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Effect of solvent on *cis*-to-*trans* isomerization of 4-hydroxyazobenzene aggregated through intermolecular hydrogen bonds†

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ABSTRACT: The half-life ($\tau_{1/2}$) for thermal isomerization of *cis*-4-hydroxyazobenzene (*c*-HOAB) to its *trans* isomer is highly dependent on the solvent used. For non-aromatic solvents, the *cis* isomer is extremely unstable at 293 K ($\tau_{1/2} < 1$ min in methanol and acetonitrile and 6 min in cyclohexane), whereas the *cis* isomer is surprisingly stable in benzene ($\tau_{1/2} = 125$ min). However, addition of hydrogen chloride and triethylamine in benzene causes a remarkable decrease in $\tau_{1/2}$. On the basis of *ab initio* molecular orbital calculations of the binding energies and the optimum structures of *c*-HOAB–solvent complexes, a mechanism for the thermal *cis*-to-*trans* isomerization reaction involving hydrogen-bonded dimers and complexes is suggested. Copyright © 2005 John Wiley & Sons, Ltd.
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KEYWORDS: 4-hydroxyazobenzene; thermal *cis*-to-*trans* isomerization; half-life; solvent effect; intermolecular hydrogen bonds; *ab initio* MO calculation

INTRODUCTION

The reversible *cis–trans* photoisomerization and the thermal *cis*-to-*trans* isomerization of azobenzenes in matrices such as polymeric chains,[1] cyclodextrin and crown ether inclusion complexes,[2,3] liquid-crystal systems,[4] bilayer membranes,[5,6] zeolites,[7–9] and clays[10,11] have attracted considerable attention from the viewpoint of fundamental and practical studies of photochromism and thermochromism. However, there is still controversy concerning the mechanism for the photoisomerization of azobenzenes owing to the difficulties of directly observing the ultrashort-lived excited state.[12–16] One of the authors recently suggested that bimolecular photoisomerization of azobenzenes through the excimer competes with unimolecular photoisomerization, a competition which depends on the initial concentration.[17] Because of the ultrashort lifetime in the excited singlet state, it is likely that the formation of ground-state aggregates is essential for the bimolecular photoisomerization. Although the spectroscopic and photoisomerization behavior of aqueous bilayer aggregates of azobenzene-containing amphiphiles and also of azobenzene aggregates formed in liquid crystal has been studied,[4–6] there have been no investigations of aggregate formation for unsubstituted azobenzene in solution.

In order to obtain a deeper insight into the role of aggregates in the *cis–trans* photoisomerization and thermal *cis*-to-*trans* isomerization of azobenzenes in solution, we have studied the effects of solvent on the isomerization of 4-hydroxyazobenzene (HOAB), which had previously been found to form dimers or aggregates through intermolecular hydrogen bonds,[18] as shown in Fig. 1. In this paper, we report that intermolecular interaction between HOAB and benzene (PhH) suppresses the formation of aggregates and that owing to this interaction the *cis* isomer (*c*-HOAB) becomes surprisingly stable. On the basis of the effect of acid and base on the stability of *c*-HOAB and also *ab initio* molecular orbital (MO) calculations of the binding energies and optimum structures of HOAB–solvent complexes, the thermal *cis*-to-*trans* isomerization mechanism is discussed, and consideration is given to the effect of hydrogen bonds between HOAB and solvents.

