoazobenzene and 6.434 g (0.06070 moles) of sodium carbonate (Fisher) in 200 mL of dry diethyl ether. The reaction flask was heated to reflux. Then 6.482 g (0.03025 moles) of 2-(2-methoxyphenoxy)acetyl chloride in 50 mL ether was slowly added. The color of the reaction flask turned from brown to red. The flask was heated at reflux for 12 hours.

After cooling, the reaction flask was filtered and the crude product collected. This crude material was washed twice with dilute acid, twice with dilute base, and several times with water. The red product obtained weighed 5.201 g (68.87% yield). The product was recrystallized from chloroform-methanol to afford gold-orange needles. The melting point range was 219-222 °C. Thin layer chromatography on alumina slides, using a 1:9 methanol:methylene chloride eluent, showed this compound to be impure. Therefore the product was chromatographed on an alumina column with the same eluent as the TLC. The recovered material was recrystallized from chloroform-methanol to yield orange needles: mp 235-236 °C;

IR (KBr) 3310(N-H, m), 3010(C-H, w), 2940(C-H, w), 1685(C=O amide, s), 1600(aromatic skeletal vibr., s), 1530(C-N-H, s), 1130(C=C-O-C, s), 850(1,4-disubstituted benzene, m) cm^{-1} (see Appendix II);

^{1}H NMR (200 MHz, CD_3SOCD_3) δ 10.10(s, 2 H, N*H*), 7.85(s, 8 H, *p*-aromatic), 6.98(m, 8 H, *o*-aromatic), 4.70(s, 4 H, $OCH_2C{=}O$), 3.84(s, 6 H, OCH_3) (see Appendix III);

^{13}C NMR (50 MHz, CD_3SOCD_3) δ 167.3(C_5), 150.3(C_7), 148.8(C_1), 148.2(C_8), 141.1(C_4), 123.4(C_3), 122.9(C_{11}), 121.3(C_{12}), 116.7(C_{10}), 114.0(C_{13}), 70.1(C_6), 56.5(C_9) (see Appendix IV);

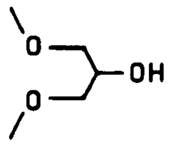
UV (Water) λ_{max} 367 nm (ε 3.73 x 10^4), (*o*-Dichlorobenzene) λ_{max} 367 nm (ε 3.60 x 10^4) (see Appendix I).

Anal. Calcd for $C_{30}H_{28}O_6N_4$: C, 66.66; H, 5.22.

Found: C, 66.25; H, 5.22.

D. Total Synthesis of bis-4,4'-[2-(1,3-dimethoxy-2-propoxy)acetamido]azobenzene

D1. Synthesis of 1,3-dimethoxy-2-propanol



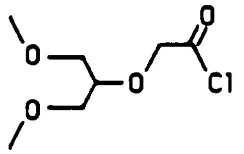
The reaction flask was a 500-mL three-neck round bottom flask. It was equipped with a mechanical stirrer, nitrogen inlet valve, and a reflux condenser with a drying tube attached. Into the flask, 200 mL of dry methanol was added. The nitrogen valve was periodically removed to allow the addition of sodium metal chunks. Over a period 0.5 hours, 9.285 g (0.4040 moles) of sodium was added to the reaction flask. When the sodium was consumed, the nitrogen valve was replaced with a pressure equalizing dropping funnel, which contained 18.53 g (0.2003 moles) of epichlorohydrin (Reidel de Haan) in methanol. After the slow addition of the epichlorohydrin, the funnel was removed. The mixture was heated on a steam bath for 15 hours.

After cooling, 10.51 g (0.1018 moles) of concentrated sulfuric acid was added to neutralize the excess methoxide. The milky solution was filtered through filter cell to remove the inorganic salts. The salts were washed twice with methanol. The washings were combined with the mother liquor. Next the methanol was removed by distillation at atmospheric pressure to yield a yellow oil. This oil was vacuum distilled to give 19.27 g (80.07% yield) of a clear liquid. Gas chromatography of this liquid, on a carbowax column at 80 °C, showed the presence of water and methanol. This impure liquid was dried over anhydrous magnesium sulfate and passed through a column of molecular sieve 4Å. The subsequent gas chromatograph did not show the presence of water or methanol: bp 76 °C (20 mmHg); $n^{20}_D = 1.4206$ (lit(52): $n^{20}_D = 1.4196$);

IR (thin film) 3450(O-H, br), 2900(C-H, s), 1450(CH_3, m), 1000(C-O-C, br) cm^{-1};

^{1}H NMR (60 MHz, $CDCl_3$) δ 4.1 (quintet, 1 H, $OCH_2C\mathit{H}CH_2O$), 3.6 (m, 10 H, $C\mathit{H}_2OC\mathit{H}_3$).

D2. Synthesis of 2-(1,3-dimethoxy-2-propoxy)acetyl chloride



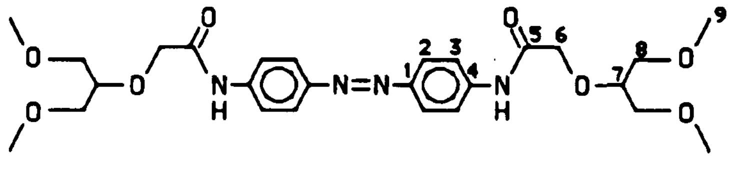
The reaction flask was a 1000-mL three-neck round bottom flask, equipped with a mechanical stirrer, nitrogen inlet valve and a reflux condenser with a drying tube attached. Into the flask was placed 16.82 g (0.4049 moles) of sodium hydride (Alpha Ventron) in 200 mL of dry dimethoxyethane. When a nitrogen atmosphere was established, the valve was removed and replaced with a pressure equalizing dropping funnel. The funnel contained 24.62 g (0.2049 moles) of 1,3-dimethoxy-2-propanol in 100 mL of dimethoxyethane. Over a period of 20 minutes, the 1,3-dimethoxy-2-propanol solution was dripped into the reaction flask. The mixture was stirred at room temperature for 0.5 hour. Through a similar dropping funnel 18.90 g (0.2000 moles) of chloroacetic acid (Aldrich) in 60 mL of dimethoxyethane was added. The reaction mixture was then heated at reflux for 12 hours. After cooling, the solvent was removed with a rotary evaporator. The carboxylate salt was then dried at 100 °C(1 mmHg) for 12 hours. The gray salt was then dissolved in 400 mL of dimethoxyethane and placed in a 1000-mL three-neck round bottom flask equipped as before. After the reaction flask was heated to reflux, 26.21 g (0.2203 moles) of thionyl chloride (Fisher) in 65 mL of dimethoxyethane was slowly added through the dropping funnel. The mixture was then heated at reflux for 12 hours.

After the reaction flask cooled to room temperature, the sodium chloride precipitate was filtered and the dimethoxyethane was removed with a rotary evaporator. The yellow oil was vacuum distilled to provide 20.42 g of a yellow liquid (51.90% yield): bp 114 °C(0.45 mmHg);

IR (thin film) 2920(C-H, s), 1810(C=O acid, s), 1130(C-O-C, s);

^{1}H NMR (60 MHz, $CDCl_3$) δ 4.5(s, 2 H, O-CH_2-C=O), 3.5(m, 11 H, $CH(CH_2OCH_3)_2$).

D3. Synthesis of bis-4,4'-[2-(1,3-dimethoxy-2-propoxy)acetamido]azobenzene



The reaction flask was a 1000-mL three-neck round bottom flask, equipped with a mechanical stirrer, dropping funnel and a reflux condenser with a drying tube attached. Into the flask was placed 4.269 g (0.0201 moles) of 4,4'-diaminoazobenzene and 8.488 g (0.0901 moles) of sodium carbonate (Fisher) in 350 mL of dimethoxyethane. The salt did not completely dissolve. The mixture was heated to reflux. Then 7.863 g (0.0399 moles) of 2-(1,3-dimethoxy-2-propoxy)-acetyl chloride in 50 mL of dimethoxyethane was slowly added to the reaction flask at reflux. The color changed from brown to blood red. The mixture was then heated at reflux for 12 hours.

Upon cooling, the reaction flask was filtered and the inorganic salts were discarded. The red filtrate was evaporated to dryness and the red solid residue was recovered. This crude product was washed twice with dilute hydrochloric acid and then several times with water. This crude material was then recrystallized from ethanol-water to afford 8.540 g of an orange product (80.17% yield). The melting point range was 148-151 °C.

Thin layer chromatography, on alumina slides using a 1:9 methanol:methylene chloride eluent, showed this product to be impure. Therefore, this material was chromatographed on a column of alumina using the same eluent as the TLC. The product was again recrystallized from ethanol-water to afford orange needles: mp 152-153 °C;

IR (KBr) 33110(N-H, s), 3010(C-H, w), 2920(C-H, m), 1695(C=O amide, s), 1600(aromatic skeletal vibr., s,), 1540(C-N-H, s), 1155(C-O-C, s), 865(1,4-disubstituted benzene, m) cm^{-1} (see Appendix II);

^{1}H NMR (200 MHz, $CDCl_3$) δ 9.59(s, 2 H, N*H*), 7.92(d of AB q, 4 H, J=8.9 Hz, aromatic), 7.76 (d of AB q, 4 H, J=8.9 Hz, aromatic), 4.26(s, 4 H, $OCH_2C=O$), 3.79(quintet, 2 H, J=5.2 Hz, $OCH(CH_2O)_2$), 3.53(d, 8 H, J=5.2 Hz, $OCH_2CH(OCH_2)CH_2O$), 3.46(s, 12 H, OCH_3) (see Appendix III);

^{13}C NMR (50 MHz, $CDCl_3$) δ 168.9(C_5), 148.9(C_1), 140.1(C_4), 123.6(C_3), 119.6(C_2), 79.3(C_6), 72.3(C_8), 69.4(C_7), 59.2(C_9) (see Appendix IV);

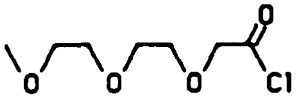
UV (Water) λ_{max} 367 nm (ε 3.68 x 10^4), (*o*-Dichlorobenzene) λ_{max} 367 nm (ε 3.51 x 10^4) (see Appendix I).

Anal. Calcd for $C_{26}H_{36}O_8N_4$: C, 58.64; H, 6.81.

Found: C, 58.92; H, 6.58.

E. Total Synthesis of bis-4,4'-[2-[2-(2-methoxyethoxy)ethoxy]acetamido]azobenzene

E1. Synthesis of 2-[2-(2-methoxyethoxy)ethoxy]acetyl chloride



The reaction flask was a 500-mL three-neck round bottom flask equipped with a mechanical stirrer, reflux condenser and a nitrogen inlet valve. Into the flask was placed 9.96 g (0.2358 moles) of sodium hydride (Alpha Ventron) in 100 mL of dimethoxyethane. The nitrogen valve was used to provide an inert atmosphere. Then the nitrogen valve was replaced with a dropping funnel containing 14.85 g (0.1236 moles) of 2-(2-methoxyethoxy)ethanol (Aldrich) in 50 mL dimethoxyethane. The solution was added dropwise while cooling the reaction flask. Similarly a solution of 10.61 g (0.1122 moles) of chloroacetic acid (Aldrich) in 50 mL dimethoxyethane was added. The reaction flask was heated on a steam bath for 24 hours.

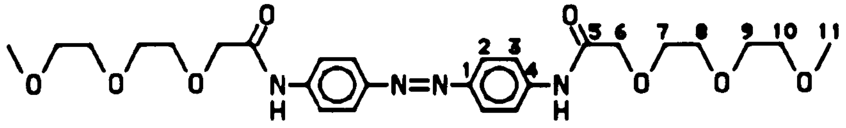
After cooling to room temperature, 0.6173 g (0.0114 moles) of 88% formic acid was added to neutralize the excess alkoxide. Next, the solvent was distilled at atmospheric pressure. The removal of the excess alcohol was accomplished at 100 °C and 1 mmHg over a period of 12 hours. The dried residue was dissolved in dimethoxyethane and treated with 14.68 g (0.1234 moles, excess of 10%) of thionyl chloride in 30 mL dimethoxyethane. The flask was heated on a steam bath for 15 minutes.

After cooling the sodium chloride was filtered. The filtrate was distilled at atmospheric pressure to yield an oily residue. The oil was vacuum distilled to afford 12.57 g (62.87% yield) of a yellow liquid: bp 112 °C (10 mmHg);

IR (thin film) 2920(C-H, w), 1800(Cl-C=O, s), 1140(C-O-C, s) cm^{-1};

^{1}H NMR (60 MHz, $CDCl_3$) δ 4.5 (s, 2 H, $OCH_2C{=}O$), 3.6 (m, 11 H, $OCH_2CH_2OCH_2CH_2OCH_3$)

E2. Synthesis of bis-4,4'-[2-[2-(2-methoxyethoxy)ethoxy]acetamido]azobenzene



The reaction vessel was a 500-mL three-neck round bottom flask equipped with a reflux condenser with a drying tube attached, a mechanical stirrer, and a pressure equalizing dropping funnel. Into the flask was 6.811 g (0.0321 moles) of 4,4'-diaminoazobenzene, 13.10 g (0.1236 moles) of sodium carbonate (Fisher) and 300 mL of dimethoxyethane.

The reaction flask was heated to reflux, then 12.57 g of 2-[2-(2-methoxyethoxy)ethoxy] acetyl chloride (0.0639 moles) in 40 mL dimethoxyethane was added through the dropping funnel. After the addition was complete, the dropping funnel was removed and the reaction flask was heated on the steam bath overnight.

The red solution was filtered. The precipitate collected was washed with 200 mL of 1.0 N hydrochloric acid. The red product was combined to the residue obtained after evaporation of the mother liquor. This product was recrystallized from methanol-water to afford 11.75 g (69.05% yield) and mp 71-72 °C.

The use of thin layer chromatography, on alumina slides using 1:1 ether:methylene chloride eluent, showed the compound to be impure. Therefore, the compound was chromatographed on a column of alumina using the same eluent as the TLC. The main band was then collected and evaporated to dryness. The residue was recrystallized from methanol-water to yield orange needles: mp 82-83 °C;

IR(KBr) 3320(N-H, s), 3020(C-H, w), 2910(C-H, m), 1663(C=O amide, s), 1600(aromatic skeletal vibr., s), 1540(C-N-H, m), 1140(C-O-C, s), 1100(C-O-C, s), 855(1,4-disubstituted benzene, s) cm^{-1} (see Appendix II);

^{1}H NMR (200 MHz, $CDCl_3$) δ 8.98(s, 2 H, N*H*), 7.92(d of AB-q, 4 H, J=8.9, aromatic), 7.78(d of AB-q, 4 H, J=8.9, aromatic), 4.15(s, 4 H, $OCH_2C=O$), 3.76(m, 12 H, OCH_2), 3.60(m, 4 H, OCH_2), 3.39(s, 6 H, OCH_3) (see Appendix III);

^{13}C NMR(50 MHz, $CDCl_3$) δ 168.5(C_5), 149.1(C_1), 139.9(C_4), 123.7(C_3), 120.0(C_2), 71.7(C_6), 71.2(C_7), 70.7(C_8), 70.4(C_9), 70.1(C_{10}), 58.9(C_{11}) (see Appendix IV);

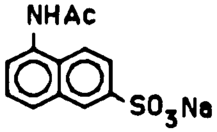
UV (Water) λ_{max} 367 nm (ε 3.47 x 10^4), (*o*-Dichlorobenzene) λ_{max} 367 nm (ε 3.17 x 10^4) (see Appendix I).

Anal. Calcd for $C_{26}H_{36}O_8N_4$: C, 58.64; H, 6.81.

Found: C, 58.09; H, 6.70. (Since Cm-4 is hydroscopic and the melting point is 82 °C, this compound is difficult to dry. This information could explain the poor analysis.)

E. Total Syntheses of Dyes

E1. Synthesis of sodium 5-acetamido-2-naphthalenesulfonate

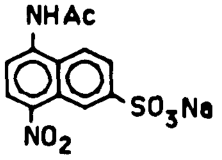


In a 1000-mL round bottom flask was placed 33.5 g (0.150 moles) of 5-amino-2-naphthalenesulfonic acid (Kodak) and 12.3 g (0.150 moles) of sodium acetate (Fisher) with 200 mL of water. The flask was warmed and swirled to dissolve the reactants. The cooled flask was then equipped with a reflux condenser, dropping funnel, and magnetic stirrer. Through the funnel was added 20.5 g (0.20 moles) of acetic anhydride (Fisher). The reaction flask was then stirred for 2 hours. Next the solvent was removed with a rotary evaporator. The crude solid was dissolved in 1300 mL of methanol and the white product was precipitated with isopropyl ether. The product was dried at 100 °C (1 mmHg). Two crops were obtained of the sodium 5-acetamido-2-naphtalene-sulfonate for a total weight of 36.0 g (83.6% yield). This sodium salt did not melt up to 360 °C;

IR (KBr) 3240(N-H, m), 3020(C-H, w), 2940(C-H, w), 1650(C=O amide, s), 1530(C-N-H, m), 1200(S=O, s), 1045(S=O, s) cm^{-1};

^{1}H NMR (60 MHz, CD_3SOCD_3) δ 10.0(s, 1 H, N*H*C=O), 8.4-7.4(m, 6 H, aromatic), 2.3(s, 3 H, O=CCH_3).

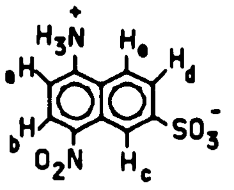
F2. Synthesis of sodium 5-acetamido-8-nitro-2-naphthalenesulfonate



In a 500-mL three-neck round bottom flask was placed 100 mL of concentrated sulfuric acid. The reaction flask was equipped with an efficient mechanical stirrer and cooled to -10 °C in an ethylene glycol-CO_2 bath. Small portions of sodium 5-acetamido-2-naphthalenesulfonate powder were slowly added over a 4 hour period until 25.8 g (0.090 moles) had dissolved. Next 12.0 mL (0.10 moles HNO_3) of a 1:1 solution of concentrated HNO_3:concentrated H_2SO_4 was added through a dropping funnel while maintaining a temperature between -10 °C and 0 °C. The reaction flask was then allowed to stir at this temperature for 1.5 hours.

In a 3000-mL beaker was placed 260 g (2.45 moles) of sodium carbonate (Fisher), 200 g of ice and 100 mL of water. The beaker was cooled in an ice bath and equipped with a mechanical stirrer. The entire brown sulfuric acid solution was slowly neutralized in the ice-carbonate mixture. The temperature was maintained below 5 °C by the addition of ice. The carbonate mixture was periodically checked to make sure it was still alkaline. The final volume of the green mixture was 1300 mL. The mixture was allowed to warm to room temperature with constant stirring. The green precipitate was collected through filtration and was found to consist mostly of sodium sulfate. Therefore the entire precipitate was extracted with boiling methanol and filtered. The orange methanol filtrate was concentrated and the orange product was precipitated with diisopropyl ether. The product was dried at 100 °C (1 mmHg) and weighed 24.7 g (83.5% yield). However, analysis proved the product to consist of the desired compound and some of the hydrolyzed product. Therefore no further purification was attempted and this mixture was used in the next step of the synthesis.

F3. Synthesis of 5-amino-8-nitro-2-naphthalenesulfonic acid

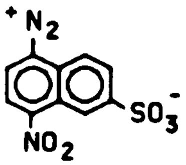


In a 1000-mL round bottom flask was placed 24.6 g (0.0743 moles) of crude sodium 5-acetamido-8-nitro-2-naphthalenesulfonate. Next 500 mL of 9N ammonia was added to dissolve the compound. This solution was allowed to stand at ambient temperature for 24 hours. The solvent was removed with a rotary evaporator. The crude material was dissolved in the smallest amount of water and acidified to pH 3 with concentrated HCl. The 5-amino-8-nitro-2-naphthalene-sulfonic acid precipitated and was collected through filtration. The product weighed 17.8 g (0.0662 moles) which was an 89.10% yield. The orange product was recrystallized from ethanol-diisopropyl ether. There was a 76.9% recovery from the recrystallization. The compound did not melt but charred black above 250 °C;

IR (KBr) 3600-2500(NH_3, br), 1200(S=O, s), 1520(NO_2, s), 1340(NO_2, s), 1040(S=O, s) cm^{-1};

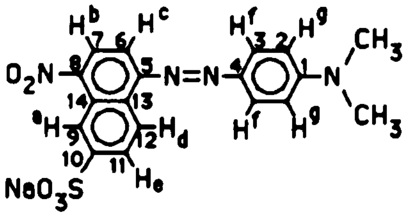
^1H NMR (60 MHz, CD_3SOCD_3) δ 9.4(s, 1 H, H_c), 8.5(d, 1 H, H_b), 8.4(d, 1 H, H_d), 7.8(d, 1 H, H_e), 7.6(s, 3 H, NH_3), 6.9(d, 1 H, H_a).

