

CONTROL OF THE THERMAL *CIS* TO *TRANS* ISOMERIZATIONS OF AZOBENZENE AND THIOINDIGO DERIVATIVES BY THE FORMATION OF SUPRAMOLECULAR H-BONDED ASSEMBLIES

JACQUELINE ROSENGAUS AND ITAMAR WILLNER*

Institute of Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

2,3-Bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (1a) forms intermolecular H-bonded complexes with 3,3'-diacetyl-*cis*-azobenzene (4b) and 6,6'-diethoxy-*cis*-thioindigo (5b), (association constants $K = 4.9 \times 10^4$ and $3.5 \times 10^5 \text{ l mol}^{-1}$, respectively). The thermal *cis* → *trans* isomerization of 4b and 5b to 3,3'-diacetyl-*trans*-azobenzene (4a), and 6,6'-diethoxy-*trans*-thioindigo (5a), is inhibited in the intermolecular complex 1a–4b and 1a–5b. Molecular mechanics calculations support the formation of the intermolecular H-bonded complexes between 1a and 4b or 5b.

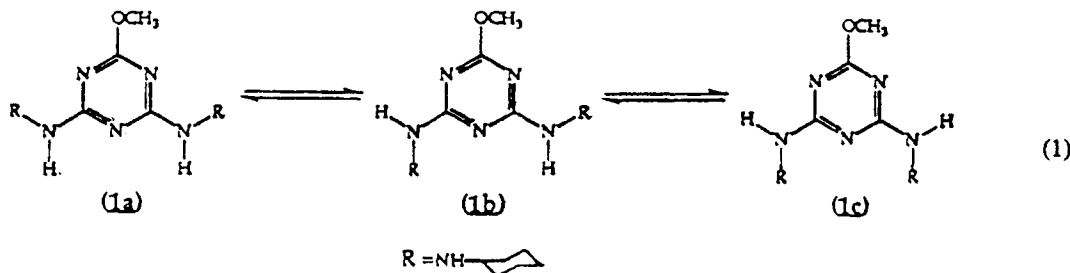
INTRODUCTION

The design of supramolecular assemblies stabilized by intermolecular complementary H-bonds is a subject of extensive research.^{1–3} Experimental^{4,5} and theoretical⁶ studies have revealed the roles of the structural features, the nature of chemical functionalities and the complementarity of the chemical functionalities on the stabilities of the resulting H-bonded assemblies. In this context, H-bonded intermolecular assemblies provide model systems for biological self-assembling materials such as DNA or proteins. Recent studies have revealed that aminotriazines and other H-donor compounds self-assemble in the presence of carbonyl acceptor compounds in the form of two-dimensional arrays,⁷ strands⁸ and helix structures.⁹ Of particular interest is the control

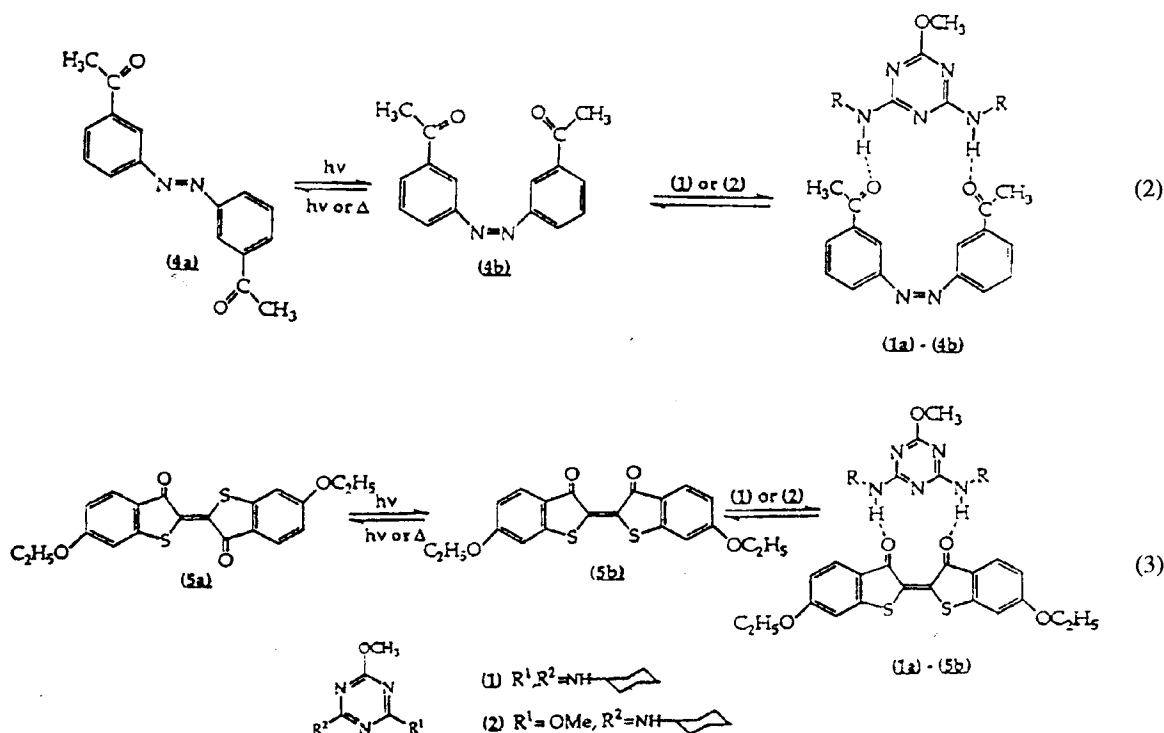
of chemical reactivity within supramolecular assemblies.^{10,11} Intermolecular H-bonded complexes have been used as catalytic assemblies for various chemical transformations such as self-replication,¹² phosphoryl transfer,¹³ intermolecular alkylations,¹⁴ control of pericyclic reactions¹⁵ and energy transfer from an excited chromophore.¹⁶

