Characterization of simple photoresponsive systems and their applications to metal ion transport

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Some new photoresponsive azobenzenes (**1**–**5**) have been synthesized and characterized. On irradiation at 330 nm these systems undergo conversion from the *E* to the *Z* form to a varying extent which depends upon the nature and position of substitution on the azobenzene rings. They revert back to the *E* form on thermal isomerization in the dark. Photochemical equilibria have been studied and compared in acetonitrile and *o*-dichlorobenzene; *E* forms are stabilized more in *o*-dichlorobenzene than in acetonitrile. Two of the molecules (**1** and **4**) show enhanced transport of Cu^{2+} ions across a liquid membrane on irradiation.

The development of systems which change their physical and chemical properties in response to photoirradiation is of great interest because of a range of applications.[1,2] Azo compounds and their derivatives provide one such system which undergoes conversion from the *E* to *Z* form by irradiation at 310 nm and reverts to the *E* configuration on irradiation at 440 nm. This photochemical switching leads to two photostationary equilibria (PSE) characterized by the *E*/*Z* populations. The starting state can be attained by thermal isomerization.[3–6] The rate of thermal isomerization of the azobenzene unit depends both on the size of the macrocycle in the unit and on whether the cavity of the macrocycle is occupied.

Cations are known to be transported through membranes by photoresponsive carriers. The light driven ion transport is attributed to the enhanced binding ability of the *Z*-form to extract ions from the source phase and transport them to the receiving phase. At the receiving phase, the radiation is changed so as to isomerize the *Z*-form to the *E*-form. This initiates decomplexation thereby enriching the receiving phase with the transported ions. A specific example is (*E*)-azo(benzo-18-crown-6) which forms a 1:1 metal–crown complex with Na^+ and K^+ while the (*Z*) isomer forms an intramolecular 1:2 metal–crown sandwich complex.[7] Therefore *E*–*Z* isomerization releases a metal ion. Other photochemically active azobenzene derived systems include cyclophanes,[8] double-decker porphyrins,[9] macrobicyclic molecules,[3] catenanes,[4] *etc.* The most efficient light-driven ion transport is possible for moderately stable complexes.

Since most of the reported photoresponsive systems contain large macrocyclic systems, it is of interest to examine the possibility of photoinduced *E*–*Z* isomerization and metal ion transport involving smaller molecular systems. Here we report a few examples of photoresponsive aldehydes and Schiff base molecules and photoinduced metal ion transport by some of these molecules across a liquid membrane.

Experimental

4,4′-Bis(chlorocarbonyl)azobenzene

This was prepared by a modified procedure.[10] *p*-Nitrobenzoic acid (15 g) and NaOH (50 g) were mixed in water (225 cm^3) and the solution was heated on a water bath until the solid dissolved; hot aqueous glucose (100 g in 150 cm^3 of water) was then added slowly at 50 °C whereupon a yellow precipitate was obtained which immediately changed to a brown solution upon further addition of glucose. This reaction is highly exothermic. Then a stream of air was passed into the mixture for 3 h and a light brown precipitate was obtained. This was filtered, dissolved in water and acidified with acetic acid (25 cm^3) whereupon a light pink precipitate was obtained. This was filtered, washed with plenty of water (300 cm^3) and dried in an oven at 105 °C (yield 9 g). The acid thus obtained (9 g) was mixed with 17.5 g of PCl_5 in 115 cm^3 of 1,2-dichloroethane at 0 °C and then refluxed for 2 h. The bright red crystals obtained were filtered and recrystallized repeatedly from toluene (yield 8.7 g); ν/cm^{-1} 1780 (CO) and 1600 (N=N); δ_H(200 MHz; $CDCl_3$; 25 °C) 8.097 (d, 4 H, Ar) and 8.340 (d, 4 H, Ar). [Calc. (Found) (%): C, 54.72 (54.75); H, 2.60 (2.6); N, 9.12 (9.1)].

4,9-Dioxo-3,10-dioxa-6,7-diaza-2,11(1,2),5,8(1,4)-tetrabenzenadodecaphan-6-ene-1,12-dial 1

Salicylaldehyde (2 mmol) was stirred with triethylamine (1 cm^3) in toluene (100 cm^3) under N_2 at room temperature for 30 min. Then 4,4′-bis(chlorocarbonyl)azobenzene (1 mmol) in toluene (100 cm^3) was added dropwise under N_2 and stirred for 24 h at room temperature. The bulk precipitate obtained was filtered, washed repeatedly with water and toluene, dried and recrystallized from hot toluene as light pink needles.