F4. Diazotisation of 5-amino-8-nitro-2-naphthalenesulfonic acid



In a 50-mL Erlenmeyer flask was place 1.00 g (0.0037 moles) of 5-amino-8-nitro-2-naphthalenesulfonic acid, 0.202 g (0.0019 moles) of sodium carbonate (Fisher) and 30 mL of water. The flask was warmed on a steam bath to dissolve the reactants. At this point, 0.273 g (0.0039 moles) of sodium nitrite (Fisher) was added and dissolved. The reaction flask was cooled to 0 °C in an ice bath. In a separate 125-mL Erlenmeyer flask was placed 0.67 mL (0.008 moles) of concentrated HCl and 20 g of ice. This flask was stirred and the cold sodium salt solution was poured into the acid and ice mixture. The diazotized mixture was maintained at 0 °C while stirring for at least 1 hour. The solution was then ready for coupling.

E5. Synthesis of 5-(4'-N,N-dimethylaminophenylazo)-8-nitro-2-naphthalenesulfonic acid



The diazotisation of 5-amino-8-nitro-2-naphthalenesulfonic acid was accomplished as described above. To the diazonium salt solution was added a mixture of 3.68 g (0.008 moles) of N,N-dimethylaniline (Baker) and 3.85 mL (0.0611 moles) of glacial acetic acid. A deep purple color formed as the mixture stirred for an additional 1.5 hours. Then 25 g of sodium carbonate (Fisher) was slowly added to the reaction flask which had a final volume of approximately 350 mL. The flask was heated to boiling to dissolve all of the salt. The mixture was allowed to slowly cool to room temperature and then cooled in an ice bath to 0 °C. The mixture was filtered to collect the sodium salt of the dye, which was washed twice with additional cold saturated sodium carbonate solution. The sodium salt of the dye was immediately dissolved in 250 mL of water. To this solution was added 250 mL of concentrated HCl to precipitate a fine brown powder which was centrifudged, filtered and washed with water five times. This crude zwitterion weighed 6.068 g (0.01515 moles) which was a 52.42% yield. The crude material was purified by chromatography as its tetra-n-butylammonium salt. The absorbent utilized was silica gel 60 with particle size 0.040 - 0.063 mm, the eluent was 4% methanol in acetone. The purified tetra-n-butylammonium salt had a melting point of 173-174 °C. The salt was converted back to the zwitterion with 6 N hydrochloric acid. The final weight of dried product was 2.09 g which was a 34.5% recovery. The sodium salt of the dye was obtained by titration of the zwitterion with sodium hydroxide. The sodium salt was dried at 100 °C (1 mmHg); the salt did not melt at 360 °C;

IR (KBr) 3040(C-H, w), 2930(C-H, w), 1600(aromatic skeletal vibr., s), 1520(NO_2, m), 1450(CH_3, s), 1370(C-N, s), 1130(S=O, s), 1040(S=O,m) cm^{-1} (see Appendix II);

^1H NMR (200 MHz, D_2O) δ 8.84(s, 1 H, H_a), 8.48(d of AB-q, 1 H, H_e), 7.89 (d of AB-q, 1 H, H_d), 7.60(d of AB-q, 1 H, H_b), 6.77(d of AB-q, 1 H, H_c), 6.70(d of AB-q, 2 H, H_f), 5.74(d of AB-q, 2 H, H_g), 2.66(s, 6 H, CH_3) (see Appendix III);

^1H NMR (200 MHz, CD_3SOCD_3) δ 8.96(s, 1 H, J=8.9 Hz, H_e), 8.79(s, 1 H, H_a), 8.39(d of AB-q, 1 H, J=8.5 Hz, H_b), 8.05(d of AB-q, 1 H, J=8.9 Hz, H_d), 7.98(d of AB-q, 2 H, J=9.0 Hz, H_f), 7.74(d of AB-q, 1 H, J=8.5 Hz, H_c), 6.92(d of AB-q, 2 H, J=9.0 Hz, H_g), 3.11(s, 6 H, CH_3) (see Appendix III);

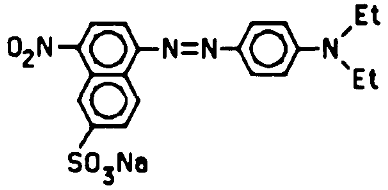
^{13}C NMR (50 MHz, CD_3SOCD_3) δ 153.3(C_1), 150.5(C_8), 148.7(C_{10}), 145.2(C_5), 130.0(C_{14}), 125.9(C_3), 125.3(C_6), 125.1(C_7), 124.6(C_{13}), 123.8(C_{12}), 118.6(C_{11}), 111.4(C_2), 109.9(C_9), 40.0(CH_3) (see Appendix IV);

UV (Water) λ_{max} 520 nm (ε 2.89 x 10^4) (see Appendix I).

Anal Cald. for $C_{18}H_{16}O_5N_4S$ (acid): C, 53.99; H, 4.03.

Found: C, 53.10; H, 4.11. (Although this zwitterion was thoroughly dried, it was prepared from the sodium salt by acid treatment. Traces of the salt could be responsible for the poor analysis.)

F6. Synthesis of sodium 5-(4'-N,N-diethylaminophenylazo)-8-nitro-2-naphthalenesulfonate

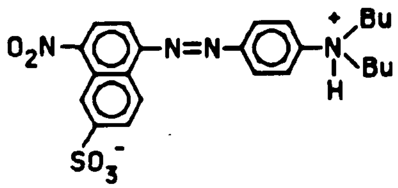


A diazonium salt solution was prepared as previously described using 1.00 g (0.0037 moles) of 5-amino-8-nitro-2-naphthalenesulfonic acid. To the cold stirring diazonium salt solution was added a mixture of 0.568 g (0.0038 moles) of N,N-diethylaniline (Baker) and 0.50 mL (0.085 moles) of glacial acetic acid. A deep purple color formed as the mixture stirred for an hour at 0 °C. Next 10 g of sodium carbonate (Fisher) was added and the mixture was boiled for ten minutes. The flask was cooled in an ice bath and filtered to collect the product. The weight obtained was 0.462 g (0.0010 moles) which was 27.5% yield. The compound was dried for 24 hours at 100 °C(1 mmHg). The compound did not melt at 360 °C;

IR (KBr) 3040(C-H, w), 2940(C-H, w), 1600(aromatic skeletal vibr., s), 1520(NO_2, s), 1385(NO_2, s), 1310(C-N, s), 1130(S=O, s), 1030(S=O, m) cm^{-1};

^1H NMR (60 MHz, CD_3SOCD_3) δ 9.5-6.9(m, 9 H, aromatic), 3.5(s, 4 H, NCH_2), 1.3(t, 6 H, CH_3).

F7. Synthesis of 5-(4'-N,N-dibutylaminophenylazo)-8-nitro-2-naphthalenesulfonic acid

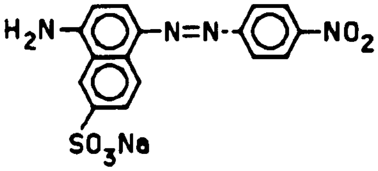


A diazonium salt solution was prepared as previously described using 2.0 g (0.0076 moles) of 5-amino-8-nitro-2-naphthalenesulfonic acid. To the stirring cold diazonium salt was added a mixture of 1.57 g (0.0076 moles) of N,N-dibutylaniline (Kodak) and 1.0 mL (0.017 moles) of glacial acetic acid. A deep purple color formed as the mixture stirred for an hour at 0 °C. The solvent was then removed with a rotary evaporator. The crude solid was dissolved in the smallest amount of water and acidified to pH 3. The acidic solution was then extracted three times with methylene chloride. The purple methylene chloride extracts were combined and taken to dryness. The solid was then dried at 100 °C (1 mmHg) for 24 hours. The product weighed 1.56 g (0.0032 moles) a 42.3% yield. The product did not melt at 360 °C;

IR (KBr) 3400(N-H, s), 3040(C-H, w), 2930(C-H, m), 1600(aromatic skeletal vibr., s), 1520(NO_2, m), 1330(NO_2, s), 1310(C-N, s), 1140(S=O, s), 1040(S=O, m) cm^{-1};

^{1}H NMR (60 MHz, CD_3SOCD_3) d 9.4-6.9(m, 9 H, aromatic), 3.5(m, 4 H, NCH_2), 2.2-0.8(m, 14 H, $CH_2CH_2CH_3$).

F8. Synthesis of sodium 8-amino-5-(4-nitrophenylazo)-2-napthalene-sulfonate



In a 250-mL Erlenmeyer flask was placed 3.912 g (0.02832 moles) of 4-nitroaniline (Eastman) and 8 mL (0.104 moles) of concentrated hydrochloric acid. The solution was diluted with water to 125 mL and cooled to 0 °C in an ice bath. As the temperature dropped there was precipitation of 4-nitroanilinuim chloride. Similarly, 1.976 g (0.02864 moles) of sodium nitrite (Fisher) was dissolved in 20 mL of water and cooled to 0 °C in an ice bath.

In a 1000-mL Erlenmeyer flask 5.660 g (0.02535 moles) of 8-amino-2-naphthalenesulfonic acid (CTC Organics) and 22.29 g (0.2103 moles) of sodium carbonate (Fisher) were combined with 400 mL of water. This mixture was heated until all of the sulfonic acid dissolved. This solution was then cooled in an ice bath to 0 °C.

Next, the 250-mL Erlenmeyer containing the 4-nitroanilinium chloride solution was stirred in an ice bath at 0 °C. The entire sodium nitrite solution was added in one portion. This solution was stirred at 0 °C for 0.5 hour. All of the precipitate dissolved to yield a yellow solution of 4-nitrodiazonium chloride.

After the sodium 8-amino-2-naphthalenesulfonate solution reached 0 °C, the 4-nitrodiazonium chloride solution was added slowly. The reaction flask was stirred thoroughly after each addition. An immediate violet precipitate formed after each addtion. Once all of the diazonium salt was added, the resulting mixture was warmed to room temperature with constant stirring.

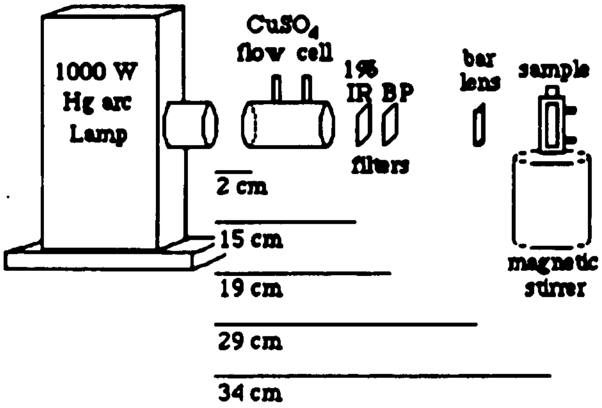
The reaction flask was heated to boiling to dissolve the precipitate plus 10 g of sodium chloride. The solution was again cooled to 0 °C and filtered. The solid precipitate was dissolved in 2-methoxyethanol (Aldrich) and 60 g of silica gel (EM Reagents) was added The mixture was taken to dryness depositing the product on the silica gel. The impregnated silica gel was placed on a large silica gel column. The column was eluted with 9:1 ratio of acetone:chloroform. The final main band was removed by changing the eluent to 2-methoxyethanol. The solution was taken to dryness on a rotary evaporator. The resulting product weighed 11.80 g which was 118% yield. The presence of sodium chloride was detected with silver nitrate. Therefore, the product was then dissolved in approximately 500 mL of water and acidified with hydrochloric acid. The 8-amino-5-(4-nitrophenylazo)-2-

naphthalenesulfonic acid precipitated out of solution. The product was filtered and washed with water until no more chloride was present in the wash. The product was dried and weighed 7.414 g (78.54% yield). The product did not melt when the temperature was raised to 360 °C;

IR (KBr) 3400(N-H, br), 3040(C-H, w), 1610(aromatic skeletal vibr., m), 1580(C-N-H, s), 1515(NO_2, m), 1435(N=N, w), 1325(NO_2, s), 1190(S=O, s), 1140(S=O, s), 860(C-N-O, w), 700(aromatic, s).

Irradiation

Figure 7`



The light source was a Schoeffel LH 151N 1000 W high pressure mercury arc lamp. The light was passed through a cooled $CuSO_4$ solution (15g/100 mL) in a 10 cm flow cell, a 1% transmitting IR filter and a 350 nm band pass filter. The light was focused with a bar lens (5.0 cm focal point) on the sample. The sample was in a jacketed flask maintained at 25.0 °C with a water circulating bath. The sample was stirred with a magnetic stirrer during irradiation. The sample was irradiated until the UV-Vis spectum of an aliquot of the sample no longer changed. The photostationary state was reached in any time up to 3 hours, depending on the size and concentration of the sample. For a solution of Cm with a concentration of 6 x 10^{-3} M the time would be 3 hours.

Experiment and Calculation of the Rate of the Thermal Isomerization

The following method was a typical example of the kinetic thermal isomerization experiment. A solution of the complexing agent at a concentration of 6.6 x 10^{-3} M was irradiated until the photostationary state was reached (accomplished by periodically removing small aliquots and monitoring the UV spectrum until no further change was observed). The light scource was extinguished and the initial time was recorded. An aliquot of the solution was successively diluted to a concentration of 2 x 10^{-5} M. The solution was placed in a 1 cm cuvette inside of an ultraviolet spectrophotometer which had thermally jacketed cuvette holders maintained at 25.0 °C. Successive spectra were obtained, spanning from 300-450 nm, in 0.5 hour intervals. The exact time was noted at the start of each spectrum. An infinity spectrum was also obtained at a minimum of 24 hours later.

The data was plotted where y-axis ■ $\ln[A_\infty/(A_\infty - A_t)]$ and x-axis ■ t. The term 'A_∞' was the absorbance of the trans isomer(@360 nm) at time infinity; 'A_t' was the absorbance of the trans isomer at any time t, as measured from the time the light scource was extinguished; 't' was the time(minutes) that a spectrum was obtained, as measured from the time the light scource was extinguished. The data provided a straight line which conformed to the equation :

$$\ln[A_\infty/(A_\infty - A_t)] = kt + b. \qquad \text{(eq 40)}$$

The variable 'k' was the slope of the line and was equal to the rate constant of the thermal isomerization in units of min^{-1}. The following expression provided the value of the rate constant (sec^{-1}): rate constant = k/60 . The intercept 'b' was related to the photostationary state and was expressed as the percentage of conversion from trans to cis isomers, given by: % conversion = $100/e^{b}$.

A least square determination of the data was carried out. The following equations were employed to calculate the correlation coefficient(r), the slope(k), the uncertainty in the slope(σk), the intercept(b) and the uncertainty in the intercept(σb).

$$r = \frac{[\Sigma xy-(\Sigma x\Sigma y)/n]}{\{[\Sigma x^2-(\Sigma x)^2/n]\,[\Sigma y^2-(\Sigma y)^2/n]\}^{1/2}} \qquad \text{(eq 41)}$$

$$k = \frac{n\Sigma xy-\Sigma x\Sigma y}{n\Sigma x^2-(\Sigma x)^2} \qquad \text{(eq 42)}$$

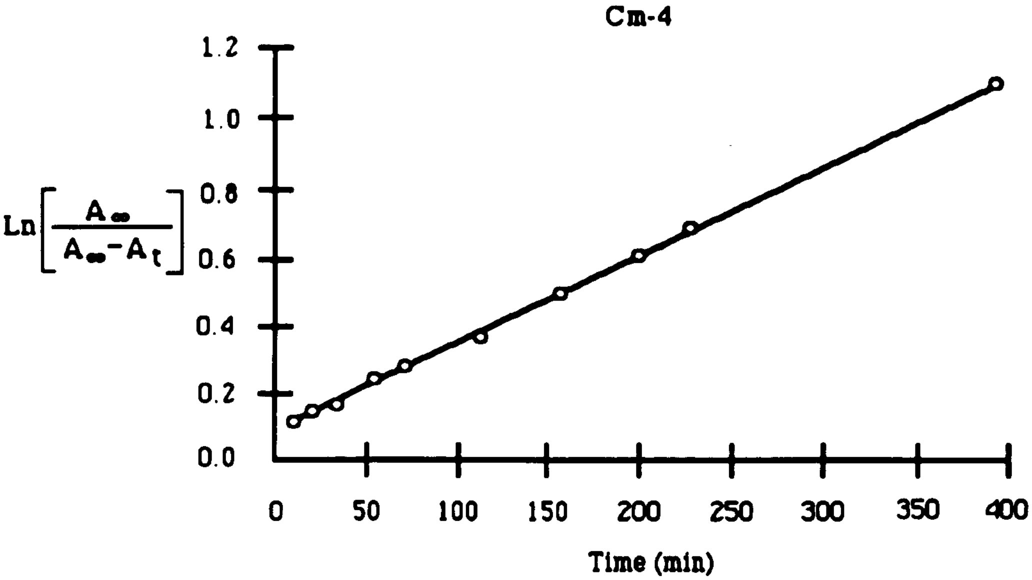
$$b = (\Sigma y-k\Sigma x)/n \qquad \text{(eq 43)}$$

$$\sigma k = \frac{(\Sigma y^2-b\Sigma y-k\Sigma xy)^{1/2}\,/(n-2)}{[\Sigma x^2-(\Sigma x)^2/n]^{1/2}} \qquad \text{(eq 44)}$$

$$\sigma b = \{(\Sigma y^2-b\Sigma y-k\Sigma xy)^{1/2}/(n-2)\}\,\{\Sigma x^2/[n\Sigma x^2-(\Sigma x)^2]\}^{1/2} \qquad \text{(eq 45)}$$

The plot in Figure 8 and the data in Table XVI were the typical results of a kinetic thermal isomerization, here shown for Cm-4 at 25 °C.

<u>Figure 8</u>



Solvent: 1% cyclohexanol in *o*-dichlorobenzene.

Concentration: 2.679 x 10^{-5} mol L^{-1}

Absorbance infinity trans(A_∞) @367 nm : 0.835

Epsilon(@367 nm): 3.1168 x 10^4 L mol^{-1} cm^{-1}

Table XVI

Points	X-axis Time(min)	Y-axis $\ln[A_\infty/(A_\infty - A_t)]$	Absorbance	% Reaction
1	12.00	0.1127	0.089	3.47
2	21.00	0.1371	0.107	5.80
3	35.83	0.1735	0.133	9.17
4	53.83	0.2187	0.164	13.16
5	69.11	0.2582	0.190	16.54
6	110.4	0.3731	0.260	25.60
7	161.0	0.5108	0.334	35.17
8	199.8	0.6160	0.384	41.64
9	223.8	0.7211	0.429	47.47
10	387.4	1.118	0.562	64.68

Least Square Data

$k = 2.688 \times 10^{-3} \pm 2.787 \times 10^{-6}$ (0.10%)

$b = 7.736 \times 10^{-2} \pm 4.785 \times 10^{-4}$ (0.62%)

$r = 0.9999$

Calculated Results

Percent conversion trans-cis = 92.56%

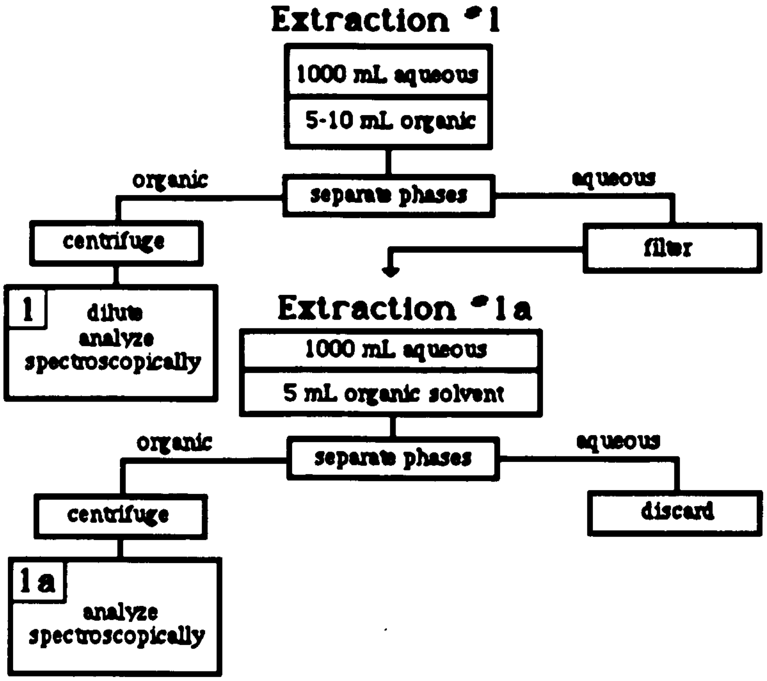
Half Life = 257.9 minutes

Rate Constant = 4.48×10^{-5} sec^{-1}

Extraction Experiments

A. Extraction Method 1 - Determination of K_1

Scheme VI



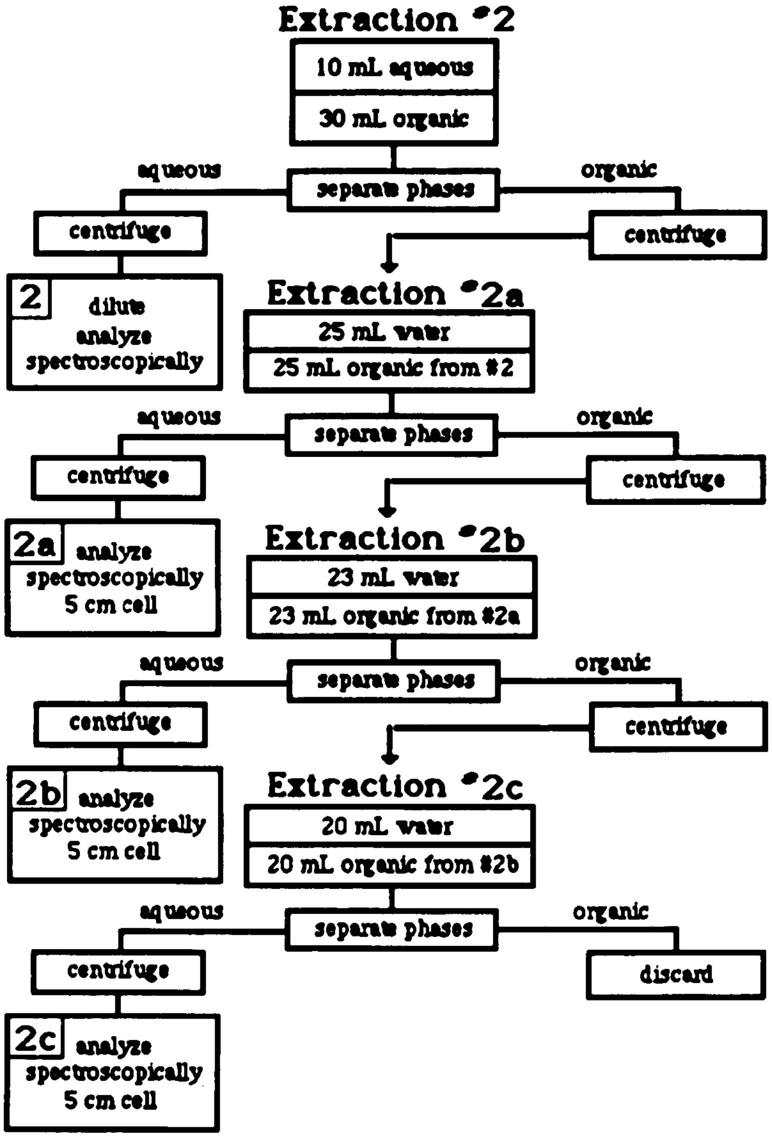
The partition coefficents (K_1) of the complexing agents, illustrated that Cm heavily favored solubility in the organic phase. Therefore, the extraction sequence of Scheme VI was used to determine K_1. The extraction #1a served to concentrate the small amount of Cm in the aqueous phase of extraction #1 so that accurate data could be obtained spectroscopically.