Diaminotriazines provide three atom sites for the organization of intermolecular H-bonded complexes.¹⁷ Previous studies have indicated that 2,4-bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (1) exists in solution in three different conformations [equation (1)]. It was shown that 1,3-diketones form intermolecular H-bonded complexes with the discrete conformation (1a) of the diaminotriazine host.

In this paper we report the formation of intermolecu-



* Author for correspondence.



lar assemblies between 1 and 3,3'-diacetyl-*cis*-azobenzene (4b) and 6,6'-diethoxy-*cis*-thioindigo (5b). We examine the effects of the formation of the intermolecular H-bonded assemblies on the thermal *cis* $\rightarrow$ *trans* isomerization reaction of the respective azobenzene and thioindigo derivatives [equations (2) and (3)]. The kinetic analyses allow us to characterize the association constants of 4b and 5b to 1a.¹⁸

EXPERIMENTAL

General. UV-visible spectra were recorded on a Uvikon 860 spectrophotometer, equipped with a thermostated cell holder. All chemicals were purchased from Aldrich, except 6,6'-diethoxythioindigo (5), which was purchased from Chroma Chemicals. 3,3'-Diacetyl-*trans*-azobenzene¹⁹ (4), 2,4-bis(amino-cyclohexyl)-6-methoxy-1,3,5-triazine (1) and 2-amino-cyclohexyl-4,6-dimethoxy-1,3,5-triazine¹⁷ (2) were prepared as described in the literature. Chloroform and 1,2-dichloroethane were of analytical grade and were further purified prior to use. Purification of the solvent was performed by shaking the organic layer with concentrated H_2SO_4 to remove trace amounts of alcohol. The organic layer was then repeatedly washed with water until the aqueous layers turned neutral, dried with MgSO_4 or CaCl_2 and distilled twice over P_2O_5 . The

distilled organic solvent was stored in the dark, to avoid photochemical formation of phosgene, and used within 2 weeks from purification. Association constants were calculated from kinetic data as described earlier.¹⁸

Kinetic studies. Typically, four to five samples (3 ml) of 3,3'-diacetyl-*trans*-azobenzene (4b), $8.36 \times 10^{-5} \text{ M}$ in 1,2-dichloroethane, and 6,6'-diethoxy-*trans*-thioindigo (5a), $1.71 \times 10^{-4} \text{ M}$ in chloroform, were placed in 3.5 ml glass cuvette equipped with a micro magnetic stirrer. To each cell different molar ratios of 1 or 2 were added and the samples were then sealed under vacuum. Photoisomerization of 4a to 4b was accomplished by irradiation of each sample for about 5 min with a Nd:YAG laser at 355 nm (pumped at 1 Hz frequency). Photoisomerization of 6,6'-diethoxy-*trans*-thioindigo (5a) to 5b was achieved by illumination of the respective samples with a xenon arc lamp equipped with a 515 nm cut-off filter. Thermal *cis* $\rightarrow$ *trans* isomerizations of 4b and 5b to 4a and 5a, respectively, were followed spectroscopically at 50 °C.

RESULTS AND DISCUSSION

Azobenzenes²⁰ and thioindigoids²¹ undergo reversible photochemical *trans* $\rightleftharpoons$ *cis* and thermal *cis* $\rightarrow$ *trans* isomerization reactions. The photochemical *trans* $\rightleftharpoons$ *cis* isomerization of thioindigoids is inhibited in the

presence of added ethanol,²² whereas the thermal *cis* → *trans* isomerization is catalysed by acid.²³ Similarly, dryness of the organic solvent is essential to eliminate perturbations in the formation of intermolecular H-bonded assemblies.²⁴ It is therefore of extreme importance to purify the solvents used, as described, in order to characterize the effects of formation of H-bonded assemblies between **1** and **4b** or **5b** on the isomerization rates. The rate constant for the *cis* → *trans* isomerization of 3,3'-diacetyl-*cis*-azobenzene (**4b**) at 50 °C is $k = 1.1 \times 10^{-4} \text{ s}^{-1}$ in 1,2-dichloroethane and for the isomerization of 6,6'-diethoxy-*cis*-thioindigo (**5b**) $k = 4.3 \times 10^{-4} \text{ s}^{-1}$, in chloroform (50 °C).

