

Phototropic Molecules. 3. Complexation between Alkali Metal Ions and *trans*- and *cis-p,p'*-Bis(Polyether)Azobenzenes*

PAUL HABERFIELD** and THOMAS P. RIZZO

Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn NY 11210, U.S.A.

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Abstract. Three polyether complexing agents were prepared whose shapes could be photochemically altered by means of an azobenzene fragment incorporated into the middle of the polyether chain. The compounds are **1**, bis-4,4'-[2-(methoxyethoxy)acetamido]azobenzene, **2**, bis-4,4'-[2-(1,3-dimethoxy-2-propoxy)acetamido]azobenzene and **3**, bis-4,4'-{2-[2-(2-methoxyethoxy)ethoxy]acetamido}azobenzene. Extraction equilibrium constants, K_{EXT} , for the extraction of Li^+ , Na^+ , K^+ , and Cs^+ ions from water into an organic solvent were measured for these three agents under irradiation and in the dark. Compounds **1** and **2** were found to give substantially larger K_{EXT} values on irradiation than in the dark. The $K(\text{light})/K(\text{dark})$ ratios for the three compounds ranged from 0.47 to 16.6.

Key words. Phototropic complexation, azobenzenes, polyethers, photochem, alkali metal extraction.

1. Introduction

The well-known ability of polyethers (glymes) to solvate alkali metal ions [2] is due to the fact that the molecules can wrap themselves around these ions, thus providing more than one ligand for the cation's solvation shell. This effect is enhanced by crown ethers of the appropriate size [3], and still more by cryptands [4]. The relative effectiveness of these three classes of complexing agents is in the ratio of about $1 : 10^4 : 10^9$ [4]. One might also reasonably suppose that there would be a difference, albeit a smaller one, between a linear polyether which is free to envelop a cation, and one which has a built-in stereochemical constraint which prevents it from assuming a geometry that optimizes cation solvation. If this geometrical constraint could then be photochemically switched on and off, by means of a phototropic [5] moiety in the molecule, one would have a basis for utilizing this phenomenon for the construction of a light-powered alkali metal pump. Such photoregulated ion binding has been reported for a Zn–iminodiacetic acid complex [6] and for several alkali metal–crown ether complexes [7]. We report here work directed at determining whether the ability of a linear polyether to extract alkali metal ions from an aqueous to an organic phase is significantly modified by the introduction of a stereochemical constraint that prevents it from wrapping around a cation.

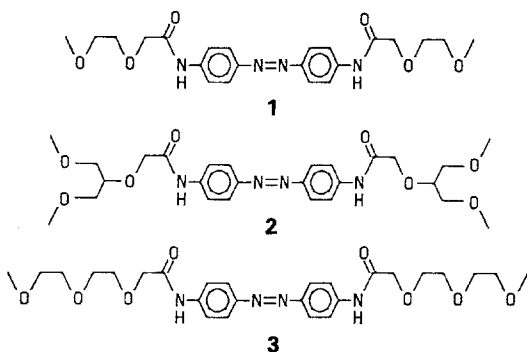
* For part 2 see ref. [1]

** Author for correspondence.

2. Results and Discussion

2.1. COMPOUNDS

We chose azobenzene as our phototropic moiety and an amide linkage as the means of attaching the polyether chains to the azobenzene. Examination of space filling models showed that when an amide carbonyl was the first oxygen, the chain would more readily form a crown ether-like ring. Thus in a model of compound *cis*-**1**, the six oxygens were found to assume a conformation similar to that found in 18-crown-6 without evident strain. Compounds **2** and **3** were selected to see the effect of adding one more oxygen to each side of the polyether chain. In compound **3** the chain was simply lengthened, while in compound **2** the effect of branching the chains was tested.



The synthesis of the three phototropic polyethers was straightforward and is shown in Scheme I.

2.2. CIS/TRANS ISOMERIZATION

Irradiation of solutions of the *trans* isomers led to a decrease in their absorbance, indicative of their isomerization to the *cis* compounds. Using a high pressure mercury arc lamp yielded only about 30% conversions to the *cis* isomers; however,

Scheme 1.

