

Effects of the Hydrogen-bonded Interactions on the Thermal *cis* to *trans* Isomerization of 3,3'-Diacetylazobenzene

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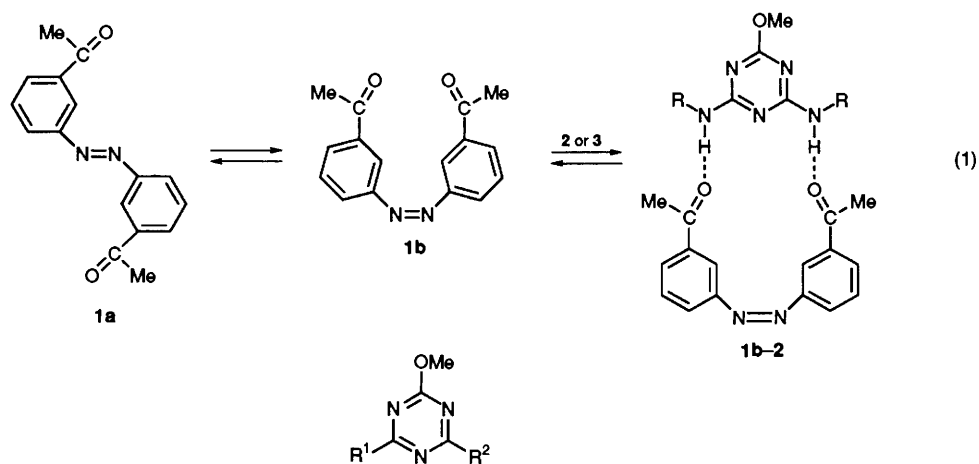
The thermal isomerization of 3,3'-diacetyl-*cis*-azobenzene **1b** is retarded in the presence of 2,4-bis(cyclohexylamino)-6-methoxy-1,3,5-triazine due to the formation of an intermolecular hydrogen-bonded assembly.

Extensive research activity is directed towards the design of supramolecular host-guest assemblies originating from complementary hydrogen-bonded interactions.^{1,2} Of particular interest is the influence of hydrogen-bonded interactions on chemical transformations; *e.g.* self-replicating systems by complementary hydrogen-bonds,³ phosphoryl transfer processes⁴ and control of pericyclic reactions⁵ represent chemical transformations in hydrogen-bonded supramolecular assemblies.

Recently, the effects of hydrogen-bonded interactions on the photophysical properties of a pyrene substituted receptor have been studied by Shinkai.⁶ In this system the fluorescence of the pyrene units is affected by intermolecular hydrogen-

bonding of the receptor with barbiturate host compounds.⁷ In a previous study we have demonstrated the formation of hydrogen-bonded assemblies between di- and tri-amino-triazines and bemegride.⁸ We have shown that these compounds provide three sites for the formation of complementary hydrogen-bonded interactions with guest substrates.

Azobenzenes undergo reversible photochemical *trans* \rightleftharpoons *cis* and thermal *cis* \rightarrow *trans* isomerization reactions.⁹ Here we report the influence of hydrogen bond interactions on the thermal isomerization of 3,3'-diacetyl-*cis*-azobenzene, **1b**. We describe the influence of the hydrogen-bonded assembly formed between 2,4-bis(cyclohexylamino)-6-methoxy-1,3,5-triazine, **2**, and **1b** on the isomerization process [eqn. (1)].



2; R¹, R² = *c*-C₆H₁₁NH
3; R¹ = OMe, R² = *c*-C₆H₁₁NH

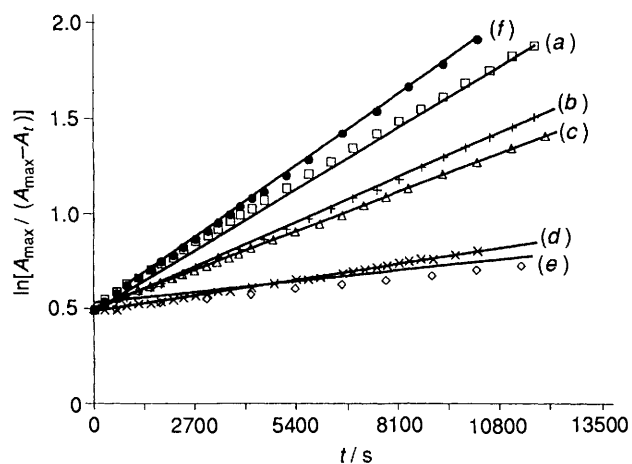


Fig. 1 Rates of isomerization of **1b**, 8.36×10^{-5} mol dm $^{-3}$ in the presence of **2**. Concentrations of **2**: (a) 0; (b) 2.09×10^{-5} ; (c) 4.18×10^{-5} ; (d) 8.36×10^{-5} ; (e) 4.18×10^{-4} mol dm $^{-3}$; (f) rate of isomerization of **1b** 8.36×10^{-5} mol dm $^{-3}$, in the presence of 2.09×10^{-5} mol dm $^{-3}$ of **3**.