Molecular mechanics (MM)²⁵ calculations were performed on both photoisomers **4b** and **5b** and also on the intermolecular structures that were formed by interacting the minimized structures of **4b** and **5b** with the minimized triazine host structures **1a** and **2**, respectively. MM uses the MMX force-field method developed by Allinger,²⁶ in which H-bonds are treated as electrostatic interactions. A stable bimolecular assembly was generated by forcing 3,3'-diacetyl-*cis*-azobenzene **4b** to short distance (*ca* 2.5 Å) from the symmetric

conformation of 2,4-bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (**1a**). The energy of the resulting assembly was minimized until a structure of minimum potential energy was obtained. Figure 1 shows the calculated structure of **4b** and the intermolecular complex **1a-4b**, exhibiting minimum potential energies. The distances between the amino hydrogens and the complementary carbonyl functionalities are 2.055 Å, which is typical of H-bond lengths,²⁶ and thus the calculations imply that the intermolecular complex is stabilized by complementary H-bonds.

The MM calculations also reveal that formation of the intermolecular complex **1a-4b** results in structural distortions into the energetically favoured configuration of **4b** itself. Whereas in **4b** the carbonyl functions of the acetyl substituents face in opposite directions relative to the two benzene rings (the dihedral angles are 35.5° and -41.2°, respectively), the two carbonyl functions in the H-bonded complex **1a-4b** have the same orientation with an almost symmetrical configuration (the dihedral angles are 23.5°). Also, the two benzene groups of **4b** are distorted relative to the azo bond by a relative angle of 61.6°, as a result of through-space H-H repulsions. In the complex **1a-4b**

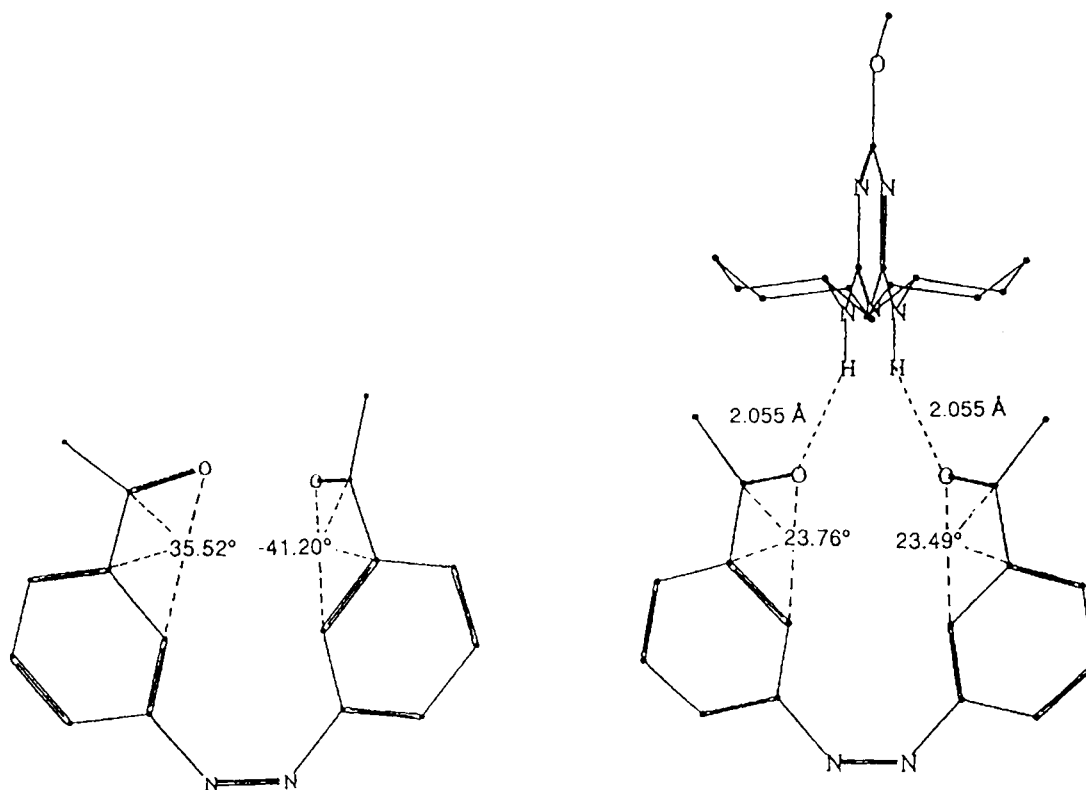


Figure 1. Calculated minimum potential energy structures of **4b** and the complex **1a-4b**

the mutual steric distortion of the two rings is decreased (52.7°) owing to stabilization of the H-bonded assembly.

The calculated enthalpy change associated with the formation of the H-bonded assembly **1a–4b** is $\Delta H = -36.65 \text{ kJ mol}^{-1}$. No stable H-bond complex was formed between **2** and **4b** or between 3,3'-diacetyl-*trans*-azobenzene **4a** and **1a**. Also, similar MM calculations were applied to test the possible association of different isomers of **4**, e.g. 2,2'-diacetyl-*cis*-azobenzene and 2,3'-diacetyl-*cis*-azobenzene, with 2,4-bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (**1a**). No stable H-bond assemblies were formed on forcing the different azobenzene derivatives to intimate intermolecular distances, and the forced complexes dissociated on energy minimization.