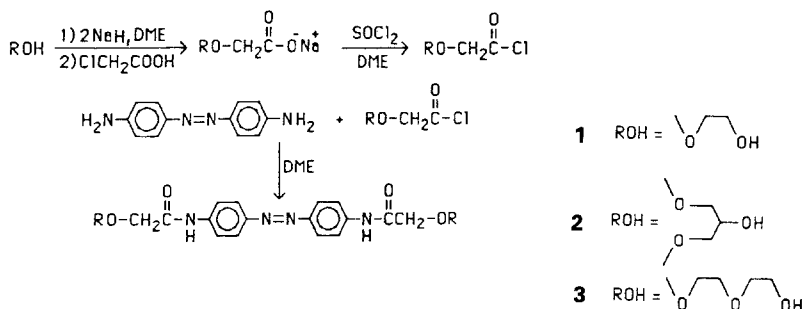


Table I. Absorbances, photostationary states and thermal *cis* → *trans* isomerization rates of polyether complexing agents in dichlorobenzene/1 wt% cyclohexanol solvent at 25.0°C

Compound	$\lambda_{\max}(\epsilon_{\max})$, nm	<i>cis</i> % ^a of <i>trans</i> isomer	$k \times 10^5$, s ⁻¹ ^b
1	367 (33 900)	89.8	3.71
2	367 (35 100)	90.0	3.81
3	367 (31 700)	88.3	2.91

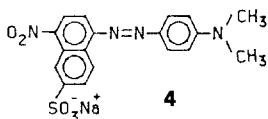
^aPercent of the *cis*-azobenzene isomer at the photostationary state.

^bFirst order rate constant for the thermal *cis* → *trans* isomerization of the azobenzene polyethers.

employing a band pass filter centered at 355 nm yielded the high conversions listed in Table I. Also listed in the table are the first order rate constants for the thermal *cis* → *trans* isomerization.

2.3. SOLVENT EXTRACTION

o-Dichlorobenzene was selected as the extraction solvent because the large difference in density between it and water made it possible to separate the two phases fairly rapidly. However pure *o*-C₆H₄Cl₂ was found to extract too little of the alkali metal complex for convenient measurement. Following the lead of Shinkai's group [7], this was remedied by the addition of an alcohol to the organic phase. Addition of 1.0 wt% of cyclohexanol to the organic phase was found to give readily measurable partition coefficients. The concentration of the metal-polyether complex in the organic phase was estimated from the absorbance of the counterion in the organic phase. The usual standby, picrate ion, was found to be unsuitable because it absorbs at the same wavelength as do our polyether complexing agents. For maximum extraction effectiveness the complexing agents were present in the organic phase in considerable excess, and hence would mask the appearance of any picrate in the organic phase. A counterion which absorbs at the blue end of the spectrum was required. A search of commercially available dyes did not reveal one possessing all the necessary characteristics: (a) that it be blue; (b) that it be an anion; (c) that it have an appropriate balance of lipophilicity/hydrophilicity; and (d) that it not be itself a complexing agent for metal ions. After a few candidates were prepared, compound 4, sodium 5-(4'-*N,N*-dimethylaminophenylazo)-8-nitro-2-naphthalenesulfonate, was found to satisfy these criteria.



The extraction of a metal ion from an aqueous phase into an organic phase with the aid of a lipophilic complexing agent is governed by three equilibria.



Equilibrium (1) is the partition of the polyether complexing agent, C, between water and the organic phase. Equilibrium (2) is the formation of the metal ion-polyether complex, C--M, in the aqueous phase. The third equilibrium, (3) is the transfer of this complex, along with the dye counterion, D, into the organic phase.

Solving the above three equilibrium equations for the amount of metal ion extracted into the organic phase yields

$$[C--M^+D^-]_{\text{ORG}} = K_1 K_2 K_3 [C_{\text{ORG}}][M_{\text{AQ}}^+][D_{\text{AQ}}^-] \quad (4)$$

and allows an extraction equilibrium constant to be defined.

$$K_{\text{EXT}} = K_1 K_2 K_3 = \frac{[C--M^+D^-]_{\text{ORG}}}{[C_{\text{ORG}}][M_{\text{AQ}}^+][D_{\text{AQ}}^-]} \quad (5)$$

The above equations are based on the assumption that a 1:1 metal ion:polyether complex is formed. A 2:1 metal ion:polyether complex will lead by analogous considerations to an extraction equilibrium constant,

$$K_{\text{EXT},2:1} = \frac{[C--M_2^{++}D_2^{--}]_{\text{ORG}}}{[C_{\text{ORG}}][M_{\text{AQ}}^+]^2[D_{\text{AQ}}^-]^2} \quad (6)$$