The organic solution was 6.6 x 10^{-3} M Cm. The aqueous phase was deionized water. The extraction flask was a 1000-mL separatory funnel equipped with a teflon stopper and stopcock. Into the flask was placed 5-10 mL of the organic solution and 1000 mL of water (Extraction #1). The flask was viqorously agitated for 3.0 minutes. The flask then remained undisturbed for 45-60 minutes to allow the phases to separate. The organic phase was removed and centrifuged. The organic phase was diluted and analyzed spectroscopically at 360 nm in a 1 cm cuvette (solution #1). The aqueous phase was slowly dripped through a porous paper filter into a similar 1000-mL separatory funnel. If an irradiated sample was being extracted, this solution was allowed to stand for a minimum of 24 hours. Otherwise the following steps were carried out immediately. A 5.0-mL aliquot of the organic solvent was added to the separatory funnel and the flask was vigorously extracted for 3.0 minutes (Extraction #1a). The flask remained undisturbed for 45-60 minutes to allow the phases to separate. The organic phase was then removed and centrifuged. The organic phase was placed into a 1 cm cuvette and analyzed with an ultraviolet spectrophotometer at 360 nm (solution #1a).

B. Extraction Method 2 - Determination of K_2K_3

The organic solution was 6.6 x 10^{-3} M Cm. The aqueous solution contained 0.01 M M^+Cl^- and 1.6 x10^{-4} M M^+D^-. First, a 30-mL aliquot of the organic solution was extracted with 10 mL of the aqueous solution. The extraction flask was an amber colored, water jacketed, eight inch test tube. The tube was equipped with a screw cap and a teflon stopcock. The tube was maintained at 25.0 °C during the extraction. The extraction was carried out by mechanically inverting the tube slowly and repeatedly. The period for one inversion was approximately 8 seconds. The extraction was carried out for 15.0 minutes (Extraction #2). After 1 minute standing the two phases were separated into test tubes and centrifuged. Then a 25-mL aliquot of the organic phase was extracted again with 25 mL of deionized water (Extraction #2a). The two phases were again separated and centrifuged. Then a 23-mL aliquot of the organic phase was extracted again with 23 mL of deionized water (Extraction #2b). The two phases were again separated and centrifuged. Finally, a 20-mL aliquot of the organic phase was extracted again with 20 mL of deionized water (Extraction #2c). The two phases were again separated and centrifuged.

Scheme VII



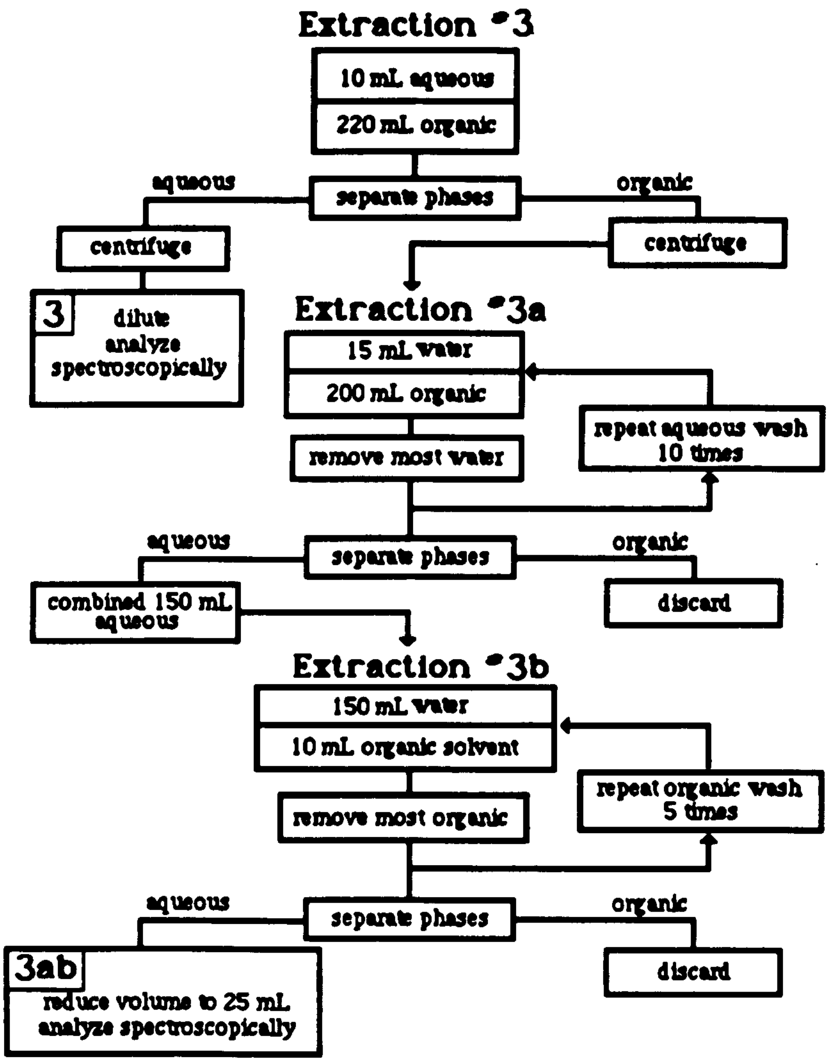
The aqueous phase from the Extraction #2 was diluted by a factor of five and the visible spectrum obtained in a 1 cm cuvette (solution #2). The aqueous phases of the susequent extractions (solutions 2a, 2b, 2c) were analyzed in a 5 cm cell spectroscopically.

C. Extraction Method 3 - Determination of K_2K_3

The concentration of the organic solution containing the complexing agent was 6.6×10^{-3} M. The aqueous solution contained 0.01 M M^+Cl^- and 1.6×10^{-4} M M^+D^-.

First, 220 mL of the organic solution was extracted with 10 mL of the aqueous solution (Extraction #3). The extraction flask was a 250-mL water jacketed separatory funnel, maintained at 25.0 °C. The flask was equipped with a screw cap and teflon stopcock. The extraction was carried out by mechanically inverting the flask slowly and repeatedly. The period of one inversion was approximately 8 seconds. The extraction was carried out for 15.0 minutes. The flask was undisturbed for 3 minutes to allow the phases to settle. Subsequently the phases were separated into test tubes and centrifuged. The aqueous phase was diluted and analyzed spectroscopically (solution #3). A 200-mL aliquot of the organic phase was placed back into the cleaned extraction flask with 15 mL of deionized water (Extraction #3a). The mixture was extracted for 3.0 minutes at an increased speed (a period of inversion of approximately 4 seconds). The phases settled and most of the aqueous phase was removed with a pipette. An additional 15.0 mL of water was added to the extraction flask and the extraction was repeated. This sequence was repeated for a total of ten extractions with water. All of the water washes were combined to provide a volume of approximately 150 mL. The combined aqueous phases were placed back into the cleaned extraction flask with 10 mL of the organic solvent (Extraction #3b). The mixture was vigorously extracted for 3.0 minutes and allowed to settle. Most of the organic phase was removed and replaced with fresh solvent. The flask was again

Scheme VIII



extracted for 3.0 minutes. This organic wash was repeated five times and the combined organic solution was dicarded. The volume of the aqueous phase was reduced to 25.0 mL. This was accomplished by placing the solution into a 250-mL round bottom flask, and slowly removing the solvent in a rotary evaporator at 50 °C

(20 mmHg). The final volume was approximately 10 mL of the solution. This solution was washed into a 25.0-mL volumetric flask and diluted to the mark with water. The final solution was placed in a 5 cm cell and analyzed in an ultraviolet spectrophotometer at 520 nm for dye content (solution #3ab).

D. Extraction Method 4 - Determination of K_{123} for Dibenzo-18-crown-6

The organic solution was 2.9×10^{-3} M dibenzo-18-crown-6 in *o*-dichlorobenzene (containing 1.00% by weight cyclohexanol). The aqueous solution contained 0.01 M M^+Cl^- and 3.5×10^{-5} M M^+D^-. First, a 10-mL aliquot of the organic solution was extracted with 10 mL of the aqueous solution. The extraction flask was an amber colored, water jacketed, eight inch test tube. The tube was equipped with a screw cap and a teflon stopcock. The tube was maintained at 25.0 °C during the extraction. The extraction was carried out by mechanically inverting the tube slowly and repeatedly. The period for one inversion was approximately 8 seconds. The extraction was carried out for 15.0 minutes. After 5 minutes standing the two phases were separated into test tubes and centrifuged. The two solutions were then analyzed spectrophotometrically.

Calculation of equilibrium Constants

A. Calculation of Partition Coefficient $K_{1,T}$

The extraction method #1 outlined previously was used to obtain the data necessary to calculate $K_{1,T}$. The following equation was employed to determine the value of $K_{1,T}$.

$$K_{1,T} = \frac{V_{org,1a}[Cm_{org,1a}]}{V_{aq,1}\{[Cm_{org,1}] - [Cm_{org,1a}]\}} \qquad \text{(eq 46)}$$

The term '$V_{org,1a}$' was the volume of the organic phase in extraction #1a (0.005 L);

'$V_{aq,1}$' was the volume of the aqueous phase for both extractions #1 and #1a (1.00 L); '$[Cm_{org,1}]$' was the equilibrium concentration of the complexing agent in the organic phase after extraction #1 (solution #1); '$[Cm_{org,1a}]$' was the equilibrium concentration of the complexing agent in the organic phase after extraction #1a (solution #1a).

The value of $[Cm_{org,1}]$ was given by:

$$[Cm_{org,1}] = \frac{A_1 D_{A1}}{\varepsilon_{Cm,org} P_{A1}} \qquad \text{(eq 47)}$$

The term 'A_1' was the absorbance maximum of Cm in the organic solvent at 360 nm (solution #1); 'D_{A1}' was the dilution factor of the organic phase; '$\varepsilon_{Cm,org}$' was the extinction coefficient of Cm in the organic solvent at 360 nm; 'P_{A1}' was the path length of the cuvette utilized.

The value of $[Cm_{org,1a}]$ was given by:

$$[Cm_{org,1a}] = \frac{A_2 D_{A2}}{\varepsilon_{Cm,org} P_{A2}} \qquad \text{(eq 48)}$$

The term 'A_2' was the absorbance maximum of Cm in the organic solvent at 360 nm (solution #1a); 'D_{A2}' was the dilution factor of the organic phase; '$\varepsilon_{Cm,org}$' was the extinction coefficient of Cm in the organic solvent at 360 nm; 'P_{A2}' was the path length of the cuvette utilized.

Sample 1: The determination of $K_{1,T}$ for Cm-4 between water and *o*-dichlorobenzene*, the value is listed in Table VII of the Results Section. The experimental data employed can be found in Appendix

V Table B. The extinction coefficient of Cm-4 was obtained from Table I of the Results Section.

$$[\text{Cm-4}_{\text{org},1}] = \frac{(0.641)\,(50.0)}{(3.17 \times 10^{4}\ \text{L mol}^{-1}\text{cm}^{-1})\,(1.00\ \text{cm})} \qquad \text{(eq 47)}$$

$$= 1.01 \times 10^{-3}\ \text{mol L}^{-1}$$

$$[\text{Cm-4}_{\text{org},2}] = \frac{(0.599)\,(10.0)}{(3.17 \times 10^{4}\ \text{L mol}^{-1}\text{cm}^{-1})\,(1.00\ \text{cm})} \qquad \text{(eq 48)}$$

$$= 1.89 \times 10^{-4}\ \text{mol L}^{-1}$$

$$K_{1,T} = \frac{(0.005\ \text{L})\,(1.89 \times 10^{-4}\ \text{mol L}^{-1})}{(1.00\ \text{L})\,\{(1.01 \times 10^{-3}\ \text{mol L}^{-1}) - (1.89 \times 10^{-4}\ \text{mol L}^{-1})\}} \qquad \text{(eq46)}$$

$$= 1.15 \times 10^{-3}$$

B. Calculation of the Partition Coefficient $K_{1,C}$

The following experiments were necessary to obtain the data for the calculation of $K_{1,C}$: (1) the irradiation of the organic solution; (2) the extraction method #1; (3) the determination of the rate of the thermal isomerization.

The following equation was derived to determine the value of $K_{1,C}$:

$$K_{1,C} = \frac{[\text{Cm}_{\text{aq}}]_{\text{obs}}}{[\text{Cm}_{\text{C,org}}]} - \frac{K_{1,T}\,[\text{Cm}_{\text{T,org}}]}{[\text{Cm}_{\text{C,org}}]} \qquad \text{(eq49)}$$

The term '$[\text{Cm}_{\text{aq}}]_{\text{obs}}$' was the observed concentration of the complexing agent in the aqueous phase; '$[\text{Cm}_{\text{C,org}}]$' was the concentration of the cis isomer of the complexing agent in the organic phase; '$[\text{Cm}_{\text{T,org}}]$' was the concentration of the trans isomer of the complexing agent in the organic phase; '$K_{1,T}$ ' was the partition coefficient for the trans isomer.

The value of $K_{1,T}$ was obtained from a separate experiment described above. The value of $[\text{Cm}_{\text{aq}}]_{\text{obs}}$ was obtained from the following expression:

$$[Cm_{aq}]_{obs} = \frac{V_{org,1a}\, A_3\, D_{A3}}{V_{aq,1}\, \varepsilon_{Cm,org}\, P_{A3}} \qquad \text{(eq 50)}$$

The term 'A_3' was the absorbance of the solution #1a; 'D_{A3}' was the dilution factor of the solution; '$\varepsilon_{Cm,org}$' was the extincton coefficient of the complexing agent in the organic solvent; 'P_{A3}' was the path length of the cuvette employed; '$V_{org,1a}$' was the volume of the organic phase for extraction #1a.; '$V_{aq,1}$' was the volume of the aqueous phase for both extractions #1 and #1a.

The values of the terms $[Cm_{C,org}]$ and $[Cm_{T,org}]$ were obtained with the aid of the thermal isomerization experiment, as described above. The isomerization was carried out on the identical solution used in the extraction experiment. A sample of the extraction solution was diluted and monitored by the spectrophotometer. The isomerization was then carried out as explained earlier. The values of the slope (k) and intercept (b) obtained allowed calculation of the concentration of the trans isomer at any time from when the light scource was extinguished. Therefore the concentration of the trans isomer was calculated at the start and finish of the extraction by the following equations:

$$Y_1 \equiv \ln[A_\infty/(A_\infty - A_{t1})] = k\, t_1 + b \qquad \text{(eq 51)}$$

$$[Cm_{T,org}]_{t1} = [Cm_{org}]_{tot}\,(1 - e^{-Y1}) \qquad \text{(eq 52)}$$

$$[Cm_{org}]_{tot} = \frac{A_4\, D_{A4}}{\varepsilon_{Cm,org}\, P_{A4}} \qquad \text{(eq 53)}$$

The term 't_1' was the time at the start of the extraction; 'Y_1' was defined as the logrithmic term solved for the value of the aborbance at t_1; '$[Cm_{T,org}]_{t1}$' was the concentration of the trans isomer in the organic phase at time t_1; ' $[Cm_{org}]_{tot}$' was the total concentration of the complexing agent in the organic solution #1 after allowing enough time for complete isomerization back to the trans isomer; 'A_4' was the absorbance of solution #1 ; 'D_{A4}' was the dilution factor of the solution #1; 'P_{A4}' was the path length of the cuvette employed for A_4; '$\varepsilon_{Cm,org}$' was the extinction coefficient of the complexing agent in the organic phase.

A similar term $[Cm_{T,org}]_{t2}$ was obtained where the value of t2 was the time the extraction ended. The average value of the concentration of the trans isomer $[Cm_{T,org}]_{av}$ was found by the following equation:

$$[Cm_{T,org}]_{av} = ([Cm_{T,org}]_{t1} + [Cm_{T,org}]_{t2}) / 2 \qquad \text{(eq 54)}$$

Therefore the average value of the concentration of the cis isomer was obtained from the difference between the total concentration of complexing agent and the average concentration of the trans isomer.

$$[Cm_{C,org}]_{av} = [Cm_{org}]_{tot} - [Cm_{T,org}]_{av} \qquad \text{(eq 55)}$$

Substitution of the above values into the equation for the partition coefficient $K_{1,C}$ provided the following equation:

$$K_{1,C} = \frac{[Cm_{aq}]_{obs}}{[Cm_{C,org}]_{av}} - \frac{K_{1,T}\,[Cm_{T,org}]_{av}}{[Cm_{C,org}]_{av}} \qquad \text{(eq 56)}$$

Sample 2: The determination of $K_{1,C}$ for Cm-4 between water and *o*-dichlorobenzene*, the value is listed in Table VII of the Results Section. The experimental data employed is found in Appendix V Table B. The extinction coefficient of Cm-4 was obtained from Table I of the Results Section.

$$[\mathrm{Cm}\text{-}4_{aq}]_{obs} = \frac{(0.005\text{ L})\,(1.567)\,(25.0)}{(1.00\text{ L})\,(3.17\text{ x }10^{4}\text{ L mol}^{-1}\text{cm}^{-1})\,(1.00\text{ cm})} \qquad \text{(eq 50)}$$

$$= 6.18\text{ x }10^{-6}\text{ mol L}^{-1}$$

$$[\mathrm{Cm}\text{-}4_{org}]_{tot} = \frac{(0.371)\,(50.0)}{(3.17\text{ x }10^{4}\text{ L mol}^{-1}\text{cm}^{-1})\,(1.00\text{ cm})} \qquad \text{(eq 53)}$$

$$= 5.85\text{ x }10^{-4}\text{ mol L}^{-1}$$

$$Y_1 = (1.77\text{ x }10^{-3}\text{ min}^{-1})\,(9.00\text{ min}) + 0.133 \qquad \text{(eq 51)}$$

$$= 0.149$$

$$[\mathrm{Cm}_T\text{-}4_{org}]_{t1} = (5.85\text{ x }10^{-4}\text{ mol L}^{-1})\,(1 - e^{-0.149}) \qquad \text{(eq 52)}$$

$$= 8.08\text{ x }10^{-5}\text{ mol L}^{-1}$$

Similarly, for t2 = 12.00 min :

$$[\mathrm{Cm}_T\text{-}4_{org}]_{t2} = 8.35\text{ x }10^{-5}\text{ mol L}^{-1} \qquad \text{(eq 51\&52)}$$

$$[\mathrm{Cm}_T\text{-}4_{org}]_{av} = (8.08\text{ x }10^{-5}\text{ mol L}^{-1} + 8.35\text{ x }10^{-5}\text{ mol L}^{-1})\,/\,2 \qquad \text{(eq 54)}$$

$$= 8.22\text{ x }10^{-5}\text{ mol L}^{-1}$$

$$[\mathrm{Cm}_C\text{-}4_{org}]_{av} = (5.85\text{ x }10^{-4}\text{ mol L}^{-1}) - (8.22\text{ x }10^{-5}\text{ mol L}^{-1}) \qquad \text{(eq 55)}$$

$$= 5.03\text{ x }10^{-4}\text{ mol L}^{-1}$$

$$K_{1,C} = \frac{6.18\text{ x }10^{-6}\text{ mol L}^{-1}}{5.03\text{ x }10^{-4}\text{ mol L}^{-1}} - \frac{(1.15\text{ x }10^{-3})\,(8.22\text{ x }10^{-6}\text{ mol L}^{-1})}{5.03\text{ x }10^{-4}\text{ mol L}^{-1}} \qquad \text{(eq 56)}$$

$$= 1.21\text{ x }10^{-2}$$

C. Calculation of Constants K_2K_3

The calculation of equilibrium constants $K_{2,T}$ and $K_{3,T}$ were performed using equation 57.

$$K_{2,T}K_{3,T} = \frac{[\mathrm{Cm}_T\mathrm{MD}_{org}]}{K_{1,T}\,[\mathrm{Cm}_{T,org}]\,[\mathrm{M}^+_{aq}]\,[\mathrm{D}^-_{aq}]} \qquad \text{(eq 57)}$$

The values of the terms in equation 57 were obtained from performing either extraction methods 2 or 3. The term which was the most difficult to handle was the concentration of complex in the organic phase ($[Cm_TMD_{org}]$). The way the multiple extraction was carried out determines the method by which the raw data was processed.