Similar MM calculations were performed with 6,6'-diethoxy-*cis*-thioindigo (**5b**) and **1a**. An intermolecular complex of minimum potential energy is obtained and its structure is depicted in Figure 2. The distances between the amino hydrogens of **1a** and the complementary carbonyl functions of **5b** are 2.056 and 2.079 Å, consistent with the formation of intermolecular H-bonds. The calculated enthalpy change associated with the formation of **1a–5b** intermolecular assembly is $\Delta H = -28.45 \text{ kJ mol}^{-1}$.

The MM calculations suggest that formation of the intermolecular complex **1a–5b** results in a structural distortion of the thioindigo backbone. Whereas in **5b** the

dihedral angle between the two carbonyl functions corresponds to 43.2° , it increases to 56° in the H-bonded complex.

No stable intermolecular complex is formed between 6,6'-diethoxy-*trans*-thioindigo (**5a**) and **1a** or between the *cis*-isomer (**5b**) and the monodentate aminotriazine derivative (**2**).

Formation of the H-bonded complexes **1a–4b** and **1a–5b** is expected to stabilize the respective *cis*-isomers and thus would inhibit their thermodynamically favoured *cis* $\rightarrow$ *trans* isomerizations. Accordingly, we studied the control of the thermal isomerization processes of **4b** and **5b** in the presence of the H-bond donor **1a**. Figure 3 shows the kinetic analysis for the isomerization of 3,3'-diacetyl-*cis*-azobenzene (**4b**) in the presence of different concentrations of 2,4-bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (**1**). The rate of isomerization is retarded as the concentration of the triazine receptor **1** is increased. Table 1 summarizes the values of the isomerization rates of **4b** in the presence and absence of **1**. The association constant, K , between **4b** and **1** was calculated from these kinetic studies.

Scheme 1 shows a general kinetic model for the formation of an intermolecular complex between an isomerizable compound such as **4b** and a hydrogen donor such as **1a**. H and G represent the triazine host **1** and the thermally isomerizable *cis*-isomer, respectively. P represents the thermally stabilized *trans*-isomer and

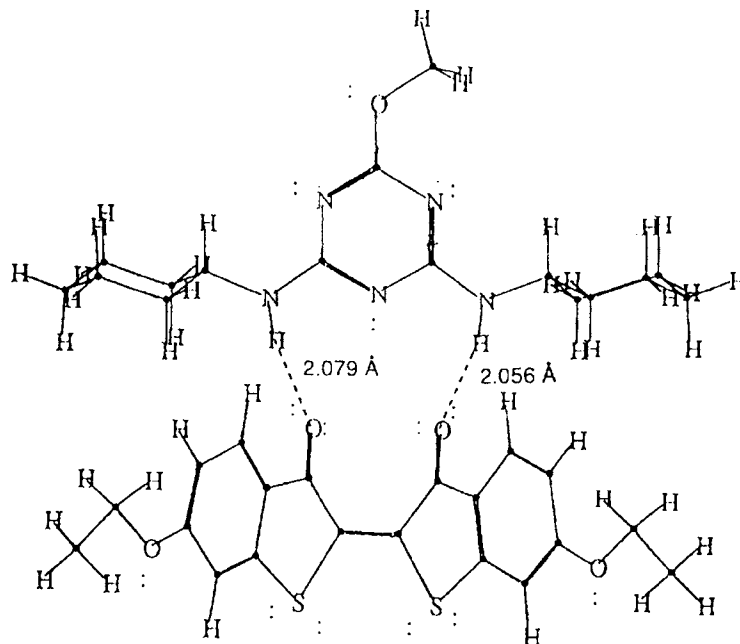


Figure 2. Calculated minimum potential energy structure of the complex **1a–5b**

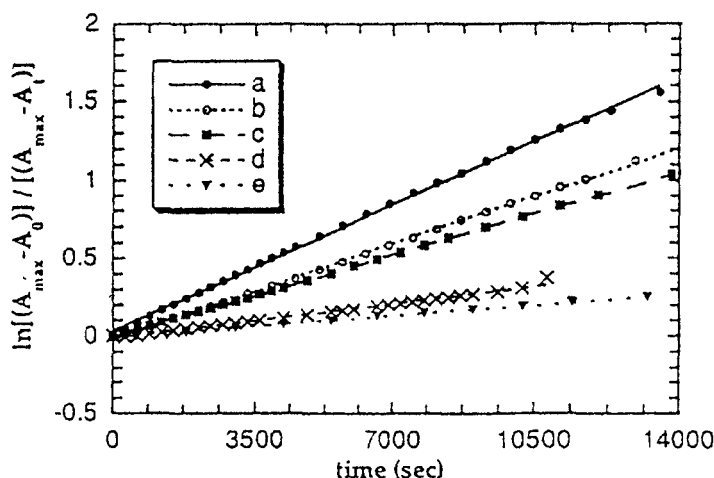
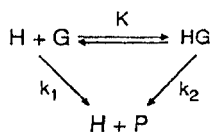


Figure 3. Kinetic analysis for the isomerization of 3,3'-diacetyl-*cis*-azobenzene (**4b**), 5×10^{-5} M, in the presence of **1**. Concentrations of **1**: (a) 0; (b) 2.09×10^{-5} ; (c) 4.18×10^{-5} ; (d) 8.36×10^{-5} ; (e) 4.18×10^{-4} M