Finally, a 1:2 metal ion:polyether complex will yield an extraction equilibrium constant,

$$K_{\text{EXT},1:2} = \frac{[C_2--M^+D^-]_{\text{ORG}}}{[C_{\text{ORG}}]^2[M_{\text{AQ}}^+][D_{\text{AQ}}^-]} \quad (7)$$

Potassium chloride was extracted from aqueous solution into *o*-dichlorobenzene/1.0 wt.% cyclohexanol using complexing agent **1** and the dye counterion **4**. The extractions were carried out in the dark and under irradiation. Extraction equilibrium constants were calculated using Equations (5), (6), and (7), representing the three possible stoichiometries of complex formation. The data in Table II show that the stoichiometry of the complex is 1:1, because only Equation (5) yields constant K_{EXT} values as the ratio of metal ion to complexing agent is varied. Similar experiments with complexing agents **2** and **3** led to the same conclusion.

Table III lists the extraction equilibrium constants of the three *trans*- and *cis*-polyether complexing agents for Li^+ , Na^+ , K^+ , and Cs^+ . For compounds **1** and **2** it was found that the ability of the linear polyether to extract alkali metal ions into an organic phase was significantly modified by the introduction of a stereochemical constraint that prevents it from wrapping around a cation. For compound **2** this effect is nearly one order of magnitude, and is fairly uniform over the four

Table II. The stoichiometry of the complex. Extraction equilibrium constants for the extraction of potassium chloride from water into *o*-dichlorobenzene/1.0 wt. % cyclohexanol using complexing agent *trans*-1 and *cis*-1 at 25.0°C

$[M^+]_{Aq} \times 10^2$ ^a	$[C]_{ORG} \times 10^3$ ^b	<i>trans</i>		<i>cis</i>			
		K_{EXT}^c	$K_{EXT,2:1} \times 10^{-7}$ ^d	$K_{EXT,1:2} \times 10^{-7}$ ^e	K_{EXT}^c	$K_{EXT,2:1} \times 10^{-7}$ ^d	$K_{EXT,1:2} \times 10^{-4}$
1.00	2.21	38.2	3.96	1.73	71.6	6.8	5.9
1.00	6.96	40.2	3.07	0.58	75.3	5.9	1.6
0.334	6.58	40.7	13.1	0.62	78.2	28.6	2.8

^aStoichiometric K^+ concentration;

^bStoichiometric concentration of compound 1;

^cCalculated with Equation (5);

^dCalculated using Equation (6);

^eCalculated using Equation (7).

Table III. Extraction equilibrium constants, K_{EXT}^a , for the *trans*- and *cis*-polyether complexing agents, C, with the alkali metal ions between water and dichlorobenzene at 25°C.

C	Li ⁺	Na ⁺	K ⁺	Cs ⁺
<i>trans</i> -1	15.2	22.9	40.0	11.7
<i>cis</i> -1	148.0	98.6	75.6	194.0
$(K_{\text{EXT}}^{\text{cis}}/K_{\text{EXT}}^{\text{trans}})$	(9.74)	(4.30)	(1.89)	(16.6)
<i>trans</i> -2	22.6	12.0	14.2	29.2
<i>cis</i> -2	143.0	129.0	121.0	194.0
$(K_{\text{EXT}}^{\text{cis}}/K_{\text{EXT}}^{\text{trans}})$	(6.33)	(10.8)	(8.52)	(6.64)
<i>trans</i> -3	625	891	991	552
<i>cis</i> -3	512	420	912	634
$(K_{\text{EXT}}^{\text{cis}}/K_{\text{EXT}}^{\text{trans}})$	(0.819)	(0.471)	(0.920)	(1.15)

^aAs defined by Equation (5), units are L² mol⁻²;

^bContaining 1.0 weight percent cyclohexanol.

alkali metals examined. Compound **1** shows an effect of about the same magnitude, but exhibits a minimum for *cis/trans* selectivity with K⁺. The longest polyether, **3** has the largest values for K_{EXT} , but exhibits hardly any *cis/trans* selectivity. It is probable that in compound **3** the longer polyether chain on each side of the azobenzene moiety is itself capable of adequately solvating the metal ion. This complex may compete favorably with one which also involves the chain on the other side, particularly when one considers the added entropic disadvantage of aligning the two longer chains.