4,9-Dioxo-3,10-dioxa-6,7-diaza-2,5,8,11(1,4)-tetrabenzenadodecaphan-6-ene-1,12-dial 2

This was prepared from 4-hydroxybenzaldehyde by a similar procedure as described above.

2^3,2^5,11^2,11^6-Tetraformyl-3,10-dioxa-6,7-diaza-2,5,8,11(1,4)-tetrabenzenadodecaphan-6-ene-4,9-dione 3

2,6-Diformyl-4-methylphenol (2 mmol) in toluene (100 cm^3) was stirred with triethylamine (1 cm^3) at room temperature for 30 min. To this 4,4′-bis(chlorocarbonyl)azobenzene (1 mmol) was added dropwise under N_2. After the addition, the reaction mixture was refluxed for 24 h and cooled. The precipitate was filtered, washed thoroughly with water and toluene and recrystallized from chloroform.

5,12-Dioxa-1^3,2,8,9,15,16^6-hexaaza-1,16(1),4,13(1,2),7,10-(1,4)-hexabenzenahexadecaphane-2,8,14-triene-6,11-dione 4

Compound **1** (1 mmol) in toluene (30 cm^3) was added to 3-aminopyridine (2 mmol) in toluene (30 cm^3) under N_2 and refluxed for 8 h. The solution was filtered and the volume of the filtrate was reduced to give compound **4**. This was recrystallized from $CHCl_3$.

5,12-Dioxa-1^3,2,8,9,15,16^3-hexaaza-1,16(1),4,7,10,13(1,4)-hexabenzenahexadecaphane-2,8,14-triene-6,11-dione 5

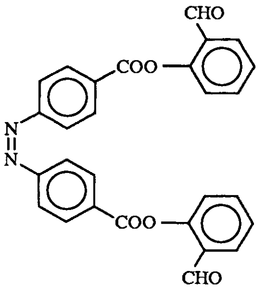
This was prepared from compound **2** by a procedure similar to the synthesis of **4**.

Characterization data for all the compounds are given in Table 1.

Table 1 Analytical and spectral data for the molecules **1–5**

Molecule	Yield (%)	Analysis[a] (%)			ν^b/cm^{-1}	δ_H(CDCl$_3$; Me$_4$Si)
		C	H	N		
1	83	70.0 (70.4)	3.9 (3.8)	5.9 (5.9)	1738, 1697, 1602	10.21 (s, 2 H, CHO), 8.38 (d, 4 H, Ar),[c] 8.12 (d, 4 H, Ar),[c] 7.98 (d, 2 H, Ar), 7.75 (t, 2 H, Ar), 7.50 (t, 2 H, Ar), 7.35 (d, 2 H, Ar)
2	72	69.9 (70.4)	3.8 (3.8)	6.0 (5.9)	1734, 1687, 1601	10.00 (s, 2 H, CHO), 8.35 (d, 4 H, Ar), 8.05 (d, 4 H, Ar), 7.95 (d, 4 H, Ar), 7.40 (d, 4 H, Ar)
3	88	67.0 (68.3)	4.0 (3.9)	5.4 (5.0)	1736, 1693, 1593	10.19 (s, 4 H, CHO), 8.41 (d, 4 H, Ar), 8.15 (d, 4 H, Ar), 8.00 (s, 4 H, Ar), 2.50 (s, 6 H, CH$_3$)
4	78	72.0 (72.3)	4.1 (4.1)	13.3 (13.3)	1732, 1620, 1602	8.60 (s, 2 H, CH=N), 8.43 (d, 4 H, Ar), 8.38 (d, 2 H, Ar), 8.18 (d, 1 H, Ar), 8.16 (d, 1 H, Ar), 8.10 (d, 4 H, Ar), 8.06 (d, 2 H, Ar), 7.65 (t, 2 H, Ar), 7.35 (m, 8 H, Ar)
5	78	72.1 (72.3)	4.1 (4.1)	13.8 (13.3)	1738, 1624, 1599	8.50 (s, 2 H, CH=N), 8.40 (d, 4 H, Ar), 8.15 (d, 4 H, Ar), 8.10 (d, 4 H, Ar), 7.30 (m, 12 H, Ar)

[a] Calculated values in parentheses. [b] Only selected peaks are presented. ν_s(C=O) ≈ 1730 cm^{-1}, ν_s(N=N) ≈ 1600 cm^{-1}. [c] Azobenzene unit.