Table 1. Rates of isomerization at 50 °C of **4b**, 5×10^{-5} M, in the presence of different concentrations of **1**

[4] : [1]	[1] (M)	k_{obs} (s^{-1})
1 : 0	0	1.1×10^{-4}
1 : 0.25	2.09×10^{-5}	8.8×10^{-5}
1 : 0.5	4.18×10^{-5}	3.6×10^{-5}
1 : 1	8.36×10^{-5}	3.1×10^{-5}
1 : 5	4.18×10^{-4}	1.7×10^{-5}



Scheme 1. Kinetic model for the formation of complexes **1a-4b** and **1a-5b** and their thermal isomerizations

HG is the complex concentration at any given concentration of the H-bond donor. The rate constants in the scheme correspond to the isomerization rate constant without added host, k_1 , and the *cis* $\rightarrow$ *trans* isomerization rate constant within the intermolecular complex structure, k_2 . The relationship between the observed isomerization rate constant, k_{obs} , and the association constant of the intermolecular H-bonded complex, K , is given by equation (4) (see Appendix). As K and k_2 are unknown, the respective values are calculated from the observed rate constants using equation (4) by an iteration procedure: first we assume $[\text{HG}] = 0$ and plot

$[\text{H}]^0 / (k_{\text{obs}} - k_1)$ vs $([\text{H}]^0 + [\text{G}]^0 - [\text{HG}])$. The value of $[\text{HG}]$ is calculated by introducing the resulting value of the slope of the former plot into equation (5) (see Appendix). This estimated complex concentration is resubstituted into equation (4). The process is repeated until the slope converges. The association constant, K , is derived from the slope and intercept of the last plot. The derived value of the association constant between **4b** and **1** is $K = 4.9 \times 10^4 \text{ l mol}^{-1}$. The rate constant for isomerization of **4b** within the intermolecular complex is $k_2 = 9.6 \times 10^{-6} \text{ s}^{-1}$. We therefore realize that the formation of an H-bonded assembly between the complementary functionalities of **4b** and **1a** retards the isomerization across the double bond by a factor of 11.5 as compared with the *cis*-azobenzene derivative.

$$\frac{[\text{H}]^0}{k_{\text{obs}} - k_1} = \frac{1}{K(k_2 - k_1)} + ([\text{H}]^0 + [\text{G}]^0 - [\text{HG}]) \frac{1}{(k_2 - k_1)} \quad (4)$$

$$[\text{HG}] = \frac{k_{\text{obs}} - k_1}{(k_2 - k_1)} [\text{G}]^0 \quad (5)$$

Further support that the intermolecular H-bonded complex retards the rate of *cis* $\rightarrow$ *trans* isomerization was obtained by a control experiment where the bidentate triazine host **1** was replaced with 2-aminocyclohexyl-4,6-dimethoxy-1,3,5-triazine (**2**). This triazine derivative is unable to form two complementary hydrogen bonds with **4b**, and therefore no or little influence in the isomerization rate is expected to be

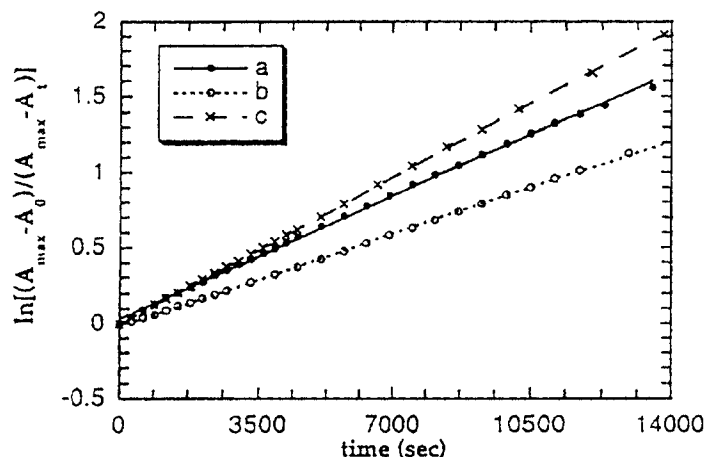


Figure 4. Kinetic analysis for the isomerization of 3,3'-diacetyl-*cis*-azobenzene (**4b**), 5×10^{-5} M, in the presence of (a) no triazine host, (b) 2.09×10^{-5} M of **1** and (c) 2.09×10^{-5} M of **2**