C1.Analysis of Complex $[Cm_TMD_{org}]$ with Multiple Extraction Method 2

There were some problems that were not mentioned previously. One problem was that the organic solvent extracts some dye on its own. Therefore a separate multiple extraction of the dye solution with the pure organic solvent was performed. This extraction accounted for the amount of dye that the solvent extracted. Another problem was that the aqueous phases were also saturated with Cm. The presence of Cm caused a baseline absorbance in the region near the dye (520 nm). A separate extraction of the organic solution of Cm with water and the value of the baseline absorbance in the aqueous phase near the dye region was obtained. This absorbance value was subtracted from the other data. The following equation then illustrated how to calculate ($[Cm_TMD_{org}]$) using extraction method 2.

$$[Cm_TMD_{org}] = \frac{(A_5+A_6+A_7)-(A_8+A_9+A_{10})-3(A_{11})}{\varepsilon_{D,aq}\, P_{A5\text{-}11}} \qquad \text{(eq 58)}$$

The first three terms 'A_5', 'A_6' and 'A_7' were the absorbances of the aqueous phases(2a, 2b 2c) from the three extractions of the dye solution with organic solution containing the complexing agent; 'A_8', 'A_9' and 'A_{10}' were the absorbances of the aqueous phases(2a, 2b, 2c) from a separate extraction involving the aqueous dye solution and the pure organic solvent; 'A_{11}' was the absorbance due to Cm in the aqueous phase at 520 nm from the separate extraction of water with the organic solution of Cm; '$\varepsilon_{D,aq}$' was the extinction coefficient of the dye in water; '$P_{A5\text{-}11}$' was the path length of the cell used.

C2. Analysis of Complex $[\mathrm{Cm_TMD_{org}}]$ with Multiple Extraction Method 3

In the multiple extraction method 3, there was also the problem of accounting for the dye extracted by the solvent. A similar extraction was completed. The dye solution was the aqueous phase and pure organic solvent was the organic phase. When this extraction was completed as discussed above, the amount of dye extracted was subtracted from the amount obtained when the complexing agent was present. The equation 59 below describes this process.

$$[\mathrm{Cm_TMD_{org}}] = \frac{(A_{12}-A_{13})\,(V_{soln})}{\varepsilon_{D,aq}\,P_{A12\text{-}13}\,V_{org}} \qquad \text{(eq 59)}$$

The term 'A_{12}' was the absorbance value obtained for solution #3ab when the complexing agent was present during the extraction; 'A_{13}' was the aborbance value obtained for solution #3ab when no complexing agent was present; '$\varepsilon_{D,aq}$' was the extinction coefficient for the dye in water; 'P_{A12-13}' was the path length of the cell employed; 'V_{soln}' was the volume of the solution that the aqueous phases were reduced to(0.025 L); 'V_{org}' was the volume of the organic phase (0.200 L).

C3. Experimental Calculation of $K_{2,T}K_{3,T}$

The term $[\mathrm{Cm_TMD_{org}}]$ was obtained from the equations 58 or 59, depending on the method of multiple extraction employed. For the term $[\mathrm{Cm_{T,org}}]$ in equation 57 the stoichoimetric value was employed since it was many times greater than the concentration of the complex. The stoichiometric concentration of salt in the original aqueous solution was employed for the term $[M^+_{aq}]$, since this concentration was so much greater than the complex. The term $[D^-_{aq}]$ was obtained from analysis of the original aqueous phase after the first extraction as illustrated in the equation 60.

$$[D^{-}_{aq}] = \frac{A_{14}\ D_{A14}}{\varepsilon_{D,aq}\ P_{A14}} \qquad \text{(eq 60)}$$

The term 'A_{14}' was the absorbance maximum of the dye at 520 nm in the aqueous phase from the first extraction; 'D_{A14}' was the dilution factor for this solution; '$\varepsilon_{D,aq}$' was the extinction coefficient for the dye at 520 nm; 'P_{A14}' was the path length of the solution. Substitution for all of the terms in equation 57 then allowed calculation of $K_{2,T}K_{3,T}$.

Sample 3: The determination of $K_{2T}K_{3T}$ for Cm-4 with potassium chloride via multiple extraction method 2. The value is listed in Table XIV of the Results Section. The experimental data can be found in Appendix V Table I. The extinction coefficients of the dye employed are experimental values close to those found in Table V of the Results Section. The partition coefficient (K_1) is obtained from Table VII of the Results Section.

$$[Cm_T\text{-}4MD_{org}] = \frac{(0.800 + 0.087 + 0.024) - (0.039 + 0.013 + 0.003) - 3(0.010)}{(2.80 \times 10^{4}\ L\ mol^{-1}cm^{-1})\ (5.00\ cm)} \qquad \text{(eq 58)}$$

$$= 5.90 \times 10^{-6}\ mol\ L^{-1}$$

$$[D^{-}_{aq}] = \frac{(0.483)\ (5.00)}{(2.72 \times 10^{4}\ L\ mol^{-1}cm^{-1})\ (1.00\ cm)} \qquad \text{(eq 60)}$$

$$= 8.88 \times 10^{-5}\ mol\ L^{-1}$$

$$K_{2T}K_{3T} = \frac{5.90 \times 10^{-6}\ mol\ L^{-1}}{(1.15 \times 10^{-3})\ (6.70 \times 10^{-3}\ mol\ L^{-1})\ (0.0100\ mol\ L^{-1})\ (8.88 \times 10^{-5}\ mol\ L^{-1})} \qquad \text{(eq 57)}$$

$$= 8.63 \times 10^{5}\ L^{2}\ mol^{-2}$$

Sample 4: The determination of $K_{2T}K_{3T}$ for Cm-4 with potassium chloride via multiple extraction method 3. The value is listed in Table XI of the Results Section. The experimental data can be found in Appendix V Table F. The extinction coefficients of the dye employed can be found in Table V of the Results Section. The partition coefficient (K_1) is obtained from Table VII of the Results Section.

$$[Cm_T\text{-}4MD_{org}] = \frac{(0.554 - 0.074)\,(0.025\ L)}{(2.89 \times 10^4\ L\ mol^{-1}cm^{-1})\,(1.00\ cm)\,(0.200\ L)} \qquad \text{(eq 59)}$$

$$= 2.08 \times 10^{-6}\ mol\ L^{-1}$$

$$[D^-_{aq}] = \frac{(0.529)\,(5.00)}{(2.76 \times 10^4\ L\ mol^{-1}cm^{-1})\,(1.00\ cm)} \qquad \text{(eq 60)}$$

$$= 9.58 \times 10^{-5}\ mol\ L^{-1}$$

$$K_{2T}K_{3T} = \frac{2.08 \times 10^{-6}\ mol\ L^{-1}}{(1.15 \times 10^{-3})\,(2.22 \times 10^{-3}\ mol\ L^{-1})\,(0.0100\ mol\ L^{-1})\,(9.58 \times 10^{-5}\ mol\ L^{-1})} \qquad \text{(eq 57)}$$

$$= 8.50 \times 10^5\ L^2\ mol^{-2}$$

C4. Calculation of $K_{2,C}K_{3,C}$

In the calculation of $K_{2,C}K_{3,C}$ the concentrations of the cis and trans isomers of Cm were necessary, as illustrated by equation 61.

$$K_{2,C}K_{3,C} = \frac{[CmMD_{org}]}{K_{1,C}\,[Cm_{C,org}]\,[M^+_{aq}]\,[D^-_{aq}]} - \frac{K_{1,T}K_{2,T}K_{3,T}\,[Cm_{T,org}]}{K_{1,C}\,[Cm_{C,org}]} \qquad \text{(eq 61)}$$

In order to perform the calculation, the following experiments were completed: (1) the irradiation of the organic solution; (2) the extraction method #3; (3) the determination of the rate of the thermal isomerization.

As previously described the times were recorded for start and finish of the extraction using the irradiated organic solution. The calculation of $[Cm_{C,org}]_{av}$ and $[Cm_{T,org}]_{av}$ can be accomplished employing the equations 51 through 55. The value of the complex concentration $[CmMD_{org}]$ was obtained as described by equations 58 or 59, depending on the method of multiple extraction that was employed. The term $[M^+_{aq}]$ was the stoichiometric concentration since its value was much larger than the complex. The $[D^-_{aq}]$ term was obtained through the use of equation 60. When all of the terms of equation 61 were obtained, the equation transformed to equation 62.

$$K_{2,C}K_{3,C} = \frac{[CmMD_{org}]}{K_{1,C}\,[Cm_{C,org}]_{av}\,[M^+_{aq}]\,[D^-_{aq}]} - \frac{K_{1,T}K_{2,T}K_{3,T}\,[Cm_{T,org}]_{av}}{K_{1,C}\,[Cm_{C,org}]_{av}} \quad \text{(eq 62)}$$

Substitution in equation 62 then allowed calculation of $K_{2,C}K_{3,C}$.

Sample 5: The determination of $K_{2C}K_{3C}$ for Cm-4 with potassium chloride via multiple extraction method 2. The value is listed in Table XIV of the Results Section. The experimental data can be found in Appendix V Table I. The extinction coefficients of the dye employed are experimental values close to those found in Table V of the Results Section. The partition coefficient (K_1) is obtained from Table VII of the Results Section.

$$[Cm_T\text{-}4MD_{org}] = \frac{(0.854 + 0.033 + 0.020) - (0.039 + 0.013 + 0.003) - 3(0.015)}{(2.80 \times 10^4\ L\ mol^{-1}cm^{-1})\ (5.00\ cm)} \quad \text{(eq 58)}$$

$$= 5.76 \times 10^{-6}\ mol\ L^{-1}$$

$$[D^-_{aq}] = \frac{(0.507)\ (5.00)}{(2.72 \times 10^4\ L\ mol^{-1}cm^{-1})\ (1.00\ cm)} \quad \text{(eq 60)}$$

$$= 9.32 \times 10^{-5}\ mol\ L^{-1}$$

$$Y_1 = (2.69 \times 10^{-3}\ min^{-1})\ (3.05\ min) + 0.120 \quad \text{(eq 51)}$$
$$= 0.128$$

$$[Cm_T\text{-}4_{org}]_{t1} = (6.70 \times 10^{-3}\ mol\ L^{-1})\ (1 - e^{-0.128}) \quad \text{(eq 52)}$$
$$= 8.05 \times 10^{-4}\ mol\ L^{-1}$$

Similarly, for t2 = 13.05 min :

$$[Cm_T\text{-}4_{org}]_{t2} = 9.62 \times 10^{-4}\ mol\ L^{-1} \quad \text{(eq 51\&52)}$$

$$[Cm_T\text{-}4_{org}]_{av} = (8.05 \times 10^{-4}\ mol\ L^{-1} + 9.62 \times 10^{-4}\ mol\ L^{-1}) / 2 \quad \text{(eq 54)}$$
$$= 8.83 \times 10^{-4}\ mol\ L^{-1}$$

$$[Cm_C\text{-}4_{org}]_{av} = (6.70 \times 10^{-3}\ mol\ L^{-1}) - (8.83 \times 10^{-4}\ mol\ L^{-1}) \quad \text{(eq 55)}$$
$$= 5.81 \times 10^{-3}\ mol\ L^{-1}$$

$$K_{2C}K_{3C} = \frac{5.76 \times 10^{-6}\ \text{mol L}^{-1}}{(1.20 \times 10^{-2})\ (5.81 \times 10^{-3}\ \text{mol L}^{-1})\ (0.0100\ \text{mol L}^{-1})\ (9.32 \times 10^{-5}\ \text{mol L}^{-1})}$$

$$- \frac{(1.15 \times 10^{-3})\ (8.62 \times 10^{5}\ \text{L}^2\ \text{mol}^{-2})\ (8.83 \times 10^{-4}\ \text{mol L}^{-1})}{(1.20 \times 10^{-2})\ (5.81 \times 10^{-3}\ \text{mol L}^{-1})} \qquad \text{(eq 62)}$$

$$= 7.61 \times 10^{4}\ \text{L}^2\ \text{mol}^{-2}$$

Sample 6: The determination of $K_{2C}K_{3C}$ for Cm-4 with potassium chloride via multiple extraction method 3. The value is listed in Table XI of the Results Section. The experimental data can be found in Appendix V Table F. The extinction coefficients of the dye employed can be found in Table V of the Results Section. The partition coefficient (K_1) is obtained from Table VII of the Results Section.

$$[\text{Cm}_C\text{-4MD}_{org}] = \frac{(0.501 - 0.074)\ (0.025\ \text{L})}{(2.89 \times 10^{4}\ \text{L mol}^{-1}\text{cm}^{-1})\ (1.00\ \text{cm})\ (0.200\ \text{L})} \qquad \text{(eq 59)}$$

$$= 1.85 \times 10^{-6}\ \text{mol L}^{-1}$$

$$[\text{D}^-_{aq}] = \frac{(0.505)\ (5.00)}{(2.76 \times 10^{4}\ \text{L mol}^{-1}\text{cm}^{-1})\ (1.00\ \text{cm})} \qquad \text{(eq 60)}$$

$$= 9.15 \times 10^{-5}\ \text{mol L}^{-1}$$

$$Y_1 = (1.76 \times 10^{-3}\ \text{min}^{-1})\ (6.00\ \text{min}) + 0.168 \qquad \text{(eq 51)}$$

$$= 0.178$$

$$[\text{Cm}_T\text{-4}_{org}]_{t1} = (2.22 \times 10^{-3}\ \text{mol L}^{-1})\ (1 - e^{-0.178}) \qquad \text{(eq 52)}$$

$$= 3.62 \times 10^{-4}\ \text{mol L}^{-1}$$

Similarly, for t2 = 16.00 min :

$$[\text{Cm}_T\text{-4}_{org}]_{t2} = 3.94 \times 10^{-4}\ \text{mol L}^{-1} \qquad \text{(eq 51\&52)}$$

$$[\text{Cm}_T\text{-4}_{org}]_{av} = (3.62 \times 10^{-4}\ \text{mol L}^{-1} + 3.94 \times 10^{-4}\ \text{mol L}^{-1}) / 2 \qquad \text{(eq 54)}$$

$$= 3.78 \times 10^{-4}\ \text{mol L}^{-1}$$

$$[\text{Cm}_C\text{-4}_{org}]_{av} = (2.22 \times 10^{-3}\ \text{mol L}^{-1}) - (3.78 \times 10^{-4}\ \text{mol L}^{-1}) \qquad \text{(eq 55)}$$

$$= 1.84 \times 10^{-3}\ \text{mol L}^{-1}$$

$$K_{2C}K_{3C} = \frac{1.85 \times 10^{-6}\ \text{mol L}^{-1}}{(1.20 \times 10^{-2})\ (1.84 \times 10^{-3}\ \text{mol L}^{-1})\ (0.0100\ \text{mol L}^{-1})\ (9.15 \times 10^{-5}\ \text{mol L}^{-1})}$$

$$= \frac{(1.15 \times 10^{-3})(8.50 \times 10^{5}\ \mathrm{L^{2}\ mol^{-2}})(3.78 \times 10^{-4}\ \mathrm{mol\ L^{-1}})}{(1.20 \times 10^{-2})(1.84 \times 10^{-3}\ \mathrm{mol\ L^{-1}})} \qquad \text{(eq 62)}$$

$$= 7.49 \times 10^{4}\ \mathrm{L^{2}\ mol^{-2}}$$

D. Calculation of K_{123} for Dibenzo-18-crown-6

The extraction method #4 was used to obtain the experimental data necessary for the calculation of K_{123} for dibenzo-18-crown-6.

The equation 63 was used to determine the constant K_{123} as shown below:

$$K_{123} = \frac{[\mathrm{CrMD_{org}}]}{[\mathrm{Cr_{org}}][\mathrm{M^{+}{}_{aq}}][\mathrm{D^{-}{}_{aq}}]} \qquad \text{(eq 63)}$$

The term '$[\mathrm{CrMD_{org}}]$' was the concentration of the complex in the organic phase; '$[\mathrm{Cr_{org}}]$' was the concentration of dibenzo-18-crown-6 in the organic phase; '$[\mathrm{M^{+}{}_{aq}}]$' was the concentration of the salt in the aqueous phase; '$[\mathrm{D^{-}{}_{aq}}]$' was the concentration of the dye in the aqueous phase.

The value of $[\mathrm{CrMD_{org}}]$ was given by:

$$[\mathrm{CrMD_{org}}] = \frac{A_{org}\ D_{org}}{\varepsilon_{D,org}\ P_{A,org}} \qquad \text{(eq 64)}$$

The term 'A_{org}' was the absorbance due to the dye complex in the organic phase; 'D_{org}' was the dilution factor of the organic phase if any; '$\varepsilon_{D,org}$' was the extinction coefficient of the dye in the organic phase; ' $P_{A,org}$' was the path length of the cuvette utilized.

The concentration of the dye in the aqueous phase, $[\mathrm{D^{-}{}_{aq}}]$ was determined by the following equation 65:

$$[D^-_{aq}] = \frac{A_{aq}\ D_{aq}}{\varepsilon_{D,aq}\ P_{A,aq}} \qquad \text{(eq 65)}$$

The term 'A_{aq}' was the absorbance due to the dye in the aqueous phase; 'D_{aq}' was the dilution factor of the aqueous phase if any; '$\varepsilon_{D,aq}$' was the extinction coefficient of the dye in the aqueous phase; ' $P_{A,aq}$' was the path length of the cuvette utilized.

The concentration of the dibenzo-18-crown-6 in the organic phase, $[Cr_{org}]$, was determined by the difference between the stoichiometric value ($[Cr_{org}]_{stoic}$) and the concentration of the complex in the organic phase ($[CrMD_{org}]$) as shown in equation 66.

$$[Cr_{org}] = [Cr_{org}]_{stoic} - [CrMD_{org}] \qquad \text{(eq 66)}$$

The stoichiometric value of the salt concentration, $[M^+_{aq}]$, was used in equation 63 since the concentration of salt was one thousand times greater than that of the dye.