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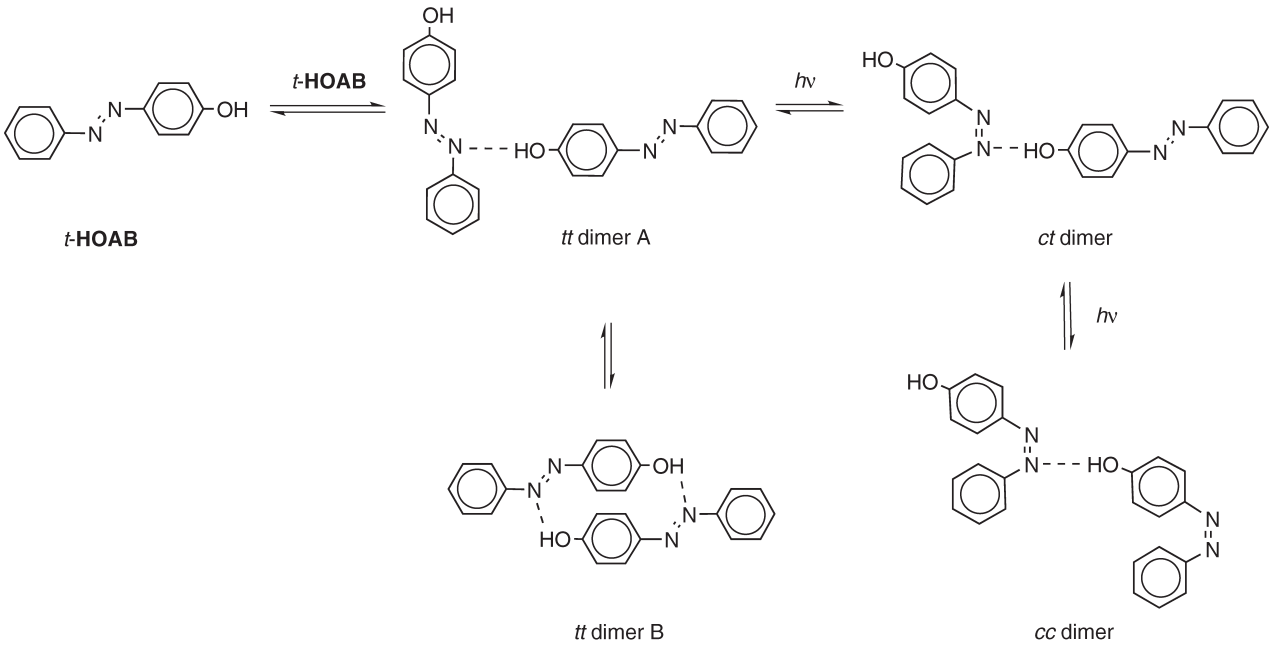


Figure 1. Schematic structure of hydrogen-bonded dimers of HOAB

EXPERIMENTAL

Materials

trans-4-Hydroxyazobenzene (*t*-HOAB) was purchased from Acros Organics and purified by recrystallization from methanol. All of the solvents used in this study were guaranteed reagents from Wako Pure Chemical Industries and Nacalai Tesque and were distilled over calcium hydride prior to use. A solution of 1.0 M hydrogen chloride (HCl) in diethyl ether and triethylamine (TEA) were obtained from Aldrich and Wako Pure Chemical Industries, respectively.

Absorption spectra at 230 K

UV–visible absorption spectra at 230 K were measured using a Jasco Ubest50 spectrometer equipped with an Oxford DN1704 liquid nitrogen bath cryostat. The temperature of the cryostat was controlled to within ± 0.1 K. Spectroscopic-grade acetonitrile (MeCN) from Dojin Chemicals was refluxed over phosphorus pentoxide under nitrogen and distilled immediately before use.

Measurement of half-lifes

Solutions containing 4×10^{-4} M *t*-HOAB were irradiated using a 400 W high-pressure mercury lamp (Riko UVL-400HA) through HOYA UV-34 and U-360 glass filters (366 nm band path) until the *cis*: *trans* ratio reached the photostationary state. The thermal decay of the *cis* isomer produced by irradiation was measured at 293 ± 1 K by observing the decrease in absorbance at 440 nm using a Shimadzu UV-2100 spectrophotometer. Linear correlation was obtained by plotting the logarithm of the decrease in molar absorptivity ($\Delta\varepsilon$) at 440 nm vs time. The correlation coefficients for PhH and cyclohexane (C_6H_{12}) were 1.000 and 0.994, respectively. In the case of methanol (MeOH) and MeCN, the decay rate was too fast to be determined at 293 K.