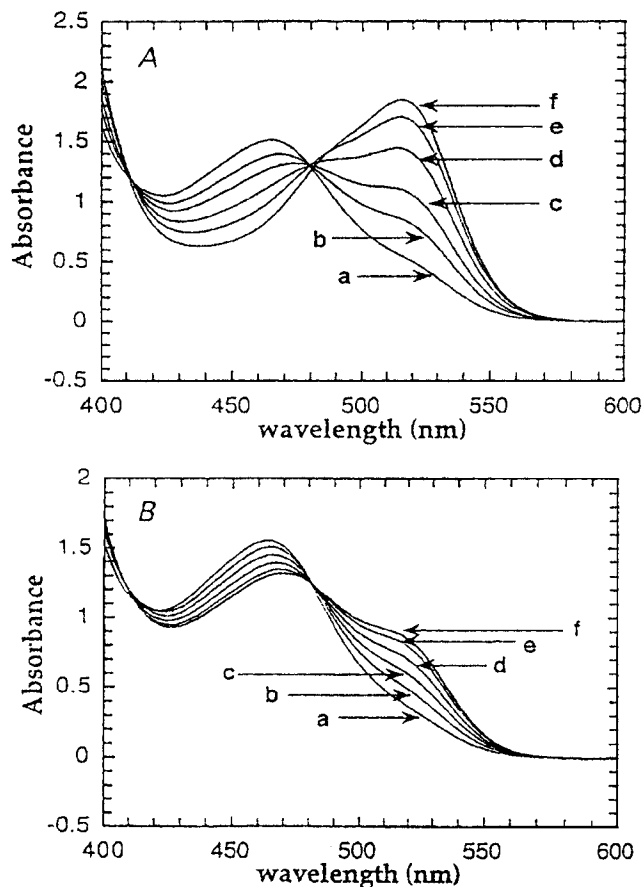


Figure 5. (A) Overlay spectra for the transformation of 6,6'-diethoxy-*cis*-thioindigo (**5b**), 1.36×10^{-4} M, to **5a**. Spectra were recorded at (a) 0, (b) 12, (c) 20, (d) 36, (e) 60 and (f) 200 min. The *cis* isomer (**5a**) was generated by illumination of **5b**, $\lambda > 515$ nm. (B) Overlay spectra for the transformation of 6,6'-diethoxy-*cis*-thioindigo (**5b**), 1.36×10^{-4} M, to **5a** in the presence of added **1**, 8.52×10^{-5} M. Spectra were recorded at time intervals of (a) 0, (b) 240, (c) 480, (d) 750, (e) 1020 and (f) 1200 min. In all experiments **5b** was generated by irradiation of **5a**, $\lambda > 515$ nm

observed. Figure 4 shows the kinetic analysis for the isomerization of **4b** in the presence of equal concentrations of the bidentate (**1**) and monodentate (**2**) triazines. Evidently, addition of the monodentate triazine **2** slightly accelerates the *cis* $\rightarrow$ *trans* isomerization of **4b**. The bidentate triazine **1**, however, inhibits the isomerization rate by a factor of 1.25 at this molar ratio.

Similarly, the *cis* $\rightarrow$ *trans* isomerization of 6,6'-diethoxy-*cis*-thioindigo (**5b**) was studied. Figure 5(A) and (B) show the spectral changes of the thermal isomerization of **5b** in the absence and presence of 2,4-bis(aminocyclohexyl)-6-methoxy-1,3,5-triazine (**1**), respectively. Addition of the H-bond donor **1** retards the isomerization rate. Figure 6 shows the kinetic analysis for the isomerization of **5b** in the presence of different concentrations of **1**.

Kinetic analysis of the thermal *cis* $\rightarrow$ *trans* isomerization of **5b** in the presence of **1** was also performed according to Scheme 1 and by application of equations (4) and (5). The observed rate constant for the isomerization of **5b** at various concentrations of **1** are summarized in Table 2. The association constant for the intermolecular H-bonded complex **1**-**5b** is $3.5 \times 10^5 \text{ l mol}^{-1}$ and the *cis* $\rightarrow$ *trans* isomerization rate within the complex is $k_2 = 1.4 \times 10^{-6} \text{ s}^{-1}$. Hence the isomerization across the double bond is *ca* 300-fold retarded in the presence of **1** as compared with free **5b**. Further control experiments were performed to support the conclusion that the formation of an intermolecular H-bonded complex between the bidentate H-donor **1a** and **5b** leads to inhibition of the isomerization rate. In these experiments the isomerization rate of **5b** was examined in the presence of the monodentate aminotriazine **2**. At a concentration of **1** or **2** of $8.52 \times 10^{-5} \text{ M}$, the isomeriz-

ation rate of **5b** is 100- and 2.5-fold retarded, respectively, as compared with the pure **5b** isomerization rate. Hence the bidentate amino functionalities in **1** play a most significant role in inhibition of the thermal isomerization of **5b**.

The values of the association constants of the intermolecular complexes **1a**-**4b** and **1a**-**5b** ($K = 4.9 \times 10^4$ and $3.5 \times 10^5 \text{ l mol}^{-1}$, respectively) should be specifically mentioned. The H-donor host molecule **1a** contains three sites for the formation of complementary H-bonds with an appropriate guest molecule. Previous studies¹⁷ have indicated that the association constants of diamino- (**1**) and triamino- (**7**) triazine derivatives through three complementary H-bonds, i.e. association with bernegrid (6), results in intermolecular complexes with association constants in the range $K = 450\text{--}920 \text{ l mol}^{-1}$. Thus, even though **4b** and **5b** are capable of forming intermolecular complexes by only two complementary H-bonds, the association constants of the resulting H-bonded assemblies are *ca* 10^3 times higher compared with the intermolecular complexes formed by three complementary H-bonds. This could be explained by the electrostatic interactions prevailing in H-bonded assemblies,^{6a} as shown schematically in Scheme 2. In the three H-bonded assembly (A), three primary attractive electrostatic interactions are perturbed by four repulsive secondary electrostatic interactions of adjacent hydrogen bonds. In the H-bonded assembly formed by two complementary H-bonds between two carbonyl functions and the bidentate amino receptor (B), the two primary attractive interactions are perturbed by only two repulsive secondary interactions, being separated by a distance of *ca* 3.2–3.8 Å (whereas in configuration A the repulsive sites are separated by a distance of