Molecular mechanics calculations show that a stable complex between the *cis* isomer **1b**, and the triazine receptor **2**, is formed through two complementary hydrogen bonds.[†] The resulting intermolecular complex **1b-2** exhibits minimum energy. The calculated **1b-2** complex shows intermolecular hydrogen bond distances of 2.055 Å between the amine groups and the complementary carbonyl functionalities. No stable complex is formed with the *trans* isomer **1a** or with 2,2'- or 2,3'-diacetylazobenzenes. The formation of the hydrogen-bonded assembly **1b-2** is evidenced by ¹H NMR spectroscopy. The amine protons of **2** are shifted downfield in the presence of **1b** as expected for a hydrogen-bonded assembly.⁸ Formation of the complex is anticipated to retard the thermal isomerization of **1b** to **1a** by the stabilization of the *cis*-azobenzene isomer in the complex structure, eqn. (1). 3,3'-Diacetyl-*trans*-azobenzene, **1a**, was prepared as described by Nakagawa.^{10‡} 3,3'-Diacetyl-*cis*-azobenzene, **1b**, was prepared by monochromatic light irradiation, $\lambda = 355$ nm, of **1a** dissolved in a dry dichloroethane solution. Sealed cells containing **1b** and different concentrations of **2** were prepared, and the thermal isomerization of **1b** to **1a** was followed spectroscopically at 50 °C. Fig. 1 shows the rates of isomerization of **1b** in the presence of different concentrations of **2**. Evidently, the rate of isomerization is slowed down as the concentration of the triazine receptor **2** is increased. The inhibition of the isomerization process of **1b** to **1a** is attributed to the formation of the hydrogen-bonded intermolecular complex **1b-2**. In this structure the *cis*-configuration is stabilized and the structural isomerization is retarded. Increase of the concentration of **2** results in higher concentration of the complex and, therefore, a decrease in the isomerization rates. The association constant for the complex

† The program PCMPI Ver. 4.2, Serena Software, Bloomington, IN, has been applied (cf. N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127).

‡ 3,3'-Diacetyl-*trans*-azobenzene, **1a**, was prepared as described by oxidation of 3-aminoacetophenone with nickel peroxide followed by SiO₂ column chromatography using light petroleum-diethyl ether (3:1) as eluent.

1b-2, has been derived from the kinetic studies[§] and corresponds to $K_a = 1.2 \times 10^6$ dm 3 mol $^{-1}$.

Further support that the inhibition of the *cis* → *trans* isomerization reaction is due to the formation of a hydrogen-bonded assembly between the triazine receptor **2** and the azo compound **1b** has been obtained by a control experiment where the monodentate receptor 2-cyclohexylamino-4,6-dimethoxy-1,3,5-triazine **3** replaces **2** as additive. The monoaminotriazine is unable to form two complementary hydrogen-bonded interactions with **1b**. Fig. 1 compares the rates of isomerization of **1b** in the presence of the triazine receptors **2** and **3** respectively, at a molar ratio corresponding to 1:0.25. No retarding effect of the rate of isomerization is observed in the presence of the monodentate receptor **3**. In fact, addition of **3** results in even a slight enhancement in the isomerization of **1b**.

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§ The association constant of **1b-2** is calculated from the kinetic data using eqn. (2) and eqn. (3), where k_1 corresponds to the isomerization rate constants of **1b** without added host, k_2 is the isomerization rate constant in the complex structure, $[H]^0$ and $[G]^0$ are the added concentrations of **2** and **1** respectively and $[HG]$ is the complex concentration at a given concentration of **2** (cf. A. K. Colter, S. S. Wang, G. H. Megerle and P. S. Ossip, *J. Am. Chem. Soc.*, 1984, **86**, 3106). K_a has been derived by an iterative calculation initiated by assuming $[HG] = 0$ and plotting $[H]^0/k_{obs} - k_1$ vs. $([H]^0 + [G]^0 - [HG])$. The resulting slope has been introduced into eqn. (3) and the resulting concentrations of $[HG]$ have been resubstituted into eqn. (2). The process has been repeated until the slope converges. The association constant is derived from the slope and intercept of the converged plot.

$$\frac{[H]^0}{k_{obs} - k_1} = \frac{1}{K_a(k_2 - k_1)} + ([H]^0 + [G]^0 - [HG]) \frac{1}{(k_2 - k_1)} \quad (2)$$

$$[HG] = \frac{k_{obs} - k_1}{k_2 - k_1} [G]^0 \quad (3)$$