Before attempting to draw any general conclusions from this data it is well to remember that the extractive power of the complexing agent is governed by three distinct equilibria, as described in Equations (1)–(5). Unfortunately we were unable to measure the most interesting of these, K_3 , separately. However we were able to determine K_1 , the partition coefficient. The partition coefficient data (Table IV) show that compound **1** has a tenfold more favorable K_1 , *cis/trans* ratio than does compound **2**, even though it does not have K_{EXT} *cis/trans* ratios which are ten times higher. Compound **3** which has a K_1 , *cis/trans* ratio which is intermediate between **1** and **2**, nevertheless lacks any *cis/trans* discrimination in its K_{EXT} values, unlike **1** and **2**. From this we conclude that the K_{EXT} *cis/trans* ratios are driven largely by the *cis/trans* differences in the complexation constants, K_2 . The *cis/trans*

Table IV. Partition coefficients, K_1^a , for the *trans*- and *cis*-polyether complexing agents, C, between water and dichlorobenzene^b at 25°C

C	<i>trans</i> , × 10 ⁴	<i>cis</i> , × 10 ⁴	<i>cis/trans</i>
1	1.41	46.8	33.2
2	0.407	1.35	3.31
3	11.5	121.0	10.4

^aAs defined by Equation (1);

^bContaining 1.0 wt% cyclohexanol

changes in the partition coefficients K_1 are largely cancelled by reciprocal changes in the partition coefficients K_3 . This is reasonable, as these changes depend on hydrophilicity/lipophilicity changes on *cis/trans* isomerization, which affect the K_1 and K_3 *cis/trans* ratios in an inverse way.

3. Conclusion

The ability of two linear polyethers to extract alkali metal ions into an organic phase was substantially altered when their shape was changed by means of a photochemically switchable azobenzene moiety. The *cis* isomers had higher K_{EXT} values than did the *trans* isomers, in which the polyether chains were sterically inhibited from wrapping around the metal ions. In a third compound, having a longer polyether chain, this effect vanished.

4. Experimental Section

4.1. COMPOUNDS 1, 2 AND 3

The three phototropic polyethers, **1**, bis-4,4'[2-(methoxyethoxy)acetamido]-azobenzene, **2**, bis-4,4'-[2-(1,3-dimethoxy-2-propoxy)acetamido]azobenzene and **3**, bis-4,4'-{2-[2-(2-methoxyethoxy)ethoxy]acetamido}azobenzene, were prepared as shown in Scheme I. As these preparations are similar, we shall describe the synthesis of **1** and simply provide analytical data for the other two.

2-(2-methoxyethoxy)acetyl chloride was prepared by the reaction of 2-methoxyethanol with chloroacetic acid, followed by conversion to the acid chloride with thionyl chloride. To 58.19 g (1.376 mol) of 57% sodium hydride (Alpha Ventron) stirred in 100 mL of dry dimethoxyethane in an ice bath and under a nitrogen atmosphere, was added, dropwise, 54.86 g (0.7210 mol) of 2-methoxyethanol (Aldrich) in 100 mL of dimethoxyethane. To this was added 62.00 g (0.6561 mol) of chloroacetic acid in 100 mL of dimethoxyethane. This mixture was heated on a steam bath at reflux for 48 h. After cooling to ice bath temperature, 94.31 g (0.7931 mol) of thionyl chloride was added, and the reaction mixture was again heated on a steam bath at reflux for 24 h. Cooling to room temperature produced a precipitate of NaCl, 94.35 g (98.3% yield). The filtrate was distilled yielding, after removal of the dimethoxyethane and the excess thionyl chloride, 41.51 g (41.5% yield) of 2-(2-methoxyethoxy)acetyl chloride: b.p. 96°C at 35 mm; IR (neat) 2940 (C—H), 1800 (C=O), 1140 (C—O—C); ¹H NMR (CDCl₃) 4.4 (2 H, s, OCH₂C=O), 3.5 (4 H, m, (OCH₂CH₂O)), 3.2 (3 H, s, OCH₃).

4,4'-diaminoazobenzene was prepared by the oxidative coupling of *p*-aminoacetanilide using sodium perborate [8], followed by hydrolysis of the resulting 4,4'-diacetamidoazobenzene. To a stirred mixture of 8.81 g (0.0415 mol) of 4,4'-diaminoazobenzene and 20.27 g (0.1931 mol) of sodium carbonate in 200 mL of dimethoxyethane heated at reflux, was added, dropwise, 15.46 g (0.1014 mol) of 2-(2-methoxyethoxy)acetyl chloride in 200 mL of dimethoxyethane. After heating at reflux for 12 h, the solution was filtered and the filtrate distilled. Recrystallization of the distillate from methanol–water yielded *compound 1*, 12.66 g (68.64% yield),