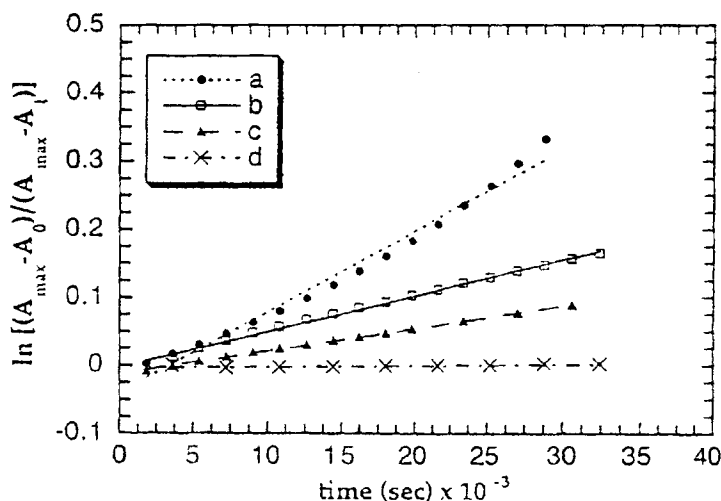
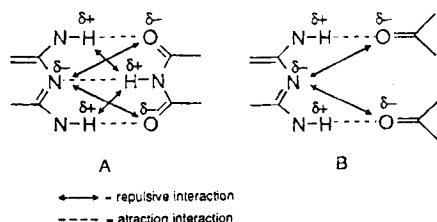


Figure 6. Kinetic analysis for the isomerization of 6,6'-diethoxy-*cis*-thioindigo (**5b**), $1.36 \times 10^{-4} \text{ M}$, in the presence of **1**. Concentrations of **1**: (a) 4.26×10^{-5} ; (b) 8.52×10^{-5} ; (c) 1.27×10^{-4} ; (d) $8.74 \times 10^{-4} \text{ M}$

Table 2. Rates of isomerization at 50 °C of **5b**, 1.36×10^{-4} M, in the presence of different concentrations of **1** and **2**

[5] : [host]	[Host] (M)	k_{obs} (s ⁻¹) ^a	k_{obs} (s ⁻¹) ^b
1 : 0	0	4.3×10^{-4}	4.3×10^{-4}
1 : 0.25	4.26×10^{-5}	9.8×10^{-6}	—
1 : 0.5	8.52×10^{-5}	4.9×10^{-6}	1.8×10^{-4}
1 : 0.75	1.27×10^{-4}	3.3×10^{-6}	—
1 : 5	8.74×10^{-4}	2.2×10^{-6}	8.5×10^{-5}
1 : 10	1.64×10^{-3}	1.6×10^{-6}	3.83×10^{-5}

^a Rate of isomerization in the presence of **1**.^b Rate of isomerization in the presence of **2**.Scheme 2. Schematic representation of the association patterns of H-bonded assemblies of **1a**

2.4–3.6 Å). This leads to higher association constants of the intermolecular complexes formed by **4b** and **5b** with **1**. Therefore, the number of complementary H-bonds in intermolecular assemblies does not reflect the strength of the resulting complexes. The relative configurations of the H-bonds and their mutual electrostatic interactions influence the stabilities of the complexes.

CONCLUSIONS

We have demonstrated the control of *cis* → *trans* thermal isomerizations of 3,3'-diacetyl-*cis*-azobenzene (**4b**) and 6,6'-diethoxy-*cis*-thioindigo (**5b**) by means of added 2,4-bis-(aminocyclohexyl)-6-methoxy-1,3,5-triazine (**1**). We have demonstrated that the *cis*-isomers **4b** and **5b** form tight complexes with **1a**. Stabilization of the *cis*-isomers retards their isomerization to the respective *trans*-isomers.

ACKNOWLEDGEMENT

This research was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities.

APPENDIX

Equations (4) and (5) were derived according to the following method.

The rate of product, P, formation is given by equations (A1) and (A2). Substitution of equation (A2) in equation (A1) yields equation (A3), which on substitution, $[G] = [G]^0 - [HG]$, yields equation (5) in the text.

$$\frac{dP}{dt} = k_{\text{obs}}[G]^0 \quad (\text{A1})$$

$$\frac{dP}{dt} = k_1[G] + k_2[HG] \quad (\text{A2})$$

$$k_{\text{obs}} = \frac{k_1[G]}{[G]^0} + \frac{k_2[HG]}{[G]^0} \quad (\text{A3})$$

The association constant, K , for the formation of the intermolecular complexes is given by equation (A4). Expression of $[H]$ and $[G]$ in terms of $[H]^0$, $[G]^0$ and the concentration of the complex, $[HG]$, and assuming that $[HG]$, $[G]^0 \gg [P]$ (early time intervals of the kinetic measurement), enable the association constant to be expressed by equation (A5).

$$K = \frac{[HG]}{[G][H]} \quad (\text{A4})$$

$$\frac{1}{K} = \frac{[G]^0[H]^0}{[HG]} - [H]^0 - [G]^0 + [HG] \quad (\text{A5})$$

Substitution of the ratio $[G]^0/[HG]$ by equation (5) in the text, followed by dividing by $(k_2 - k_1)$, yields equation (4) in the text.