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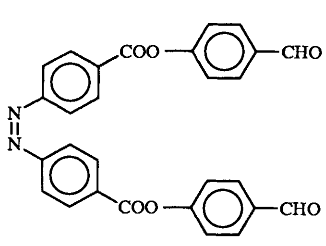

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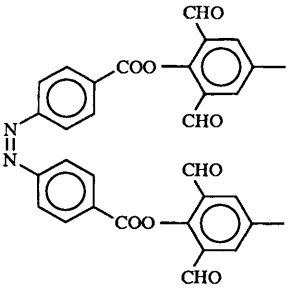

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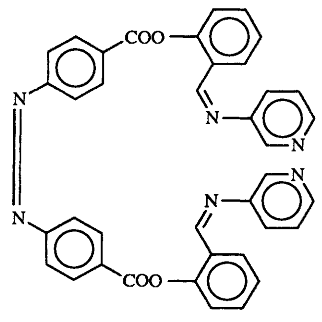

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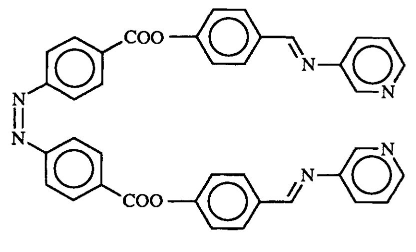

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Photoisomerization and kinetic measurements

Photoisomerization of *E* to *Z* was carried out in *o*-dichlorobenzene or acetonitrile with a 150 W Xenon short arc lamp provided with a f/4 monochromator. The distance from the source was maintained at 45 cm. The absorbance was recorded for all the ligands at room temperature in the range 600–200 nm in acetonitrile and 600–275 nm in *o*-dichlorobenzene on a JASCO model 7800 UV–VIS spectrophotometer. Subsequently the samples were irradiated at ≈330 nm and the absorbance of the band was recorded as a function of time. Irradiation was discontinued when the photostationary state was reached (when no further change in ε values of the band occurred). Photostationary states were attained in 15–100 min depending on the compounds and the solvent systems used. Then the sample was quickly transferred to a standard measuring flask and kept in the dark to carry out the kinetic measurements. The absorbance of the band at ≈330 nm was recorded as a function of time until the original spectrum was regained. The percentage compositions of *Z* and *E* isomers were calculated on the assumption that *E* isomer is 100% before irradiation. The plot of absorbance *vs.* time indicates a first-order process for forward photoisomerization (*E* to *Z*) and backward thermal isomerization (*Z* to *E*).

Transport experiments

Photoinduced transport experiments of Cu^{2+} ions by compounds **1–5** across an *o*-dichlorobenzene membrane were carried out in mini U-tubes of 3 mm diameter, 50 mm height and base width of 8 mm at 27 °C. The source phase contained 1×10^{-3} mol dm^{-3} of Cu(ClO$_4$)$_2$·6H$_2$O in water (75 µl) (1 µl = 1 mm^3), the membrane phase contained 0.5×10^{-3} mol dm^{-3} of carriers **1–5** in *o*-dichlorobenzene (0.1 cm^3) and the receiving phase contained pure distilled water (75 µl). The membrane phase was irradiated for 1 h at intervals of 24 h with a 150 W Xenon short arc lamp provided with a f/4 monochromator at 330 nm. The distance from the lamp was maintained at 45 cm. After irradiation, the U-tubes were thermostatted to 27 °C and kept in the dark. A sample of the receiving phase (30 µl) was withdrawn after 72 h and analysed for Cu^{2+} by the carbamate method.[11] Similar experiments were done without irradiation and in the absence of carrier molecules to determine the effect of irradiation on the transport of ions and the membrane phase leakage, respectively.

Results and discussion

The UV spectral features of these molecules are listed in Table 2. The absorbance band at *ca.* 330 nm is related to the π–π* transition of the N=N unit and is a measure of the composition of *E* form. It is assumed that the percentage composition of the *Z* form is negligible compared to that of the *E* form under ordinary conditions. The low intensity band at *ca.* 460 nm is due to the n–π* transition of N=N unit.