Sample 7: The determination of K_{123} for dibenzo-18-crown-6 with potassium chloride via extraction method 4. The value is listed in Table VI of the Results Section. The experimental data can be found in Appendix V Table A. The extinction coefficients of the dye employed can be found in Table V of the Results Section.

$$[CrMD_{org}] = \frac{(0.546)\,(1.00)}{(2.76 \times 10^{4}\ L\ mol^{-1}cm^{-1})\,(1.00\ cm)} \qquad \text{(eq 64)}$$

$$= 1.98 \times 10^{-5}\ mol\ L^{-1}$$

$$[D^{-}_{aq}] = \frac{(0.318)\,(1.00)}{(2.76 \times 10^{4}\ L\ mol^{-1}cm^{-1})\,(1.00\ cm)} \qquad \text{(eq 65)}$$

$$= 1.15 \times 10^{-5}\ mol\ L^{-1}$$

$$[Cr_{org}] = (1.18 \times 10^{-4}\ mol\ L^{-1}) - (1.98 \times 10^{-5}\ mol\ L^{-1}) \qquad \text{(eq 66)}$$

$$= 9.79 \times 10^{-5}\ mol\ L^{-1}$$

$$K_{123} = \frac{1.98 \times 10^{-5}\ mol\ L^{-1}}{(9.79 \times 10^{-5}\ mol\ L^{-1})\,(0.0100\ mol\ L^{-1})\,(1.15 \times 10^{-5}\ mol\ L^{-1})} \qquad \text{(eq 63)}$$

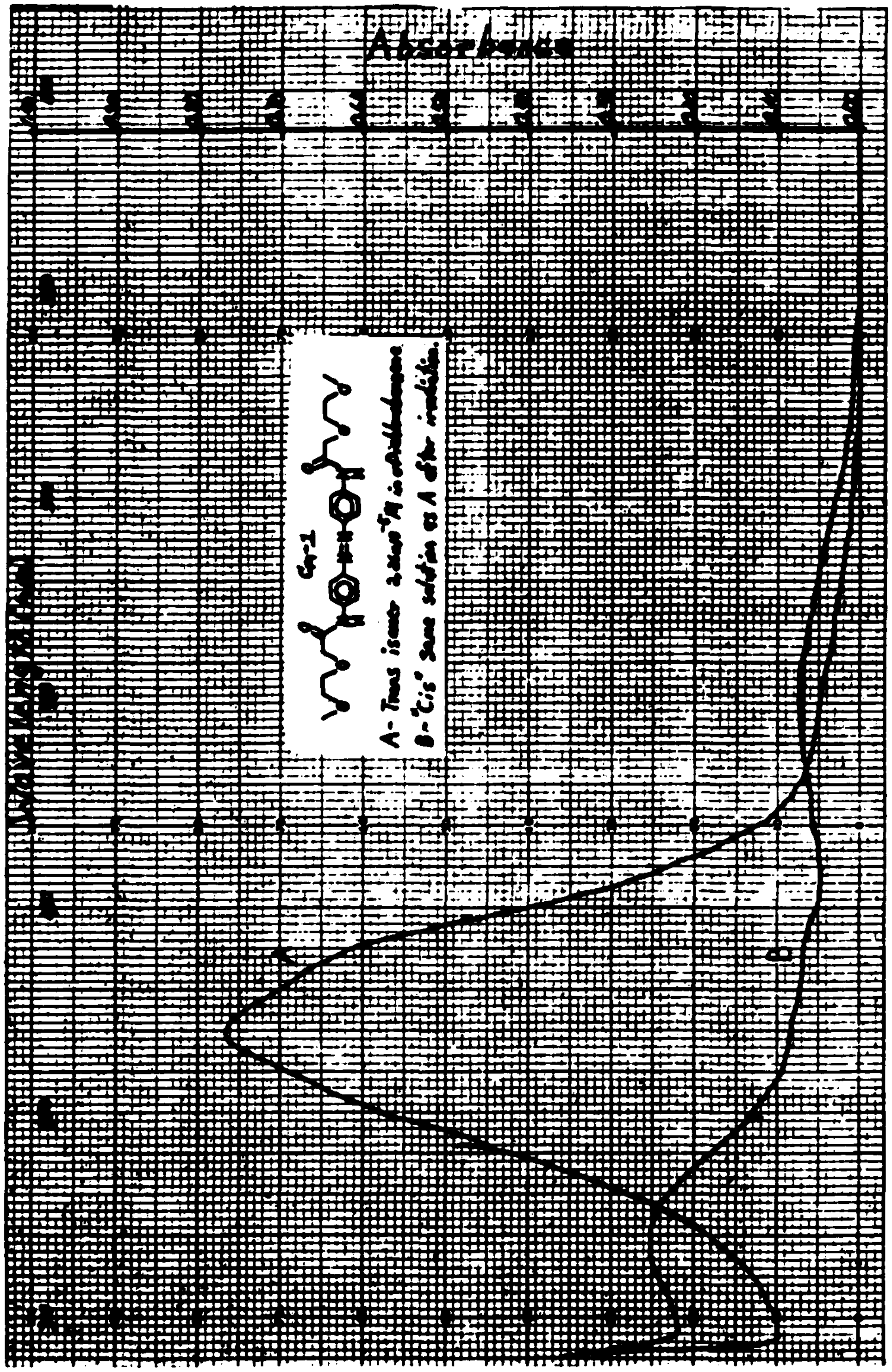
$$= 1.75 \times 10^{6}\ L^{2}\ mol^{-2}$$

Appendix I

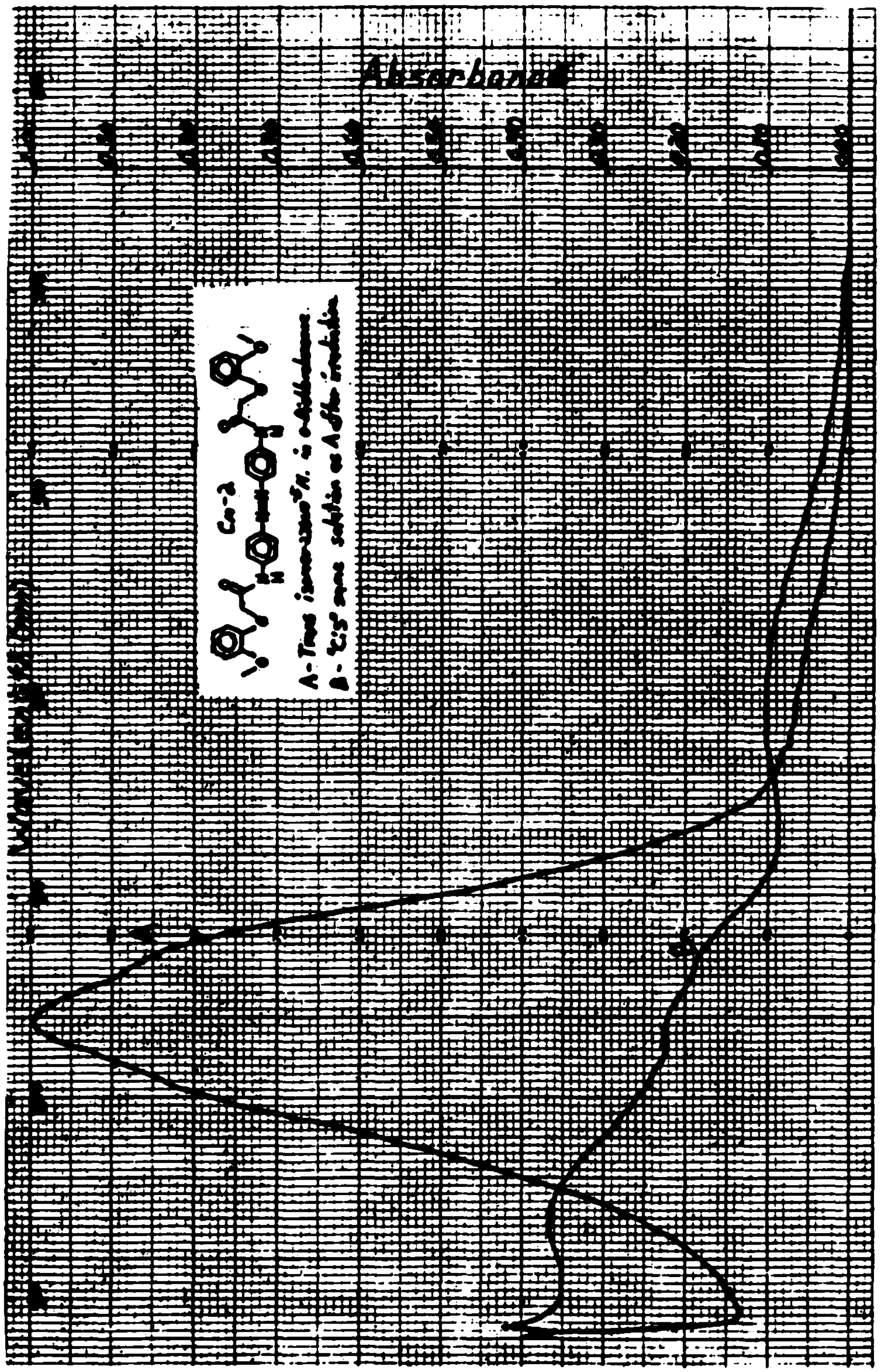
Ultraviolet - Visible Spectra

The following UV Spectra were of the compounds Cm-1, Cm-2, Cm-3, Cm-4 and dye D1. The concentrations and solvents were listed on each spectrum.

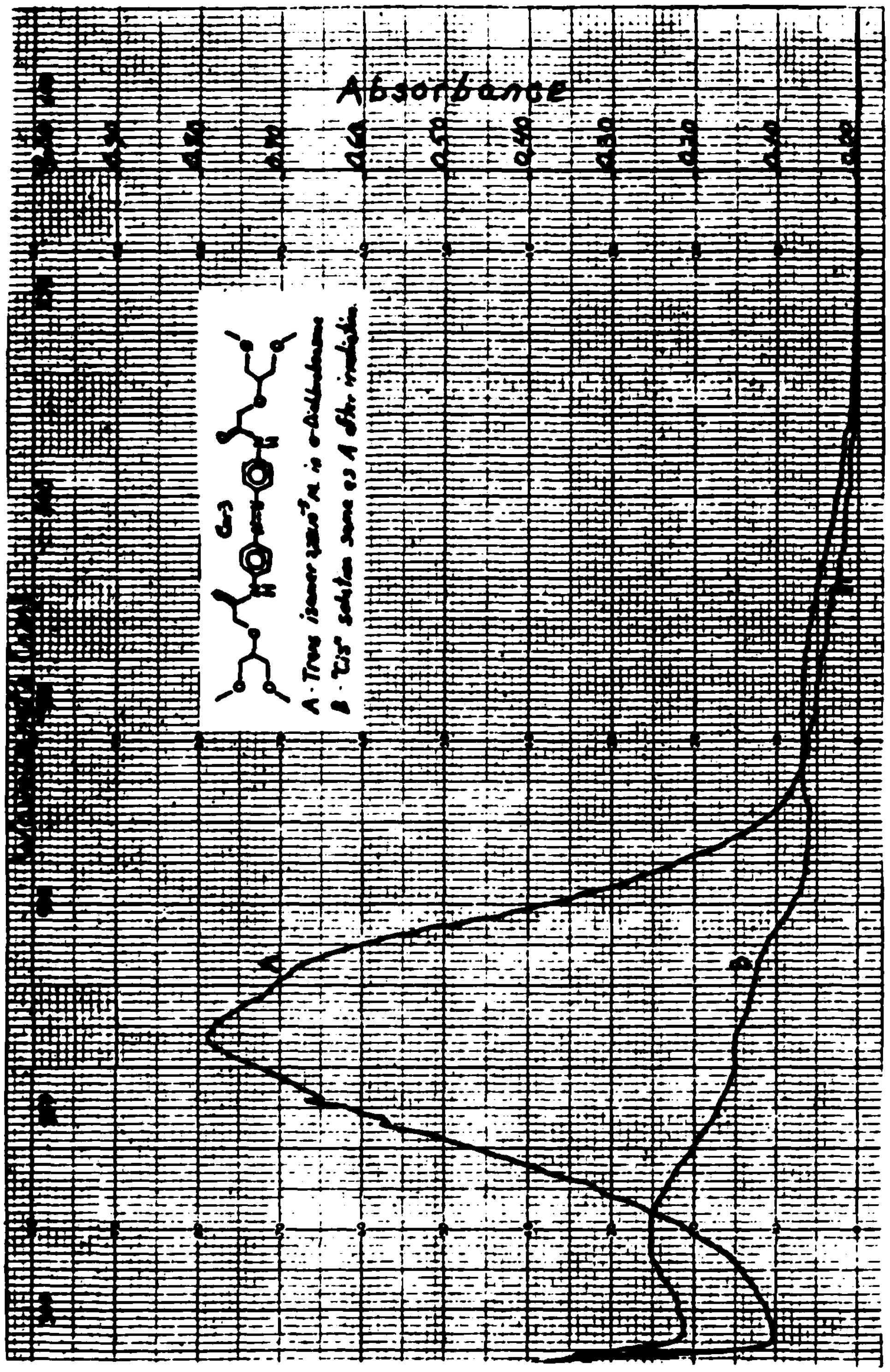
UV Spectrum of Cm-1



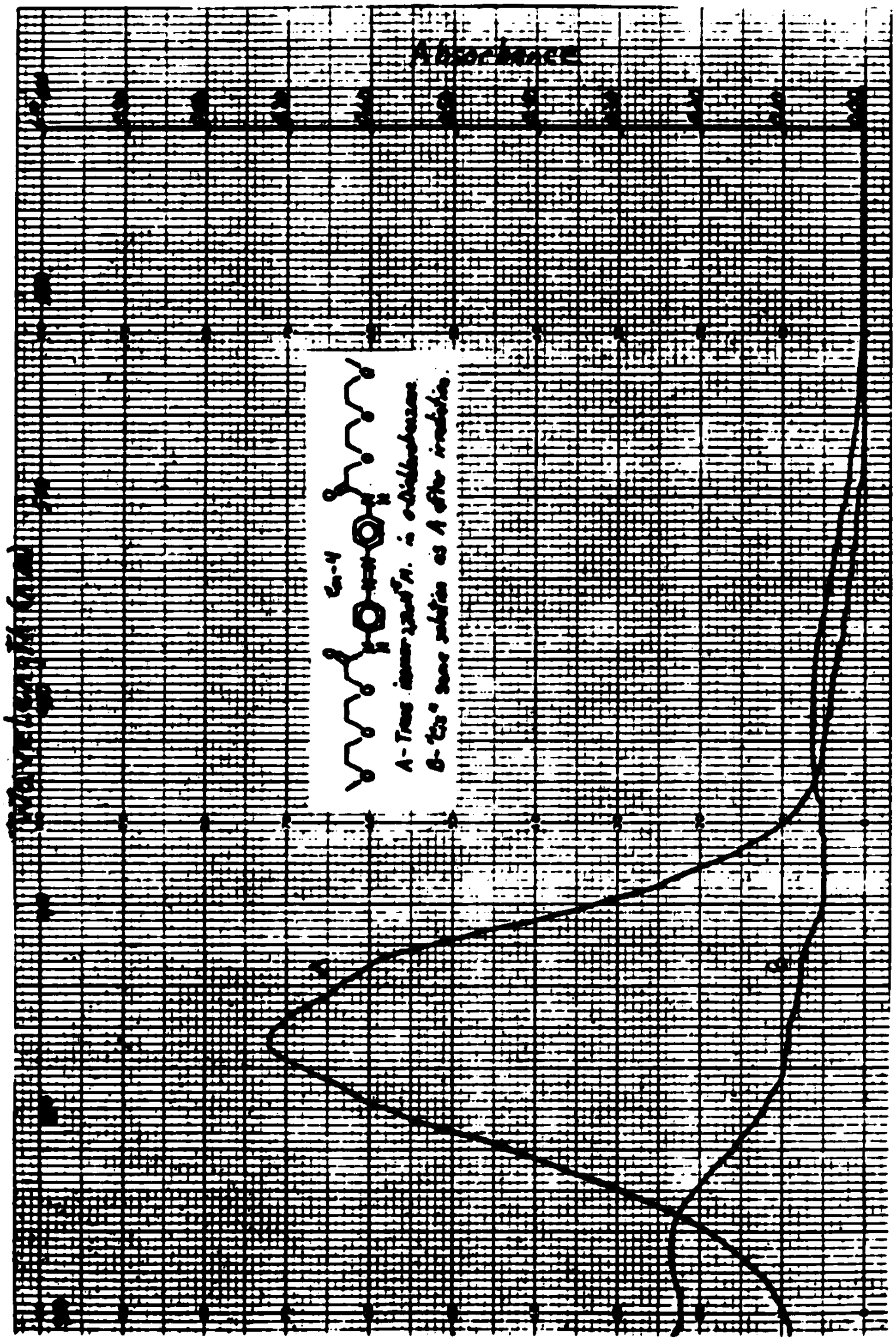
UV Spectrum of Cm-2



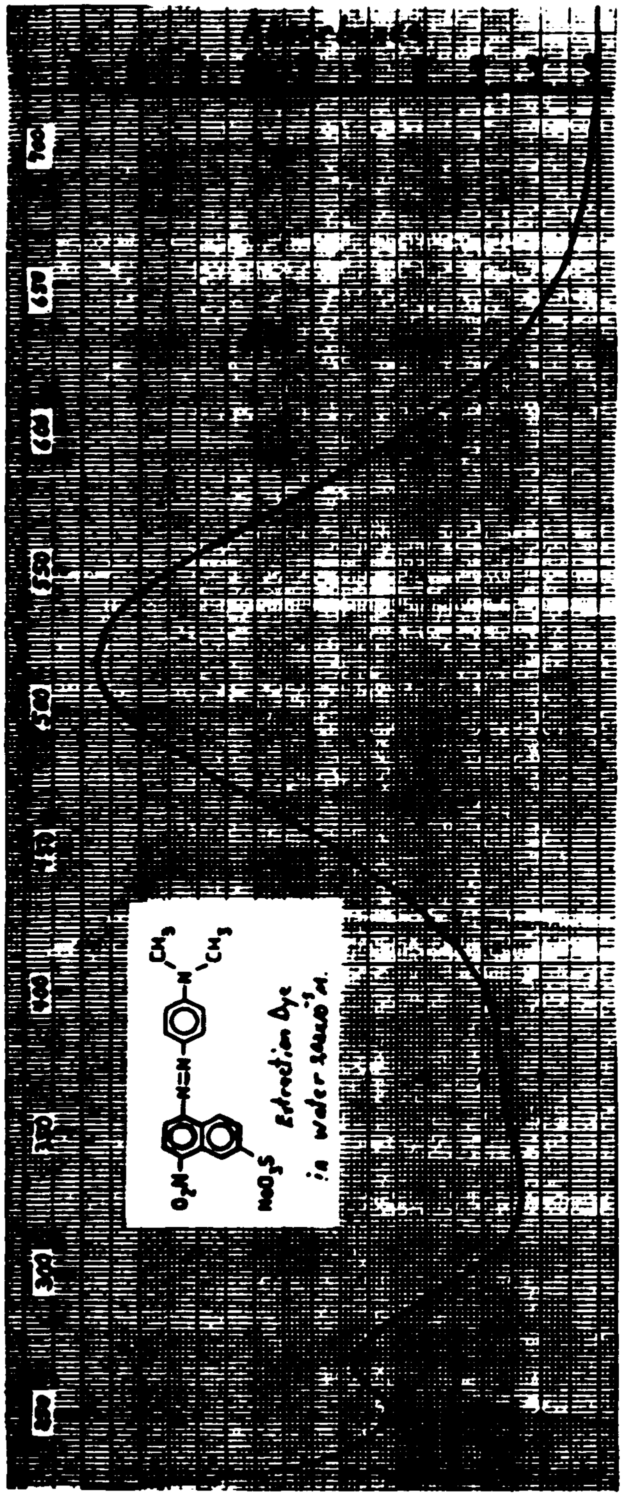
UV Spectrum of Cm-3



UV Spectrum of Cm-4



UV Spectrum of Dye - D1

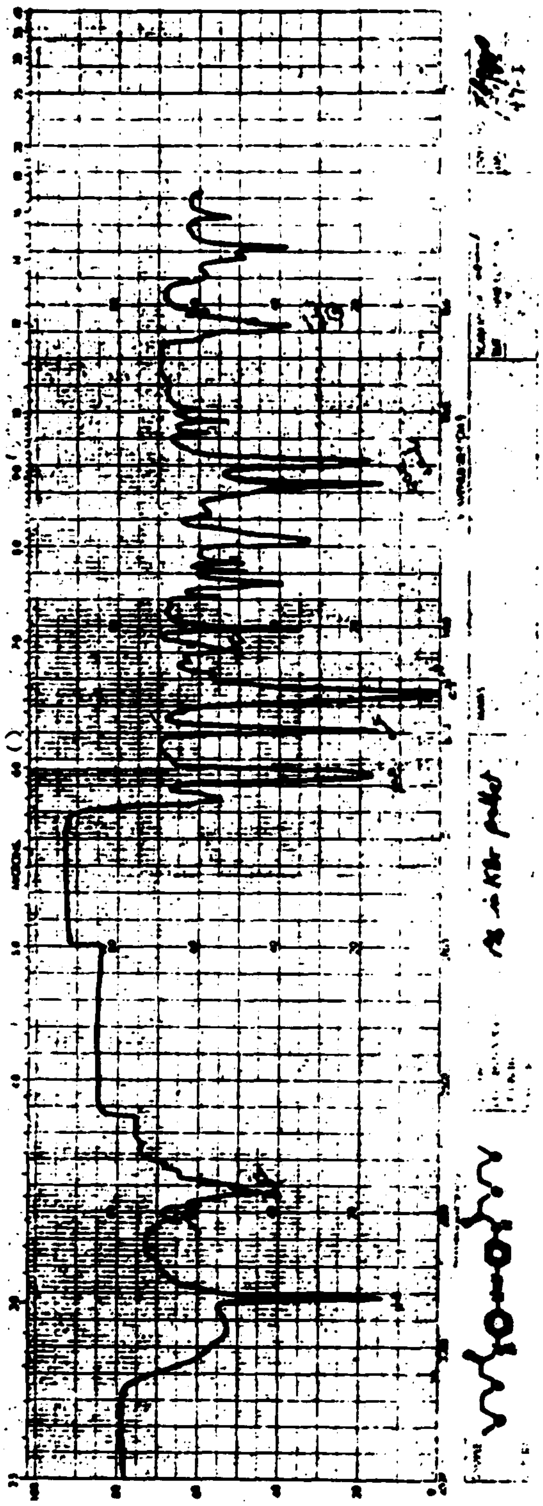


Appendix II

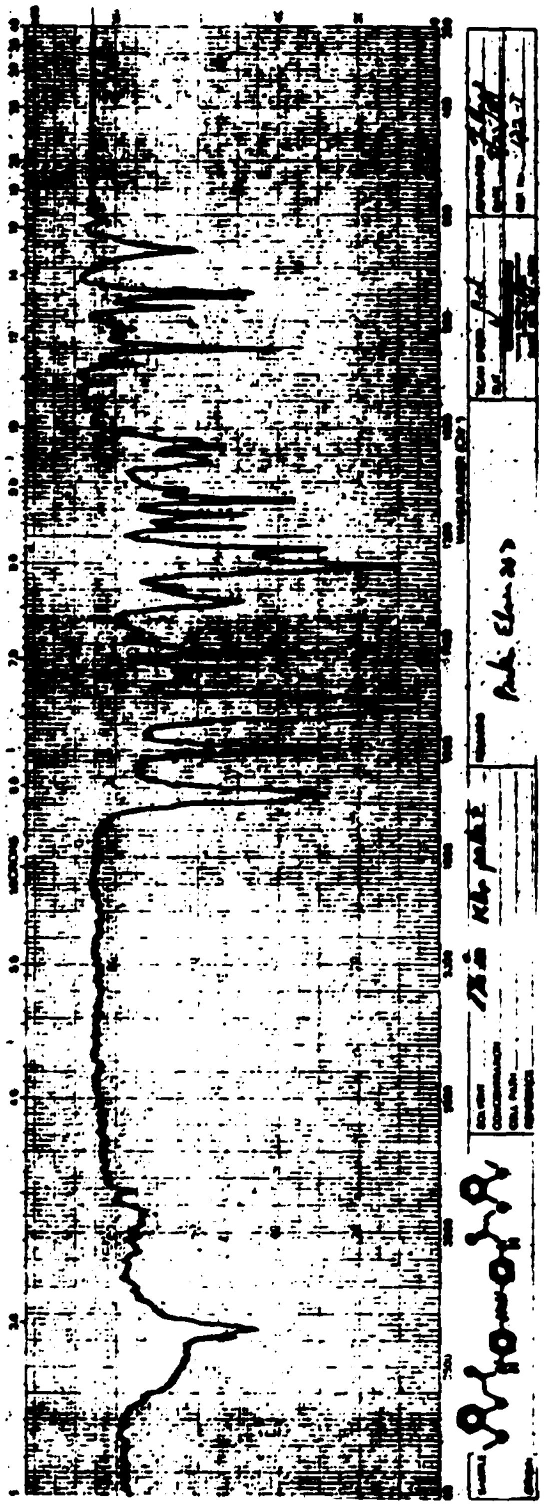
Infrared Spectra

The following IR Spectra were of the compounds Cm-1, Cm-2, Cm-3, Cm-4 and dye D1. The sample conditions were listed on each spectrum.