orange crystals, mp 155–156°C; IR (KBr) 3320 (N—H), 3013 and 2930 (C—H), 1680 (C=O), 1530 (C—N—H), 1140 and 1090 (C—O—C); ¹H NMR (CDCl₃) 3.50 (6 H, *s*, OCH₃), 3.72 (8 H, *m*, O—CH₂CH₂—O), 4.13 (4 H, *s*, OCH₂C=O), 7.84 (8 H, *q*, arom), 9.11 (2 H, *s*, NH). Anal. Calcd for C₂₂H₂₈O₆N₄: C, 59.45, H, 6.35. Found: C, 59.36, H, 6.22.

Compound 2, (80.17% yield), orange needles, mp 152–153°C; IR (KBr) 3310 (N—H), 3010 and 2920 (C—H), 1695 (C=O), 1540 (C—N—H), 1155 (C—O—C); ¹H NMR (CDCl₃) 3.46 (12 H, *s*, OCH₃), 3.53 (8 H, *d*, *J* = 5.2 Hz, —CH₂O), 3.79 (2 H, quintet OCH<), 4.26 (4 H, *s*, OCH₂C=O), 7.84 (8 H, *q*, arom), 9.59 (2H, *s*, NH). Anal. Calcd for C₂₆H₃₆O₈N₄: C, 58.64, H, 6.81. Found: C, 58.92, H, 6.58.

Compound 3, (69.05% yield), orange hygroscopic crystals, mp 82–83°C; IR (KBr) 3320 (N—H), 3020 and 2910 (C—H), 1663 (C=O), 1540 (C—N—H), 1100 (C—O—C); ¹H NMR (CDCl₃) 3.39 (6 H, *s*, OCH₃), 3.60 (4 H, *m*, O—CH₂), 3.76 (12 H, *m*, CH₂—O—CH₂CH₂—O), 4.15 (4, H, *s*, OCH₂C=O), 7.85 (8 H, *q*, arom), 8.98 (2 H, *s*, NH). Anal. Calcd for C₂₆H₃₆O₈N₄: C, 58.64, H, 6.81. Found: C, 58.09, H, 6.70.

4.2. SODIUM 5-(4'-N, N-DIMETHYLAMINOPHENYLAZO)-8-NITRO-2-NAPHTHALENESULFONATE, (4)

5-Amino-8-nitro-2-naphthalene-sulfonic acid, 5, was prepared by the stepwise acetylation, nitration and hydrolysis of 5-amino-2-naphthalenesulfonic acid. Diazotization of **5** followed by coupling with *N,N*-dimethylaniline yielded **4** in 52.4% yield. This very crude material was purified by the chromatography (silica gel, 4% methanol in acetone) of its tetra-*n*-butylammonium salt. This salt, mp 173–174°C, was converted to the zwitterion with HCl and then titrated with NaOH to produce the sodium salt. UV (water) λ_{MAX} (*E*) 520 nm (28900); IR (KBr) 3040 (C—H), 2930 (C—H), 1520 (NO₂), 1370, 1300, 1130 (SO₃), 1040 (SO₅); ¹H NMR (CD₃SOCD₃) 3.11 (6 H, *s*, CH₃), 6.92 (2 H, *d*, *J* = 9.0 Hz, 3'-phe), 7.74 (1 H, *d*, *J* = 8.5 Hz, 6-napht), 7.98 (2 H, *d*, *J* = 9.0 Hz, 2'-phe), 8.05 (1 H, *d*, *J* = 8.9 Hz, 4-napht), 8.39 (1 H, *d*, *J* = 8.5 Hz, 7-napht), 8.79 (1 H, *s*, 1-napht), 8.96 (1 H, *d*, *J* = 8.9 Hz, 3-napht); ¹³C NMR (CD₃SOCD₃) 40.0, 109.9, 111.4, 118.6, 123.8, 124.6, 125.1, 125.3, 125.9, 130.0, 143.8, 145.2, 148.7, 150.5, 153.5.