Azo compounds are shown to undergo *E–Z* isomerization on irradiation at 330 nm and *Z–E* isomerization at 460 nm or in the dark.[12] *E–Z* photochemical conversion was determined by measuring the change in absorbance at 5 min intervals during

Table 2 Electronic spectral and kinetic data for molecules **1–5** in acetonitrile and in *o*-dichlorobenzene

Molecule	Before irradiation λ(ε)[a]	At the stationary state λ(ε)[a]	$Z:E$[b] (%)	K^1[c]	K^2[d]
1 MeCN	458 (1105) 328 (50 323)	441 (1705) 327 (26 175)	47:53	2.9	0.35
1,2-Cl_2-C_6H_4	467 (1338) 335 (51 593)	467 (1577) 336 (45 283)	12:88	1.8	2.7
2 MeCN	459 (506) 327 (21 171)	451 (801) 328 (10 517)	51:49	3.8	0.56
1,2-Cl_2-C_6H_4	467 (1067) 334 (48 215)	467 (1577) 334 (42 256)	12:88	2.8	3.0
3 MeCN	331 (6912)	327 (1971)	71:29	2.7	6.43
1,2-Cl_2-C_6H_4	323 (17 622)	323 (12 844)	27:73	4.7	*e*
4 MeCN	461 (752) 326 (41 675)	447 (922) 328 (33 281)	7:93	0.6	6.61
1,2-Cl_2-C_6H_4	460 (752) 339 (54 454)	461 (842) 339 (51 522)	5:95	0.5	*e*
5 MeCN	460 (530) 327 (16 477)	460 (650) 327 (9314)	32:68	2.0	4.28
1,2-Cl_2-C_6H_4	461 (548) 337 (548)	461 (630) 337 (29 417)	15:85	2.0	*e*

[a] λ/nm; ε/mol^{-1} cm^{-1}. [b] At the photostationary state. [c] Photoinduced *E–Z* reaction (10^{-4} s^{-1}). [d] Thermal *Z–E* reaction (10^{-4} s^{-1}). [e] Not done.

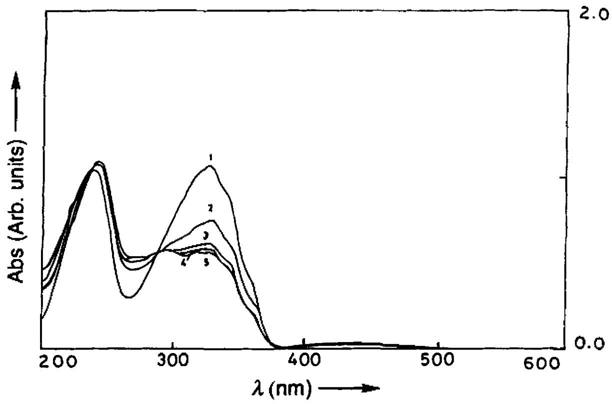

Fig. 1 UV–VIS spectra of a representative system **1** and photochemical conversion of *E–Z* form as a function of time; 1, before irradiation; 2, after irradiation for 15 min; 3, 35 min; 4, 55 min; 5, 75 min

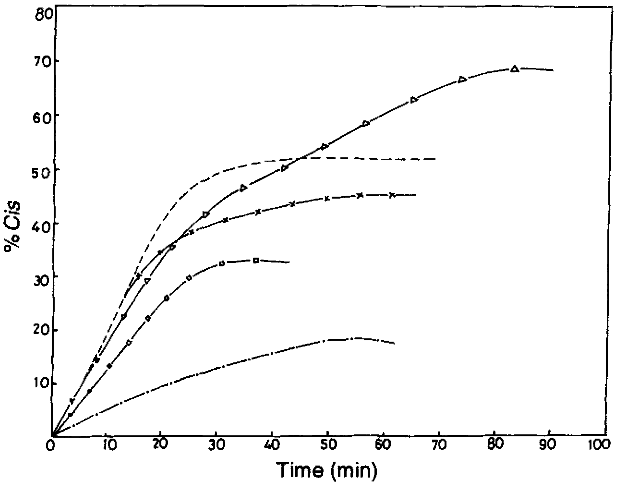

Fig. 2 Comparison of formation of *Z* forms of molecules **1–5** in acetonitrile as a function of time; 1 (×); 2 (–); 3 (△); 4 (– ·); 5 (□)

irradiation. The intensity of the π–π* transition decreased with photoirradiation at 330 nm. The UV–VIS spectra of a representative system **1** and the changes accompanying photochemical conversion of *E–Z* form is shown in Fig. 1. A comparison of formation of *Z* forms for molecules **1–5** in acetonitrile as a function of time based on the intensity decrease of the π–π* transition is depicted in Fig. 2. Table 2 presents data on the rate of photochemical generation of the *Z* form, rate of thermal regeneration of the *E* form and the percentage compositions of both the forms at the photostationary state in acetonitrile and *o*-dichlorobenzene as solvents.