Method for *ab initio* molecular orbital calculations

To obtain accurate structures of HOAB–solvent complexes, it is essential to describe accurately the intermolecular long-range interactions between solvent molecules and HOAB. In previous studies on the van der Waals interactions between rare-gas atoms,[19,20] *ab initio* MO calculations based on density functional theory (DFT) were performed using five different non-local exchange-correlation functionals included in the Gaussian 98 program package to evaluate the accuracy of the DFT exchange and correlation functionals.[21] The results clarified that the Perdew–Wang-type functionals are more accurate than the Becke-type functionals, indicating that the exchange functional proposed by Perdew and Wang produces a better description of the van der Waals interaction than Becke's functionals. In the present study, therefore, the Perdew–Wang91 functionals (PW91) were used for exchange and correlation energies.[22,23]

In the MO calculations for long-range interactions, the choice of basis set is also crucial. In particular, a diffuse basis set is needed to describe the behavior of electrons at

the long tail part of the molecular orbitals. As mentioned in previous studies,[19,20] the stacking interaction of cytosine dimer and the van der Waals interactions between rare-gas atoms cannot be described without diffuse functions. Therefore, we used the 6–31+G** basis set, the standard split valence 6–31G** basis set augmented by a set of diffuse functions.

RESULTS AND DISCUSSION

Formation of hydrogen-bonded dimers or aggregates

As found by Gabor *et al.* in 1968,[18] *t*-HOAB forms dimers or aggregates through intermolecular hydrogen bonds involving the hydroxyl group and the azo nitrogen, as shown in Fig. 1. When the absorption spectra of 2.5×10^{-5} M *t*-HOAB were measured in various solvents as a function of temperature, remarkable spectral shifts were observed.[18] In particular, when a methylcyclohexane solution was progressively cooled from 298 to 163 K, the absorption maximum around 330 nm shifted to 360 nm and a new absorption band beyond 400 nm appeared, probably owing to dimerization or aggregation.

The absorption spectra for *t*-HOAB at room temperature in MeOH, MeCN and PhH are compared with the spectrum in C_6H_{12} in Fig. 2. A slight red shift (6–10 nm) was observed in polar solvents for the absorption maximum at around 350 nm, which was attributed to a $\pi\pi^*$ band. In addition, a slight increase in absorption beyond 400 nm was observed in MeOH and MeCN. These spectral changes indicate that solvent molecules interact with *t*-HOAB and this may suppress the dimerization or aggregation of *t*- and *c*-HOAB in MeOH, MeCN and PhH. In order to understand the effect of solvent on the *cis–trans* photo- and thermal isomerization of aggregated HOAB, we measured the half-life ($\tau_{1/2}$) of the *cis* isomer in the above solvents, as described below.

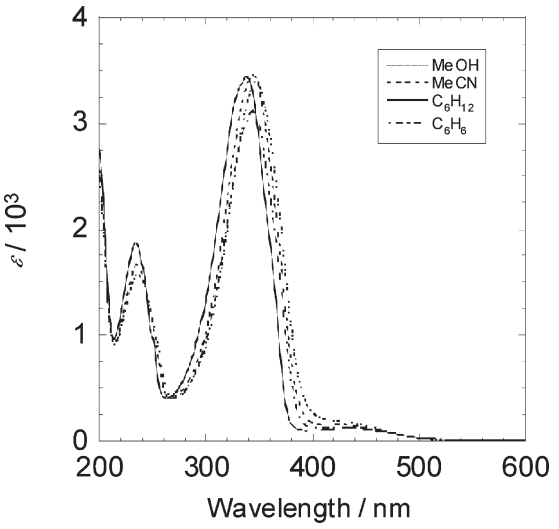


Figure 2. Absorption spectra for 2×10^{-4} M *t*-HOAB in C_6H_{12}, MeCN, PhH and MeOH measured using a 2 mm pathlength cell at room temperature