4.3. RATE OF CIS → TRANS ISOMERIZATION

A stirred solution of compound **1**, **2** or **3** in dichlorobenzene/1.0 wt% cyclohexanol in a jacketed flask maintained at 25.0°C was irradiated at 350 nm. The source was a Schoeffel LH 151N 1000 W high pressure mercury arc lamp. The light was passed through a cooled CuSO₄ solution (15 g/100 mL) in a 10 cm flow cell, through a 1% transmitting IR filter, through a 350 nm band pass filter and was focused on the sample with a bar lens. Aliquots were removed periodically and their UV spectrum was observed. When the spectrum no longer changed (the photostationary state was reached) the rate of change of the absorbance at 360 nm was monitored. Using

the first order rate equation,

$$\ln[A_{\infty}/(A_{\infty} - A_t)] = kt + b$$

where A_t is the absorbance at time t and A_{∞} is the absorbance at time infinity, yielded the first order rate constant, k . As the amount of overlap between the spectrum of the *trans* and *cis* isomers at 360 nm is slight, the intercept, b , of the above equation yielded the amount of *cis* isomer at the photostationary state, % conversion = $100/e^b$.

4.4. EXTRACTION EQUILIBRIUM CONSTANTS

Thirty millilitres of a solution of the complexing agent, C, 0.0066M, in the organic phase was shaken with 10 mL of an aqueous phase 0.01M in the alkali metal chloride, M_{AQ}^+ , and 1.6×10^{-4} M in the dye salt 4, D_{AQ}^- . The extraction flask was an amber-colored, jacketed flask maintained at 25°C, which was mechanically inverted about 7 times per min for 15 min. The two phases were separated and the organic phase centrifuged to remove any droplets of water. The organic phase was then back extracted with three successive portions of water, the total amount of dye 4 in these aqueous phases, measured spectroscopically, yielding the amount of dye-metal complex, $[C--M^+D_{ORG}^-]$, extracted into the organic phase in the first extraction. The extraction equilibrium constant, K_{EXT} , was then calculated using Equation (5). In dealing with the irradiated solutions Equation (5) had to be modified to account for the fact that these solutions contained not only the *cis* compound, but also some of the *trans* complexing agent. The extraction equilibrium constant for the *cis* compounds, $K_{EXT,CIS}$ was calculated using the equation,

$$K_{EXT,CIS} = \frac{[C--M^+D_{TOTAL,ORG}^-]}{[C_{CIS,ORG}][M_{AQ}^+][D_{AQ}^-]} - \frac{K_{EXT,TRANS}[C_{TRANS,ORG}]}{[C_{CIS,ORG}]} \quad (8)$$

where $K_{EXT,TRANS}$ was the extraction equilibrium constant for the *trans* compound obtained separately and $[C_{TRANS,ORG}]$ and $[C_{CIS,ORG}]$ were the concentrations of the *trans* and *cis* isomers, respectively, at the time of the extraction which were calculated from the composition at the photostationary state and the rate of the *cis* → *trans* isomerization.

4.5. PARTITION COEFFICIENTS, K_1

Five to ten milliliters of a solution of the complexing agent, C, 0.0066M, in the organic phase was shaken with 1.0 L of water for 3 min. The two phases were allowed to settle for about 1 h, and separated. The absorbance of the organic phase, A_1 , was measured at 360 nm. The aqueous phase was slowly dripped through a cone of filter paper to remove any droplets of organic phase and then extracted with 5.0 mL of fresh organic solvent. The absorbance of this organic phase, A_2 , was measured. The partition coefficient, K_1 , was then calculated from the relation:

$$K_1 = [5 \times A_2]/[(1000 \times A_1) - A_2] \quad (9)$$

The amplification factor implicit in this back-extraction method makes it possible to measure quite small K_1 values. Calculating the partition coefficients for the

irradiated compounds it was again necessary to allow for the fact that these solutions contained not only the *cis* compound, but also some of the *trans* isomer. The partition coefficients were measured as above, except that before measuring the A1 and A2 values, the cuvettes were left to age sufficiently to allow complete conversion to the *trans* isomer to take place. The partition coefficient, $K_{1,CIS}$, was calculated using the equation

$$K_{1,CIS} = \frac{[C_{AQ}]_{OBS}}{[C_{CIS,ORG}] - \frac{K_{1,TRANS}[C_{TRANS,ORG}]}{[C_{CIS,ORG}]}}$$

where $[C_{AQ}]_{OBS}$ was the total concentration of the complexing agent in the aqueous phase as measured using Equation 9, $[C_{CIS,ORG}]$ and $[C_{TRANS,ORG}]$ were the concentrations in the organic phase of the *cis* and *trans* isomers respectively, as determined by the partition experiment, knowledge of the composition of the photostationary state and knowledge of the rate of *cis* → *trans* isomerization, and $K_{1,TRANS}$ was the partition coefficient of the *trans* compound, obtained separately.

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