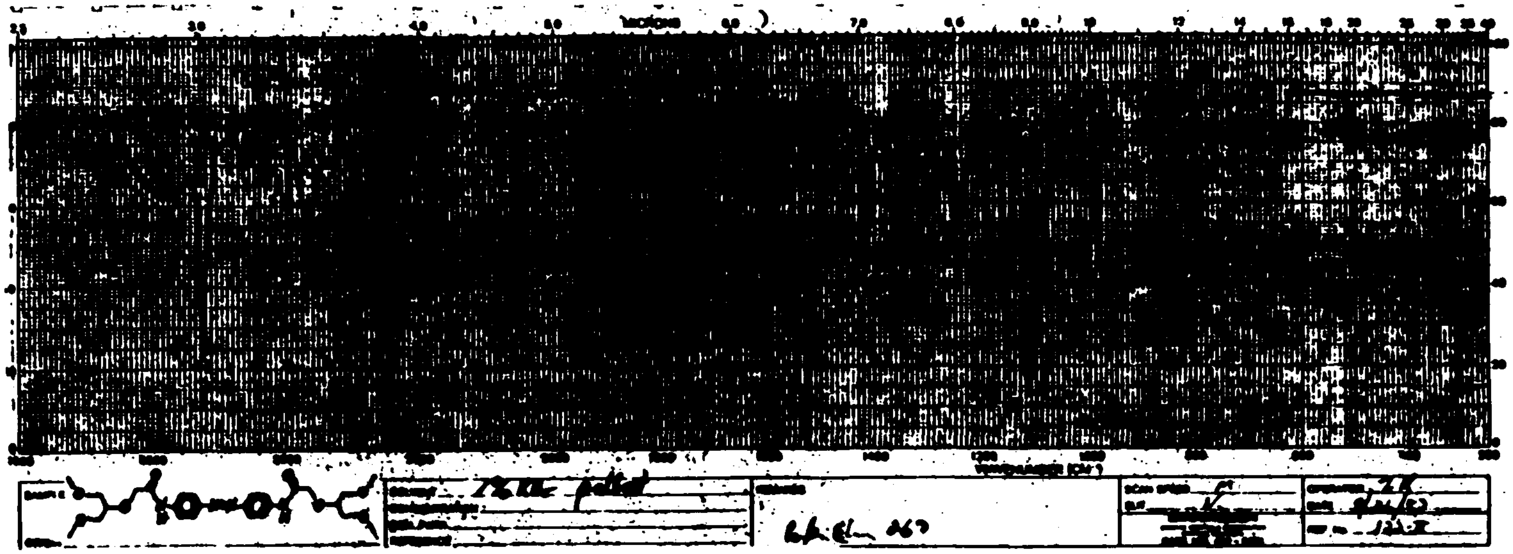
IR Spectrum of Cm-1



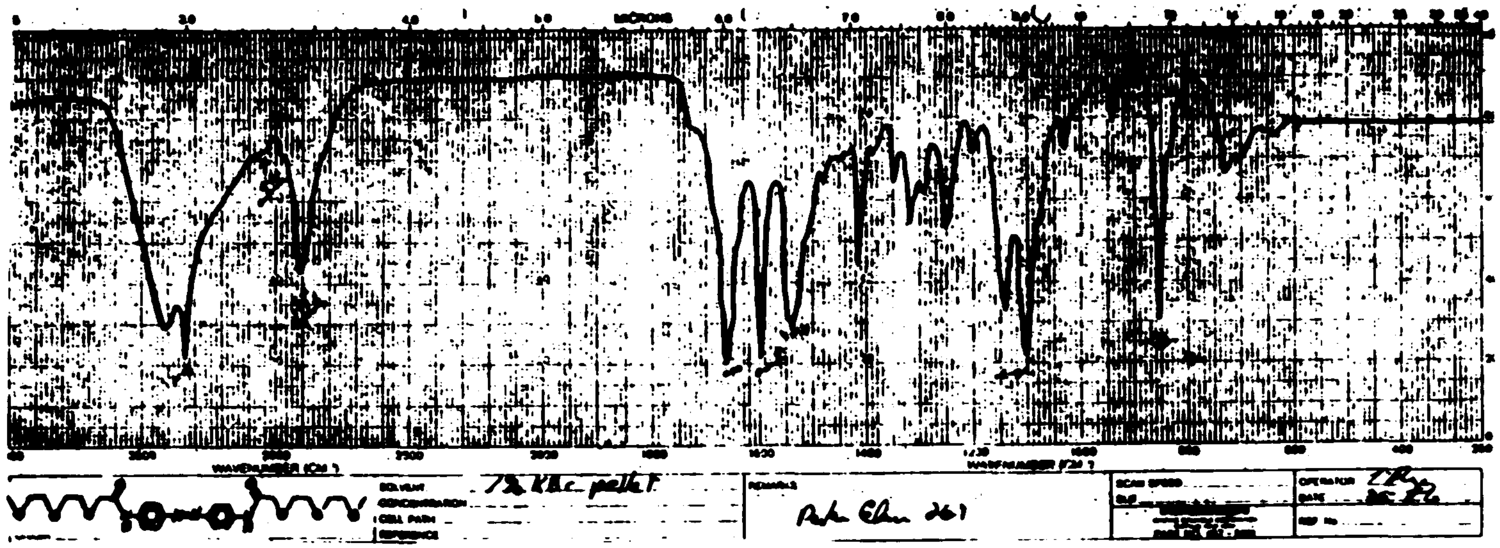
IR Spectrum of Cm-2



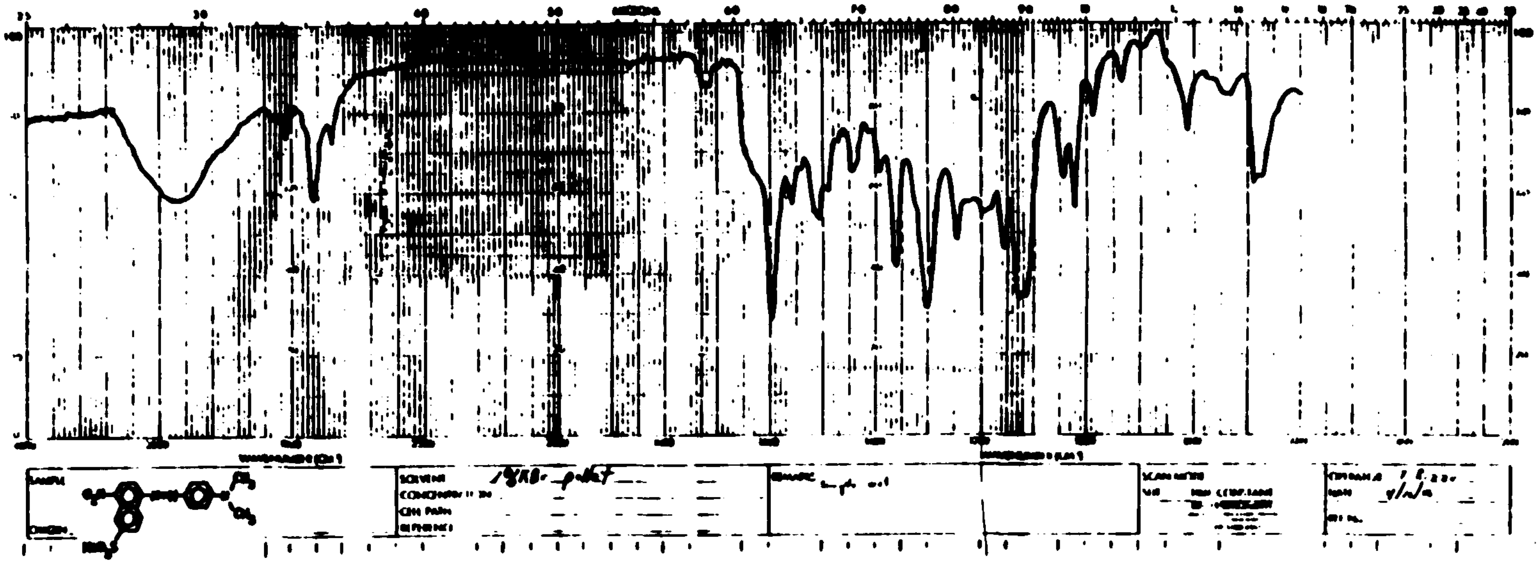
IR Spectrum of Cm-3



IR Spectrum of Cm-4



IR Spectrum of Dye - D1

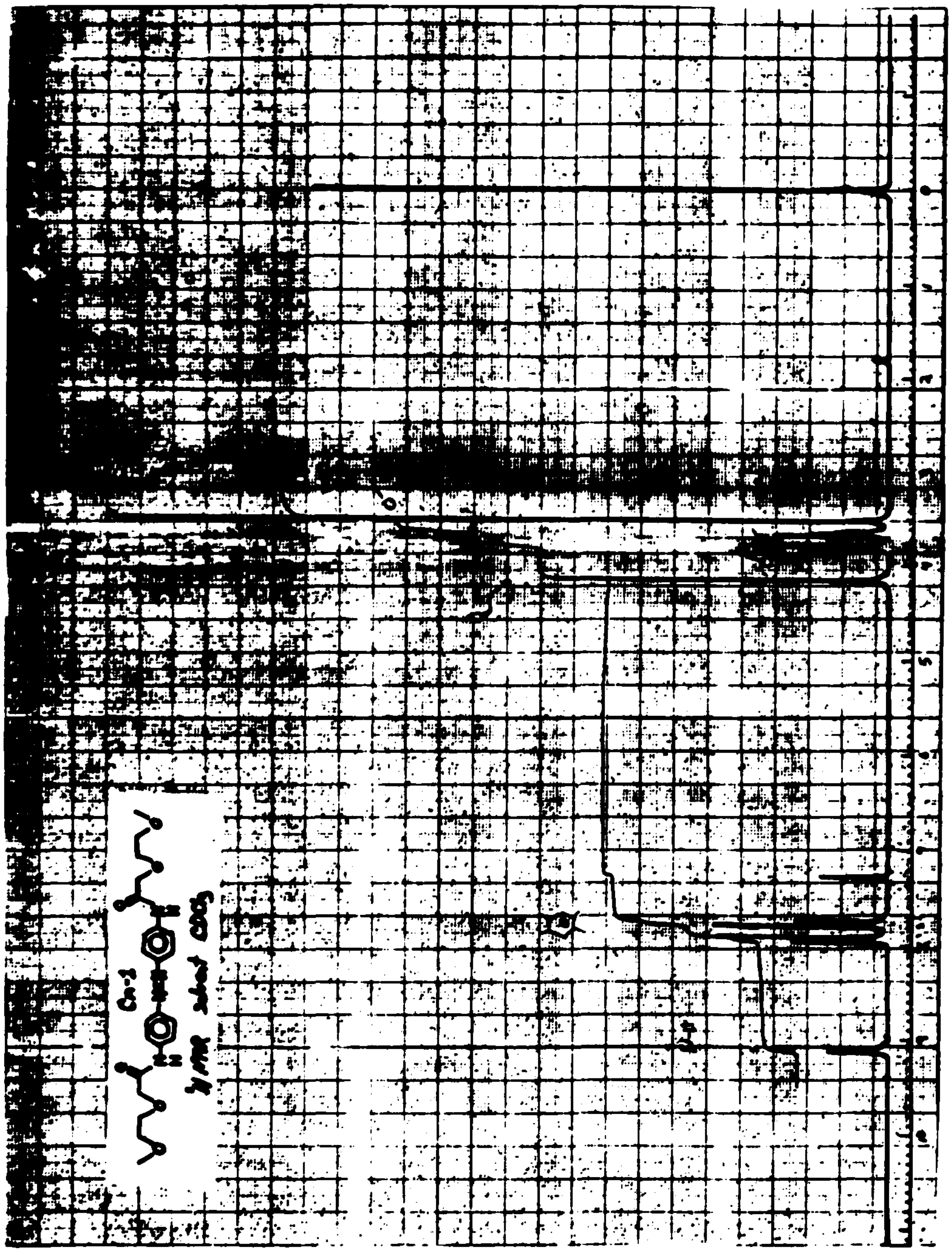


Appendix III

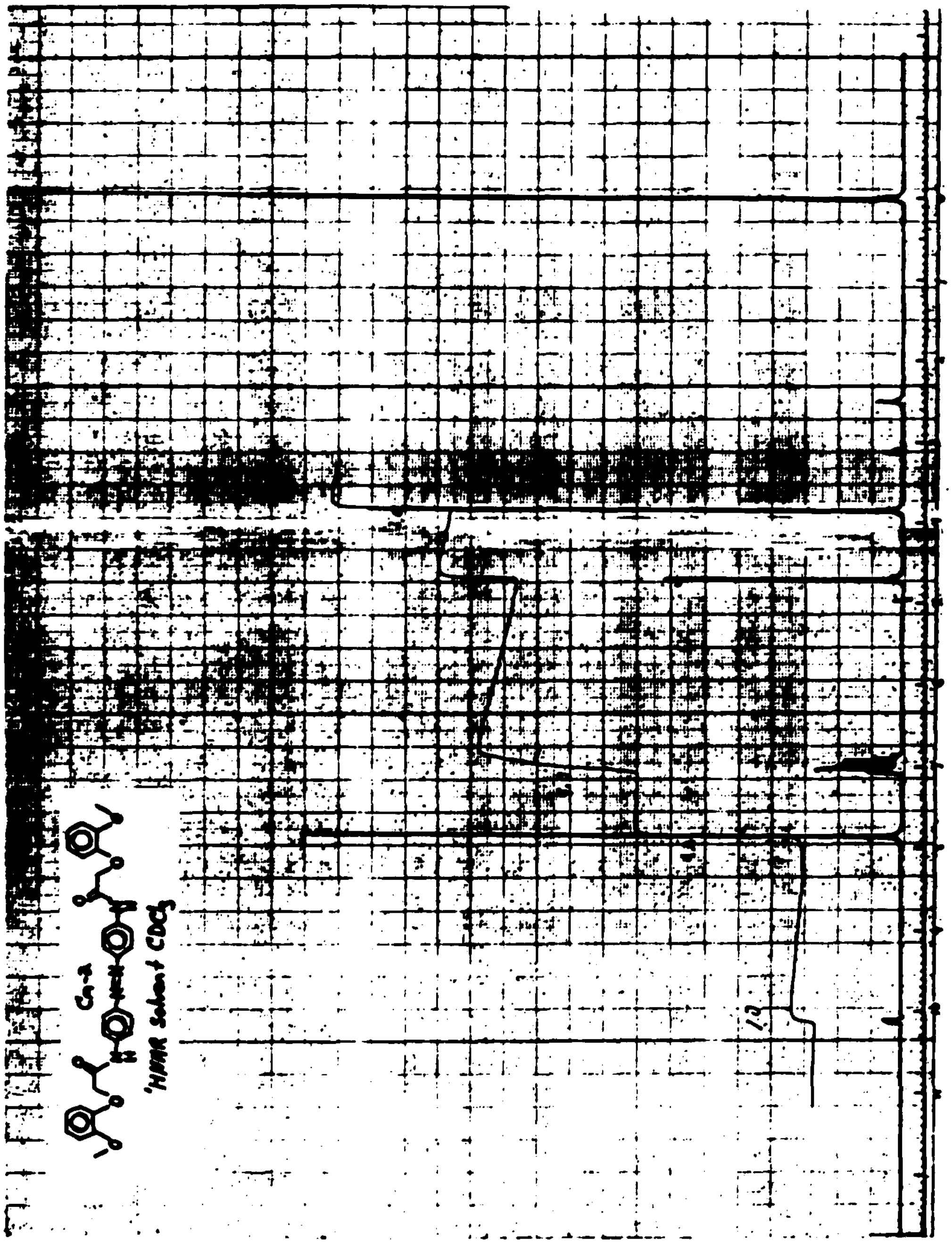
^{1}H NMR Spectra

The following ^{1}HNMR Spectra were of compounds Cm-1, Cm-2, Cm-3, Cm-4 and the dye D1. The conditions and solvents were shown on each spectrum. There were two spectra of the dye D1, one in water and one in dimethylsulfoxide.