From the data of Table 2 it can be seen that a photostationary state is reached faster in *o*-dichlorobenzene than in acetonitrile. The percentage of *Z* form is lower in *o*-dichlorobenzene than that in acetonitrile. The bands due to π–π* transitions are shifted to longer wavelengths (red-shifted) in *o*-dichlorobenzene. All these data suggest that the *E* form is stabilized more in *o*-dichlorobenzene than in acetonitrile.

Isomeric composition at the photostationary state depends largely on the nature of the substituents and their positions on the azobenzene ring. The lowest percentage of *Z* for molecule **4** compared to the other molecules may result from the destabilizing steric interactions in the *Z* form. The photoisomerization rate constant k_{E-Z} is also low. The *E* form was regenerated in less than 2 min, for this molecule in *o*-dichlorobenzene and in about 40 min in acetonitrile.

Cu^{2+} Ion transport

Since molecules **1–5** show varying extents of photoisomerization to the *Z* form, photoinduced transport of Cu^{2+} ions by these molecules at 330 nm has been investigated. In the absence of photoirradiation, the degree of Cu^{2+} ion transport is approximately 20% for molecules **1–3** and 30% for molecules **4** and **5**. Photoirradiation enhances the Cu^{2+} ion transport to 60% for molecule **1** and about 80% for molecule **4**. Other molecules **2**, **3** and **5** do not show any enhanced transport under irradiation conditions. The transport data are given in Table 3.

Molecules **4** and **5** are structurally analogous with difference only in the position of substitution. In molecule **4**, the pyridinyl group is substituted at the *ortho* position of the extended azobenzene unit while in molecule **5** this substitution is at the *para* position. The large increase in the transport of Cu^{2+} ions by molecule **4** on irradiation indicates that the pyridinyl group, being at the *ortho* position in molecule **4** may assist complex formation through the pyridine nitrogen in the *Z* isomer. This additional stabilization appears to be the driving force for the enhanced Cu^{2+} ion transport. For molecule **5**, the substitution being at the *para* position, does not have similar stabilizing force and hence shows no increase in transport on irradiation.

Table 3 Cu^{2+} ion transport data for carrier molecules **1**–**5**

Molecule	% Cu^{2+} in RP[b] with irradiation	% Cu^{2+} in RP[b] without irradiation
1	62	21
2	20	16
3	19	17
4	82	32
5	32	30

[a] Organic phase (0.1 cm^3), carriers (**1**–**5**) = 0.5×10^{-3} mol dm^{-3} in *o*-dichlorobenzene; SP (75 μl), $[Cu(ClO_4)_2 \cdot 6H_2O] = 1 \times 10^{-3}$ mol dm^{-3}; RP (75 μl), distilled water. The membrane phase was irradiated with a Xe lamp through an f/4 monochromator for 1 h at 330 nm once in 24 h; distance from the lamp was 45 cm. [b] After 72 h.

A similar explanation is offered to account for the increased Cu^{2+} ion transport for molecule **1** compared to molecule **2**. In molecule **1**, the CHO group is at the *ortho* position while in molecule **2**, it is at the *para* position. The CHO substitution at the *ortho*-position in **1** may facilitate complex formation in the *Z* isomer through oxygen atom participation enhancing photoinduced Cu^{2+} ion transport. Photoirradiation does not enhance the transport of Cu^{2+} ions by molecule **3**, which has a total of four CHO groups at the *ortho* positions of the extended azobenzene. This may be due to the steric interaction from four aldehydic groups in the *Z* form, resulting in a reduced possibility of complex formation and hence transport.

Conclusions

These results demonstrate that the molecules **1**–**5** undergo *E*–*Z* isomerization to various extents upon irradiation. Transport of Cu^{2+} ions across a membrane is enhanced only by two systems, **1** and **4**, under irradiation conditions. By proper selection of substituents on the azobenzene ring, it is possible to enhance photoinduced metal ion transport.

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