REFERENCES

- (a) J. S. Linsey, *New. J. Chem.* **15**, 153–180 (1991); (b) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science* **254**, 1312–1319 (1992).
- (a) M. C. Etter, *Acc. Chem. Res.* **23**, 120–126 (1990); (b) J. Rebek, Jr, *Science* **235**, 1478–1484 (1987).
- (a) H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.* **30**, 1417–1436 (1991); (b) J. Rebek, Jr, *Top. Curr. Chem.* **149**, 189–210 (1988); (c) J. Rebek, Jr, *Acc. Chem. Res.* **23**, 399–404 (1990).
- (a) A. D. Hamilton, N. Pant and A. Muehldorf, *Pure Appl. Chem.* **60**, 533–538 (1988); (b) K. T. Chapman and W. C. Still, *J. Am. Chem. Soc.* **111**, 3075–3077 (1989).
- (a) A. D. Hamilton, *J. Chem. Educ.* **67**, 821–828 (1990); (b) L. A. Curtiss and M. Blander, *Chem. Rev.* **88**, 827–841 (1988).
- (a) J. Pranata, S. G. Wierschke and W. L. Jorgensen, *J. Am. Chem. Soc.* **113**, 2810–2819 (1991); (b) A. C. Legon and D. J. Millen, *Acc. Chem. Res.* **20**, 39–46 (1987).
- (a) C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.* **113**, 712–713 (1991); (b) C. T. Seto and G. M. Whitesides, *J. Am. Chem. Soc.* **112**, 6409–6411 (1990).
- J.-M. Lehn, M. Mascal, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.* 479–481 (1990).

9. S. J. Geib, C. Vincent, E. Fan and A. D. Hamilton, *Angew. Chem., Int. Ed. Engl.* **32**, 119–121 (1993).
10. (a) I. Tabushi, *Tetrahedron* **40**, 269–292 (1984); (b) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.* **27**, 89–112 (1988); (c) D. J. Cram, *Angew. Chem., Int. Ed. Engl.* **27**, 1009–1020 (1988).
11. (a) F. Diederich, *Angew. Chem., Int. Ed. Engl.* **27**, 362–386 (1988); (b) R. Breslow, *Science* **218**, 532–537 (1982); (c) J.-M. Lehn, *Science* **227**, 849–856 (1985).
12. T. Tjivikua, P. Ballester and J. Rebek, Jr, *J. Am. Chem. Soc.* **112**, 1249–1250 (1990).
13. P. Tecilla, S.-K. Chang and A. D. Hamilton, *J. Am. Chem. Soc.* **112**, 9586–9590 (1990).
14. T. S. Kelly, C. Zhao and G. J. Bridger, *J. Am. Chem. Soc.* **111**, 3744–3745 (1989).
15. S. C. Hirst and A. D. Hamilton, *J. Am. Chem. Soc.* **113**, 382–383 (1991).
16. P. Tecilla, R. P. Dixon, G. Slobodkin, D. S. Alavi, D. H. Waldeck and A. D. Hamilton, *J. Am. Chem. Soc.* **112**, 9408–9410 (1990).
17. I. Willner, J. Rosengaus and Y. Eichen, *J. Phys. Org. Chem.* **6**, 29–43 (1993).
18. For a preliminary report, see J. Rosengaus and I. Willner, *J. Chem. Soc., Chem. Commun.* 1044–1045 (1993).
19. K. Nakawa and T. Tsuji, *Chem. Pharm. Bull.* **11**, 296–301 (1963).
20. A. Rau, in *Photochromism—Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent, pp. 165–192. Elsevier, Amsterdam (1990).
21. D. L. Ross and J. Blanc, in *Techniques of Chemistry. Vol. III: Photochromism*, edited by G. H. Brown, pp. 486–556. Wiley-Interscience, New York (1971).
22. D. A. Rogers, J. D. Margerum and G. M. Wyman, *J. Am. Chem. Soc.* **79**, 2464–2468 (1957).
23. K. Fukunishi, M. Tatsuma, S. M. Fatha Ur Rahman, M. Kuwabara, H. Yamanaka and M. Nomura, *Bull. Chem. Soc. Jpn.* **63**, 3701–3703 (1990).
24. S. C. Zimmerman, W. Wu and Z. Zeng, *J. Am. Chem. Soc.* **113**, 196–201 (1991).
25. *PCMPI Ver. 4.2 program*, formerly *PCMODEL-PI*, Serena Software, Bloomington, IN.
26. N. L. Allinger, *J. Am. Chem. Soc.* **99**, 8127–8134 (1977).