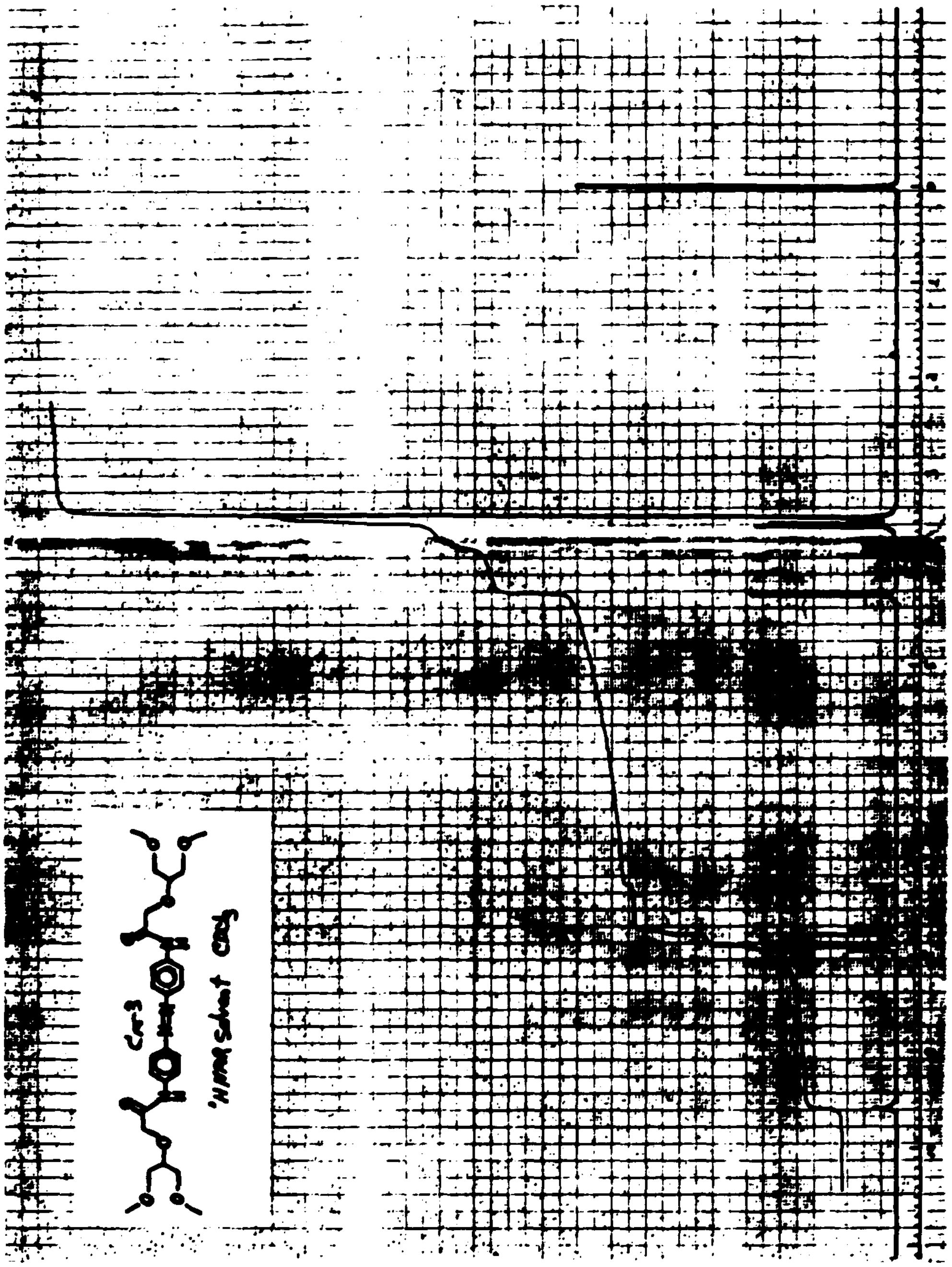
^{1}HNMR Spectrum of Cm-1



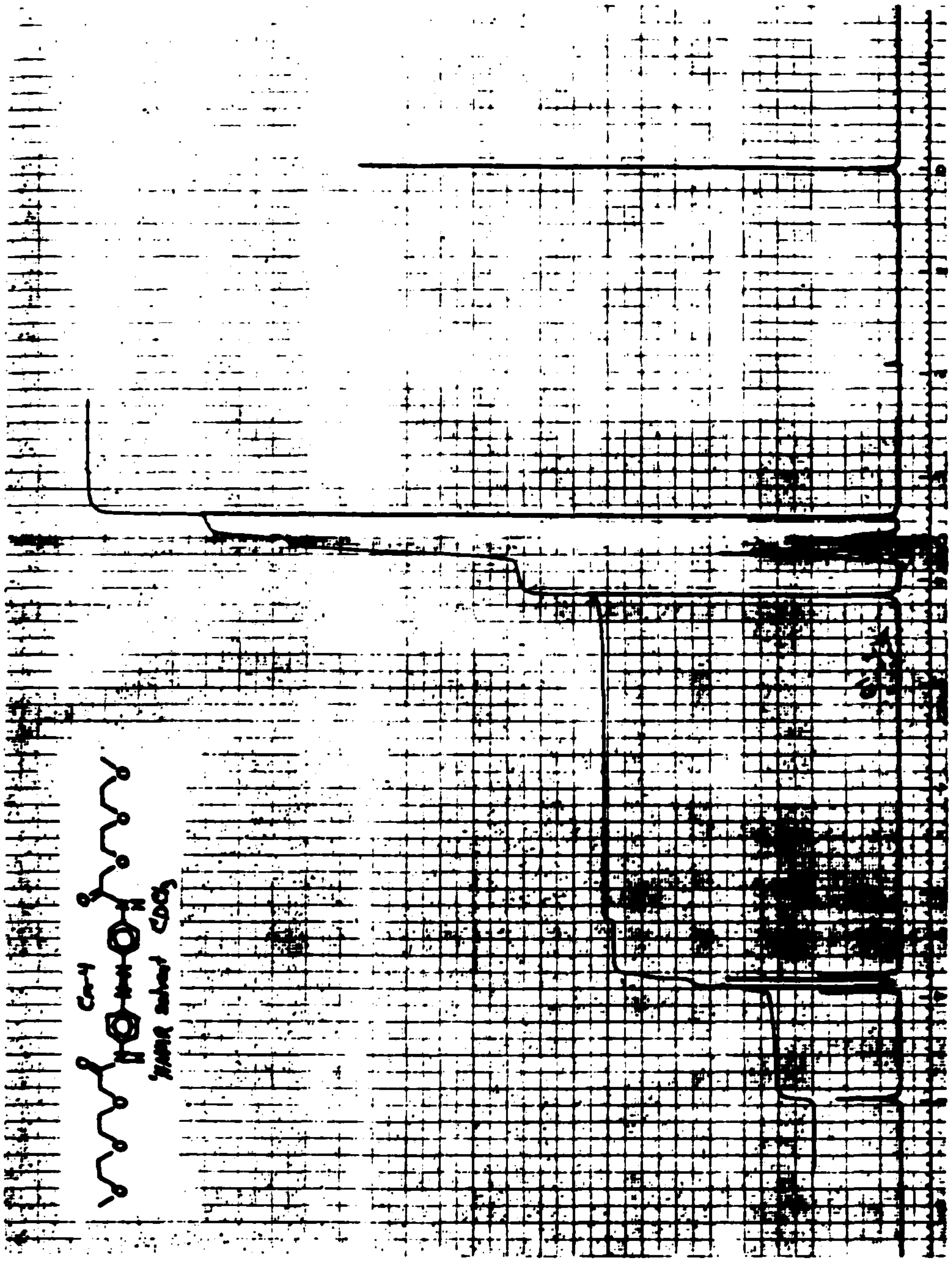
^{1}HNMR Spectrum of Cm-2



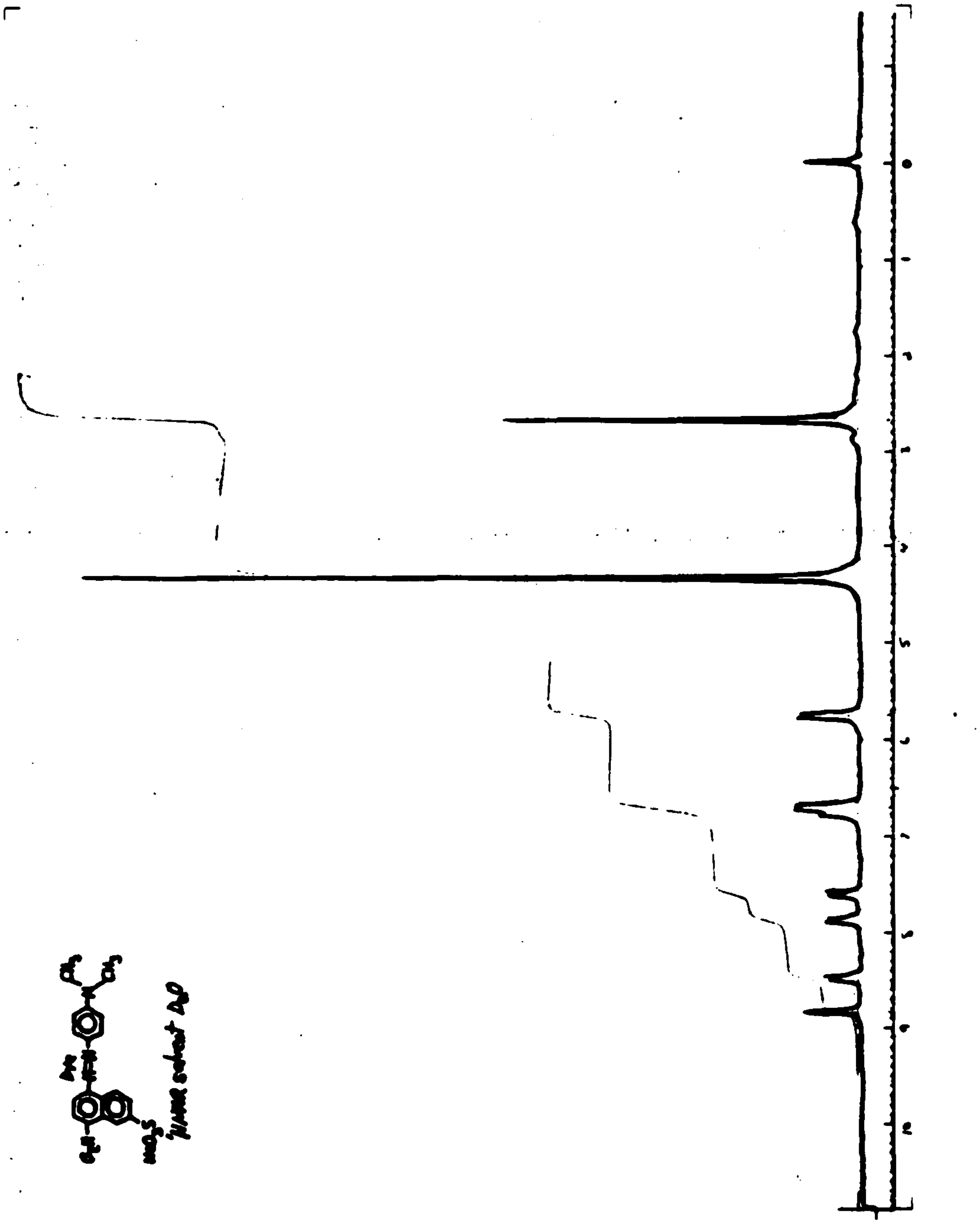
^{1}HNMR Spectrum of Cm-3



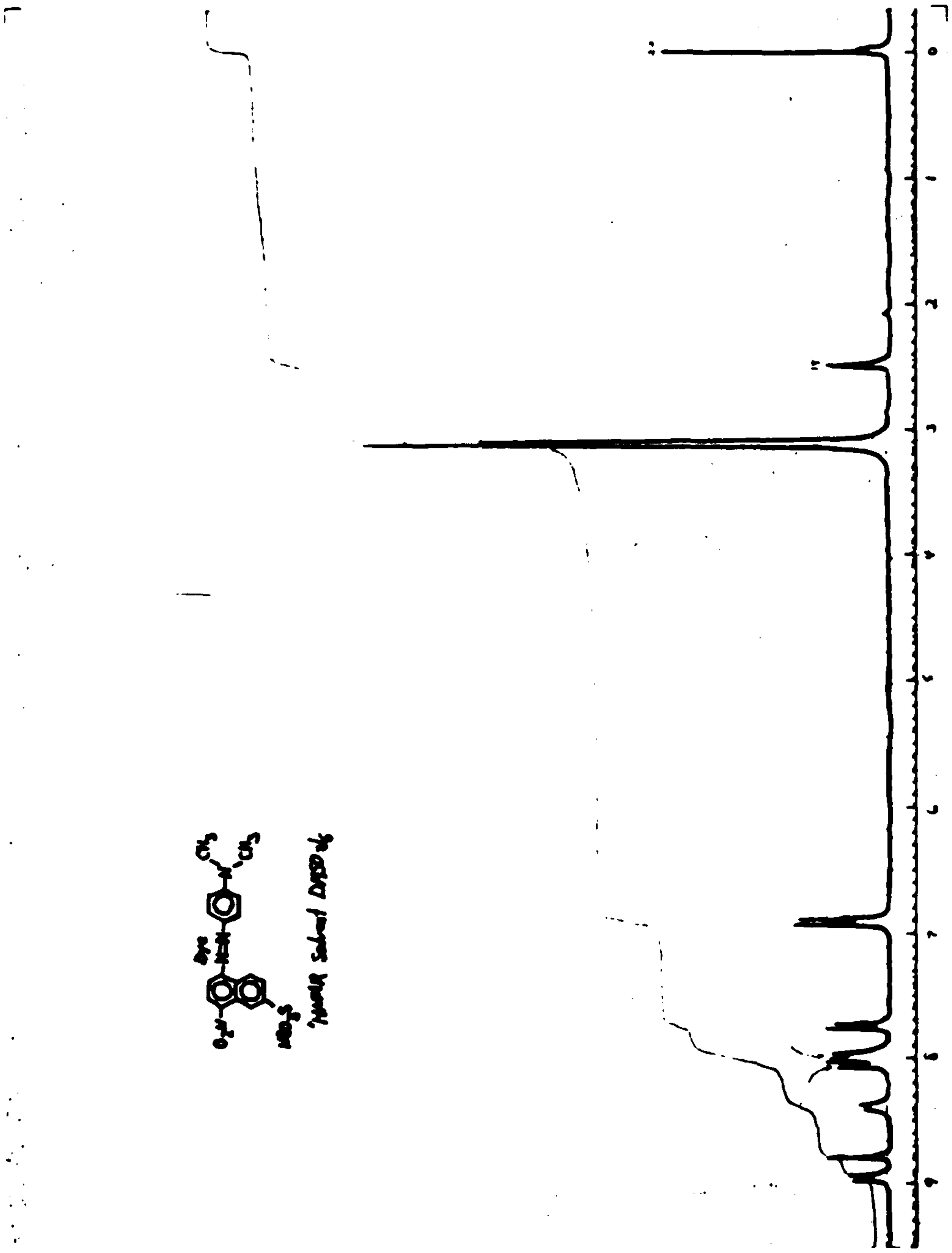
^{1}HNMR Spectrum of Cm-4



¹HNMR Spectrum of Dye D1 (water)



¹HNMR Spectrum of Dye D1 (DMSO)

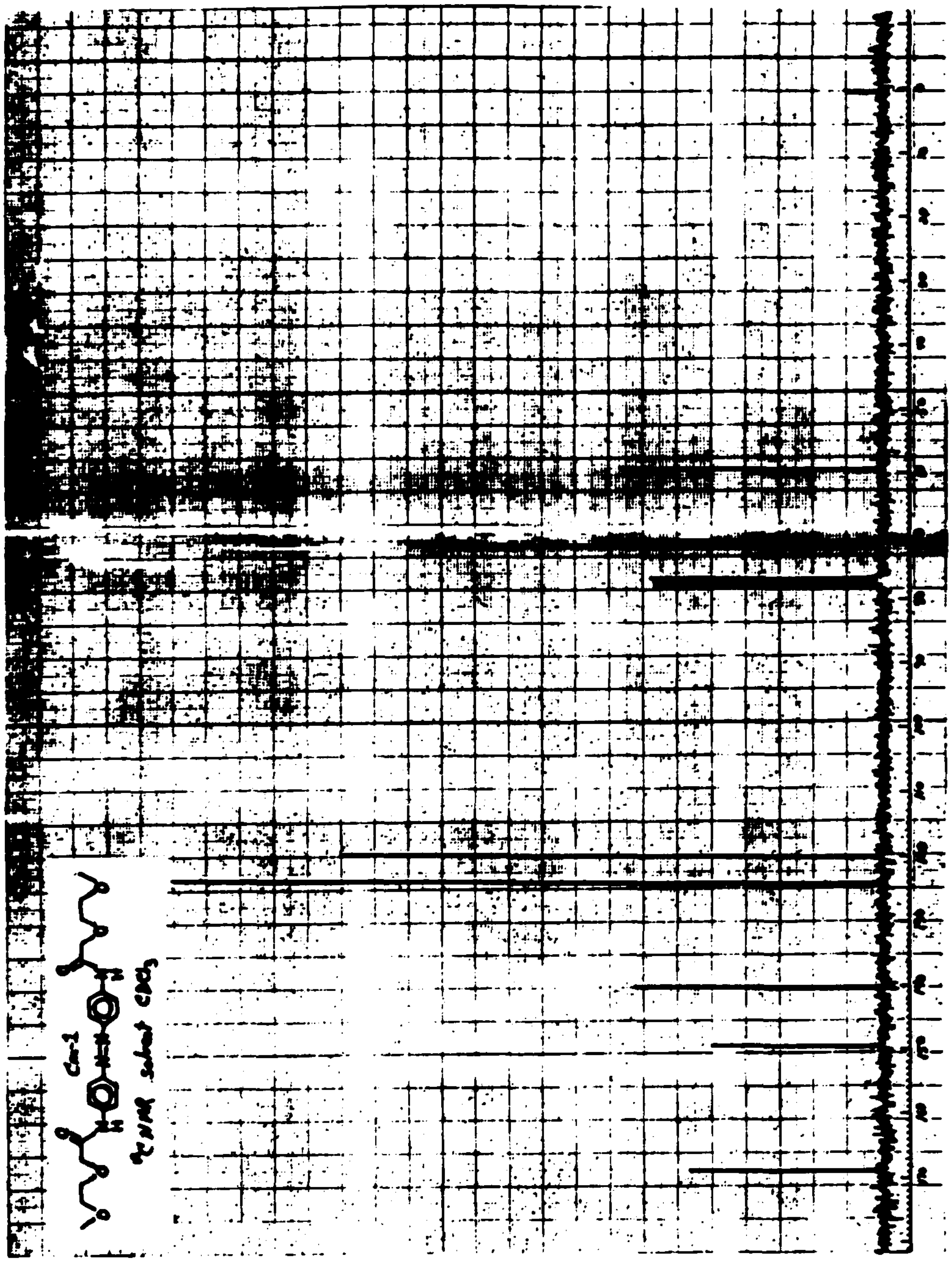


Appendix IV

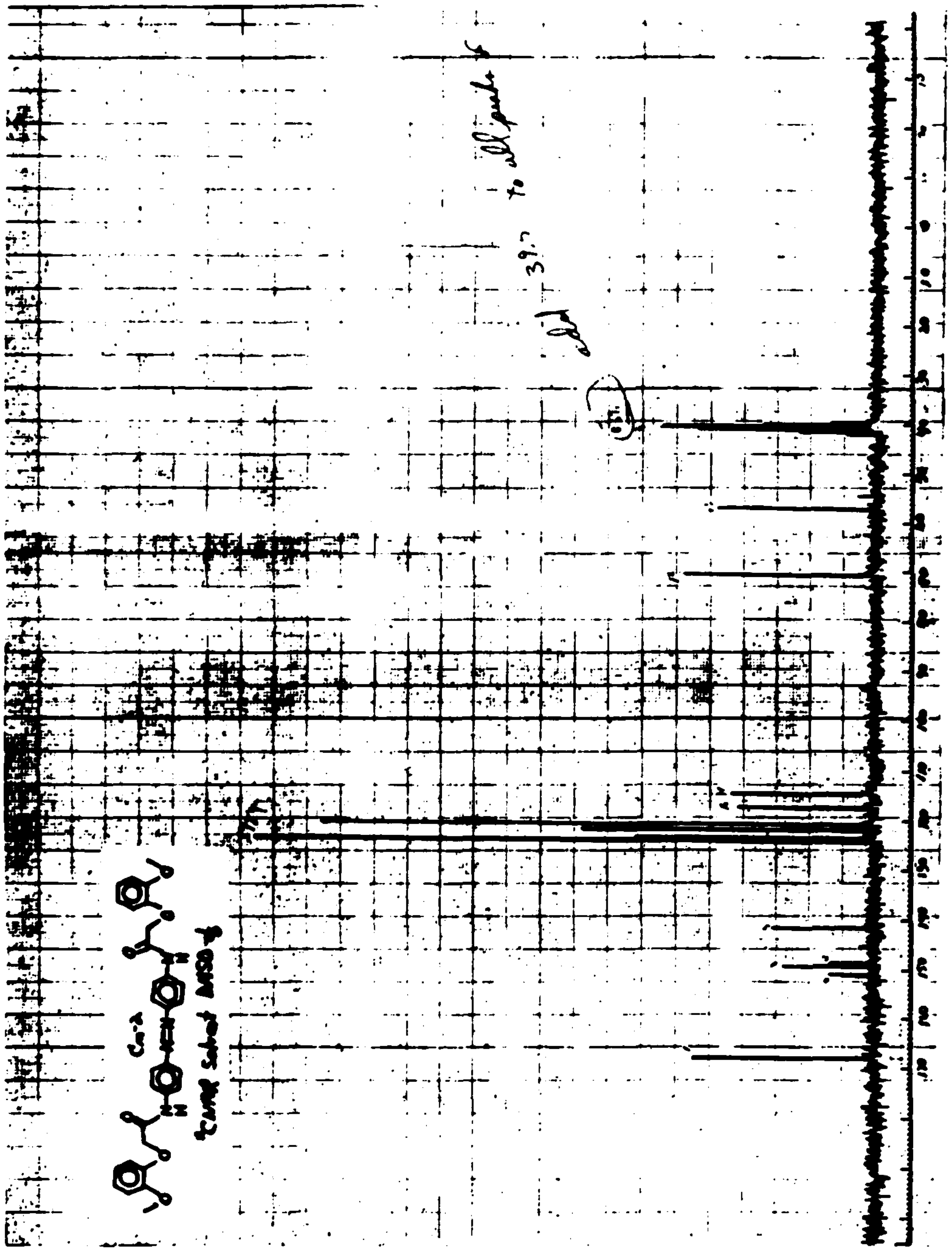
^{13}C NMR Spectra

The following ^{13}C NMR Spectra were of compounds Cm-1, Cm-2, Cm-3, Cm-4 and the dye D1. The conditions and solvents were shown on each spectrum.

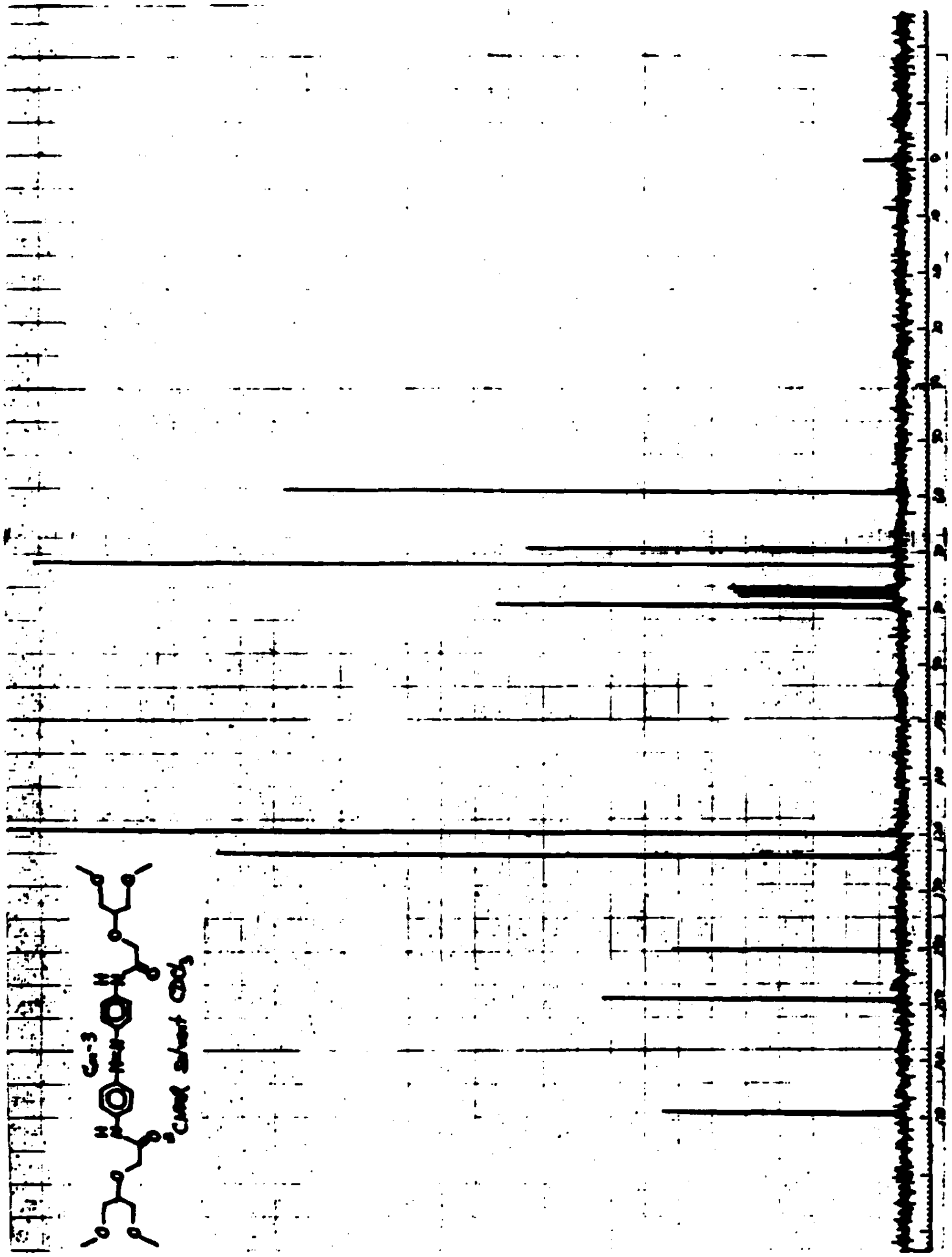
^{13}C NMR Spectrum of Cm-1



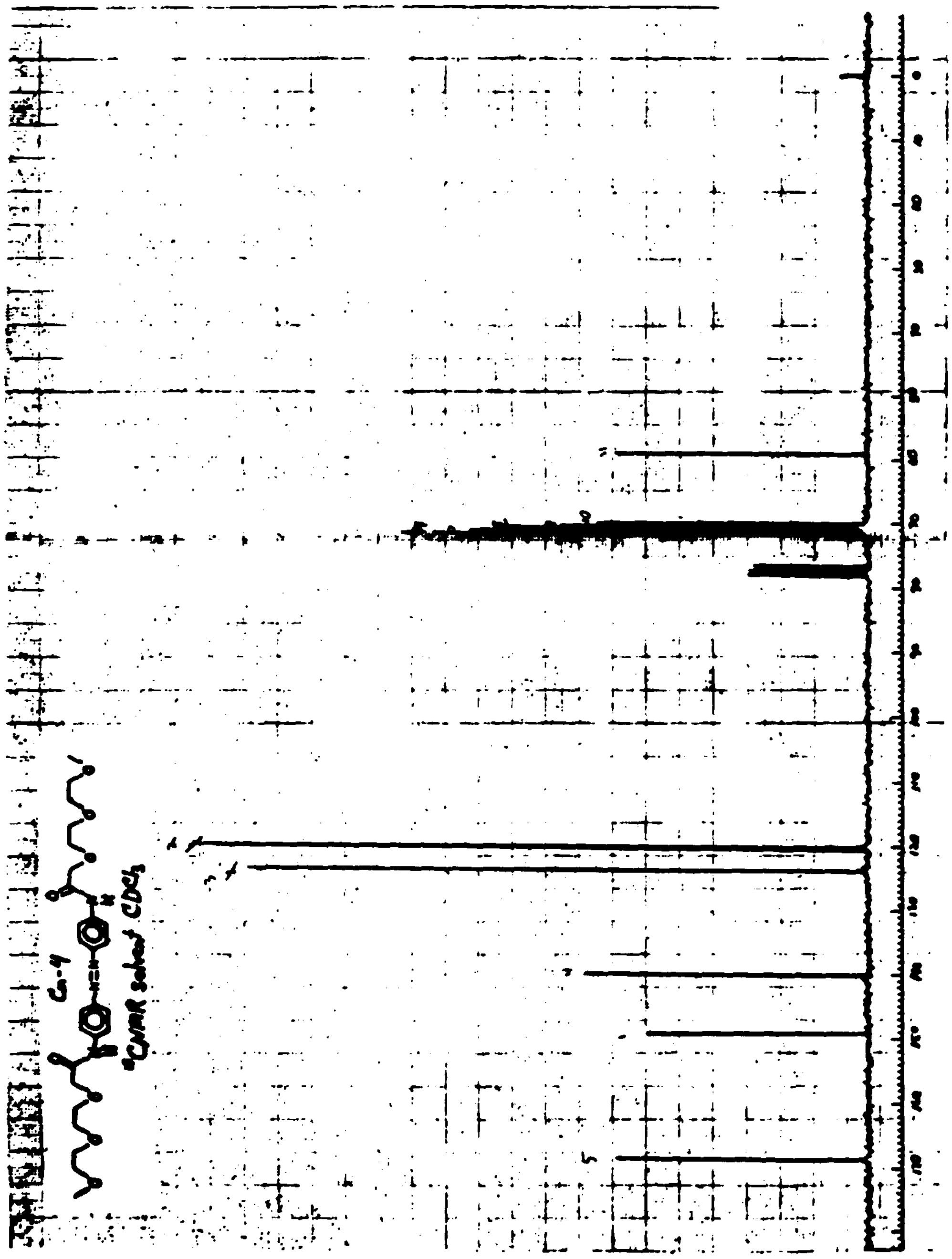
^{13}C NMR Spectrum of Cm-2



^{13}C NMR Spectrum of Cm-3



^{13}C NMR Spectrum of Cm-4



^{13}C NMR Spectrum of Dye D1

Appendix V

Experimental Data

The following tables of data were employed in the determination of various constants, provided in the Results Section, as calculated by methods described in the Experimental Section.

Table A

Data for the Calculation of K_{123} for Dibenzo-18-Crown-6, found in Table VI of the Results Section.

Species	Li	Na	K	Cs
A_{org}	0.210	0.266	0.546	0.492
D_{org}	1.00	1.00	1.00	1.00
$P_{A,org}$[a]	1.00	1.00	1.00	1.00
A_{aq}	0.592	0.438	0.318	0.284
D_{aq}	1.00	1.00	1.00	1.00
$P_{A,aq}$[a]	1.00	1.00	1.00	1.00
$[Cr_{org}]_{stoic}$[b]	12.76	3.019	0.1177	3.006
$[M^{+}_{aq}]_{stoic}$[c]	1.005	1.001	1.001	0.4990

a) Path length has units of cm.
b) Concentration in units of (mol/L) x 10^3.
c) Concentration in units of (mol/L) x 10^2.

Table B

Data for the Calculation of Partition Coefficients (K_1) for Complexing Agents between Water and *o*-Dichlorobenzene* at 25 °C, found in Table VII of the Results Section.

Species	Cm-1	Cm-2	Cm-3	Cm-4
A_1	0.813	0.612	0.532	0.641
D_{A1}	83.33	50.00	50.00	50.00
$P_{A1}{}^{a}$	1.00	1.00	1.00	1.00
A_2	1.760	0.110	0.215	0.599
D_{A2}	1.00	1.00	1.00	10.00
$P_{A2}{}^{a}$	1.00	1.00	1.00	1.00
A_3	0.525	0.225	0.543	1.567
D_{A3}	1.00	1.00	1.00	25.00
$P_{A3}{}^{a}$	1.00	1.00	1.00	1.00
A_4	0.255	0.596	0.417	0.371
D_{A4}	3.33	50.00	50.00	50.00
$P_{A4}{}^{a}$	1.00	1.00	1.00	1.00
k ($min^{-1} \times 10^3$)	18.13	1.827	2.182	1.773
b	0.2128	0.5794	0.3167	0.1327
t1 (min)	7.00	11.00	8.00	9.00
t2 (min)	10.00	14.00	11.00	12.00

*) Contains 1.00% by weight cyclohexanol.
a) Path length has units of cm.

Table C

Data for the Calculation of Partition Coefficients (K_1) for Cm-1 between Water and Various Organic Solvents at 25 °C, found in Table VIII of the Results Section.

Species	DCB*	DCB^a	OCT^b	CB^c	TOL^d	BEN^e
A_1	0.813	0.678	0.693	0.832	0.269	0.983
D_{A1}	83.33	83.33	50.00	83.33	83.33	62.50
$P_{A1}{}^f$	1.00	1.00	1.00	1.00	1.00	1.00
A_2	1.760	1.276	0.798	1.165	1.205	0.790
D_{A2}	1.00	1.00	3.33	3.33	3.33	11.11
$P_{A2}{}^f$	1.00	1.00	1.00	1.00	1.00	1.00
A_3	0.255	0.370	0.300	0.287	0.143	0.251
D_{A3}	3.33	3.33	2.50	5.00	5.00	5.00
$P_{A3}{}^f$	1.00	1.00	1.00	1.00	1.00	1.00
A_4	0.525	0.499	1.005	0.868	0.457	1.080
D_{A4}	1.00	1.00	1.00	1.00	1.00	1.00
$P_{A4}{}^f$	1.00	1.00	1.00	1.00	1.00	1.00
k (min^{-1} x 10^3)	18.13	2.242	2.011	1.969	1.915	1.778
b	0.2128	0.1289	0.1329	0.0849	0.0615	0.0436
t1 (min)	7.00	9.00	8.00	12.00	13.00	10.00
t2 (min)	10.00	12.00	11.00	15.00	16.00	13.00

) DCB stands for o-dichlorobenzene which contains 1.00 % by weight cyclohexanol.
a) DCB stands for o-dichlorobenzene.
b) OCT stands for octanol.
c) CB stands for chlorobenzene.
d) TOL stands for toluene.
e) BEN stands for benzene.
f) Path length has units of cm.

Table D

Data for the Determination of the Stoichiometry of Complexes for Cm-1 with Alkali Metals. Extraction Data for Cm-1 in *o*-Dichlorobenzene* with Aqueous KCl at 25 °C, found in Table IX of the Results Section.

	Trial 2		Trial 3	
Species	Cm_T-1	Cm_C-1	Cm_T-1	Cm_C-1
A_{12}	0.462	0.458	0.470	0.514
A_{13}	0.368	0.368	0.383	0.383
$P_{A12\text{-}13}$[a]	5.00	5.00	5.00	5.00
A_{14}	0.533	0.569	0.516	0.417
D_{A14}	5.00	5.00	5.00	5.00
P_{A14}[a]	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}$[b]	2.205	2.205	6.579	6.579
$[M^+_{aq}]_{stoic}$[c]	1.001	1.001	0.334	0.334
k (min^{-1} x 10^3)		2.226		2.226
b		0.3934		0.6215
t1		7.00		6.00
t2		17.00		16.00

*) Contains 1.00% by weight cyclohexanol.

a) Path length has units of cm.

b) Concentration is in units of (mol/L) x 10^3.

c) Concentration is in units of (mol/L) x 10^2.

Table E

Data for the Determination of the Stoichiometry of Complexes for Cm-3 with Alkali Metals. Extraction Data for Cm-3 in *o*-Dichlorobenzene* with Aqueous KCl at 25 °C, found in Table X of the Results Section.

	Trial 2		Trial 3	
Species	Cm_T-3	Cm_C-3	Cm_T-3	Cm_C-3
A_{12}	0.405	0.630	0.413	0.529
A_{13}	0.368	0.368	0.383	0.383
$P_{A12\text{-}13}{}^{a}$	5.00	5.00	5.00	5.00
A_{14}	0.544	0.568	0.549	0.523
D_{A14}	5.00	5.00	5.00	5.00
$P_{A14}{}^{a}$	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}{}^{b}$	2.209	2.209	5.626	5.626
$[M^{+}{}_{aq}]_{stoic}{}^{c}$	1.001	1.001	0.334	0.334
k (min^{-1} x 10^3)		2.286		2.286
b		0.2153		0.6072
t1		7.00		4.00
t2		17.00		14.00

*) Contains 1.00% by weight cyclohexanol.

a) Path length has units of cm.

b) Concentration is in units of (mol/L) x 10^3.

c) Concentration is in units of (mol/L) x 10^2.

Table F

Data for the Determination of the Stoichiometry of Complexes for Cm-4 with Alkali Metals. Extraction Data for Cm-4 in *o*-Dichlorobenzene* with Aqueous KCl at 25 °C, found in Table XI of the Results Section.

	Trial 2		Trial 3	
Species	Cm_T-4	Cm_C-4	Cm_T-4	Cm_C-4
A_{12}	0.554	0.501	0.527	0.431
A_{13}	0.074	0.074	0.076	0.076
$P_{A12\text{-}13}$ [a]	1.00	1.00	1.00	1.00
A_{14}	0.529	0.505	0.488	0.396
D_{A14}	5.00	5.00	5.00	5.00
P_{A14} [a]	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}$ [b]	2.217	2.217	6.582	6.582
$[M^+_{aq}]_{stoic}$ [c]	1.001	1.001	0.334	0.334
k (min^{-1} x 10^3)		1.746		1.746
b		0.1676		0.9230
t1		6.00		6.00
t2		16.00		16.00

*) Contains 1.00% by weight cyclohexanol.

a) Path length has units of cm.

b) Concentration is in units of (mol/L) x 10^3.

c) Concentration is in units of (mol/L) x 10^2.

Table G

Data for the Calculation of Equilibrium Constants K_2K_3 for Cm-1 in *o*-Dichlorobenzene* at 25 °C, found in Table XII of the Results Section.

Species	Li_T-	Li_C-	Na_T-	Na_C-	K_T-	K_C-	Cs_T-	Cs_C
A_{12}	0.651	1.829	0.653	1.196	0.875	1.060	0.547	1.926
A_{13}	0.483	0.483	0.427	0.427	0.464	0.464	0.430	0.430
$P_{A12\text{-}13}{}^a$	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
A_{14}	0.782	0.790	0.752	0.740	0.716	0.695	0.604	0.591
D_{A14}	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
$P_{A14}{}^a$	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}{}^b$	7.005	7.005	6.972	6.972	6.955	6.955	7.006	7.006
$[M^+{}_{aq}]_{stoic}{}^c$	1.001	1.001	1.000	1.000	1.002	1.002	1.000	1.000
k^d		2.055		2.387		3.333		2.943
b		0.1243		0.2059		0.2289		0.2075
t1(min)		7.83		7.00		7.00		7.00
t2 (min)		17.83		17.00		17.00		17.00

*) Contains 1.00% by weight cyclohexanol.
a) Path length has units of cm.
b) Concentration has units of (mol/L) x 10^3.
c) Concentration has units of (mol/L) x 10^2.
d) Slope has units of min $^{-1}$.

Table H

Data for the Calculation of Equilibrium Constants K_2K_3 for Cm-3 in *o*-Dichlorobenzene* at 25 °C, found in Table XIII of the Results Section.

Species	Li_{T-}	Li_{C-}	Na_{T-}	Na_{C-}	K_{T-}	K_{C-}	Cs_{T-}	Cs_{C}
A_{12}	0.703	1.188	0.536	0.683	0.590	0.877	0.684	1.106
A_{13}	0.483	0.483	0.427	0.427	0.464	0.464	0.430	0.430
P_{A12-13}[a]	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
A_{14}	0.733	0.758	0.733	0.737	0.679	0.673	0.586	0.525
D_{A14}	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
P_{A14}[a]	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}$[b]	6.571	6.571	6.565	6.565	6.345	6.345	6.287	6.287
$[M^+_{aq}]_{stoic}$[c]	1.001	1.001	1.000	1.000	1.002	1.002	1.000	1.000
k[d]		2.319		5.265		2.858		2.269
b		0.2500		0.6996		0.2087		0.3908
t1(min)		5.55		7.00		7.00		9.00
t2 (min)		15.55		17.00		17.00		19.00

*) Contains 1.00% by weight cyclohexanol.
a) Path length has units of cm.
b) Concentration has units of (mol/L) x 10^3.
c) Concentration has units of (mol/L) x 10^2.
d) Slope has units of min $^{-1}$.

Table I

Data for the Calculation of Equilibrium Constants K_2K_3 for Cm-4 in *o*-Dichlorobenzene* at 25 °C, found in Table XIV of the Results Section.

Species	Li_T-	Li_C-	Na_T-	Na_C-	K_T-	K_C-	Cs_T-	Cs_C
A_5	0.580	0.557	0.591	0.430	0.800	0.854	0.510	0.712
A_6	0.193	0.153	0.132	0.138	0.087	0.033	0.133	0.071
A_7	0.023	0.022	0.023	0.019	0.024	0.020	0.029	0.020
A_8	0.043	0.043	0.027	0.027	0.039	0.039	0.034	0.034
A_9	0.008	0.008	0.009	0.009	0.013	0.013	0.015	0.015
A_{10}	0.001	0.001	0.003	0.003	0.003	0.003	0.005	0.005
A_{11}	0.008	0.017	0.012	0.015	0.010	0.015	0.002	0.015
P_{A5-11}[a]	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
A_{14}	0.682	0.711	0.478	0.682	0.483	0.507	0.560	0.569
D_{A14}	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
P_{A14}[a]	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$[Cm_{org}]_{stoic}$[b]	6.697	6.697	6.697	6.697	6.697	6.697	6.697	6.697
$[M^+{}_{aq}]_{stoic}$[c]	1.001	1.001	1.000	1.000	1.002	1.002	1.000	1.000
k[d]		3.275		2.325		2.688		1.708
b		0.0643		0.0779		0.1199		0.1028
t1(min)		3.60		2.70		3.05		2.75
t2 (min)		13.60		12.70		13.05		12.75

*) Contains 1.00% by weight cyclohexanol.

a) Path length has units of cm.

b) Concentration has units of (mol/L) x 10^3.

c) Concentration has units of (mol/L) x 10^2.

d) Slope has units of min $^{-1}$.

Appendix VI

Shinkai's Raw Data & Calculation of K_{123}

Raw data obtained from the papers of Shinkai and co-workers[45,46] on the extraction studies of azobis(benzo-14-crown-4) (A-4) and azobis(benzo-15-crown-5) (A-5).

Extraction conditions:

	A-4	A-5
Organic solvent	o-dichlorobenzene	
Total conc of complexing agent in org phase([Cm-A])	3.74×10^{-3} M	3.00×10^{-4} M
Total conc of methyl orange in aq phase([MO])	3.74×10^{-5} M	8.10×10^{-6} M
Total conc of metal cation in aq phase([M^+])	0.05 M	0.01 M
Percent cis isomer at photostationary state(PS-%)	71	52
Ratio trans:cis isomer at photostationary state(PS-R)	0.41	0.92

Extraction Data:

Expressed as percent of methyl orange anion extracted into organic phase or percent loss from aqueous phase (%E).

	A-4		A-5	
Metal	Dark	Light	Dark	Light
Li	0	2.2	-	-
Na	0	0	29.6	17.1
K	1.3	1.0	1.3	29.0
Rb	0	5.7	29.3	49.6
Cs	1.8	3.4	24.1	29.9

Calculations:

The extraction equilibrium constants were calculated from the data above using the equations 24 and 27 (pages 21 & 22) by the following method.

A) The trans isomer(Dark) was calculated using the following substitutions in equation 24:

$$K_{123T} = \frac{[Cm_TMD_{org}]}{[Cm_{T,org}]\,[M^+_{aq}]\,[D^-_{aq}]} \qquad \text{(eq 24)}$$

$[Cm_TMD_{org}]$ = (%E /100) x [MO]
$[Cm_{T,org}]$ = [Cm-A]
$[M^+_{aq}]$ = $[M^+]$
$[D^-_{aq}]$ = [MO] x (1 - (%E /100)).

The cis isomer(Light) was calculated using the following substitutions in equation 27:

$$K_{123C} = \frac{[CmMD_{tot,org}]}{[Cm_{C,org}]\,[M^+_{aq}]\,[D^-_{aq}]} - \frac{K_{123T}\,[Cm_{T,org}]}{[Cm_{C,org}]} \qquad \text{(eq 27)}$$

$[CmMD_{tot,org}]$ = (%E /100) x [MO]
$[Cm_{T,org}] / [Cm_{C,org}]$ = (PS-R)
$[Cm_{C,org}]$ = (PS-% /100) x [Cm-A]
$[M^+_{aq}]$ = $[M^+]$
$[D^-_{aq}]$ = [MO] x (1 - (%E /100)).

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