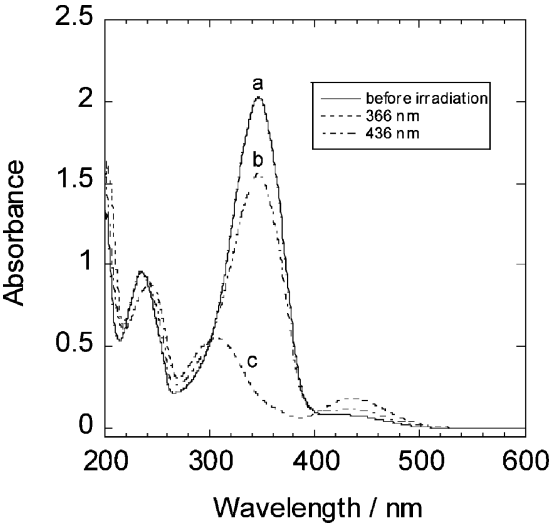


Figure 3. Absorption spectra for 2.5×10^{-4} M *t*-HOAB in MeCN measured using a 2 mm pathlength cell at 230 K: (a) before irradiation; (b) at 20 min after 436 nm irradiation; (c) at 10 min after 366 nm irradiation

Thermal stability of the *cis* isomer

When the *trans* isomer is irradiated in MeCN and MeOH using 366 nm radiation for 2 h at room temperature, there is no absorption spectral change. However, when the isomer is irradiated in MeCN at 230 K, a significant amount of the *cis* isomer (ca 90%) is produced, as can be seen from the changes in the absorption spectra shown in Fig. 3. On the other hand, when PhH is used as a solvent, the *cis*: *trans* isomer ratio in the photostationary state at room temperature was found to be ca. 85:15. These results indicate that the thermal stability of the *cis* isomer under the irradiation conditions is highly dependent on the solvents used. Therefore, we attempted to determine $\tau_{1/2}$ of the *cis* isomer in MeOH, MeCN, C_6H_{12} and PhH, as shown in Fig. 4 and Table 1. When MeOH and MeCN are employed as solvents, $\tau_{1/2}$ at 293 ± 1 K is too short to be measured (<1 min). For C_6H_{12}, $\tau_{1/2}$ increases slightly up to 6 min, whereas $\tau_{1/2}$ for PhH increases greatly up to 125 min. In a mixed solvent of C_6H_{12} and PhH, the change in $\tau_{1/2}$ depends on the ratio of the two solvents. Accordingly, it is clearly understood that benzene is a highly effective stabilizer of *c*-HOAB. As can be seen in Table 1, there is no correlation between the dielectric constants and viscosity of the solvents and $\tau_{1/2}$. However, the acidity and basicity of the solvents seem to have a profound effect on the stabilization of the *cis* isomer.

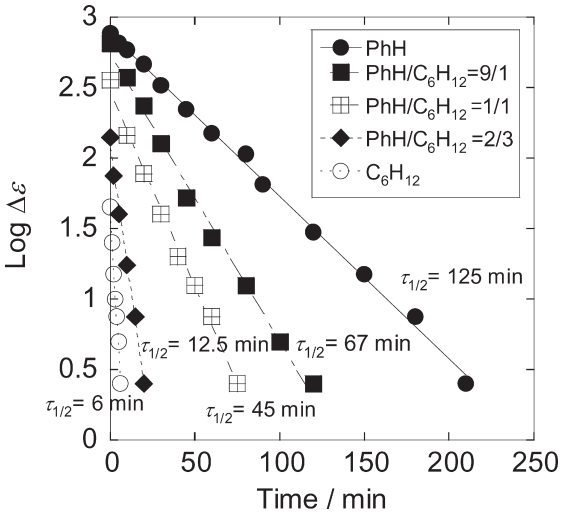


Figure 4. Plot of logarithm of decrease in molar absorptivity ($\Delta\varepsilon$) at 440 nm for *c*-HOAB vs time in PhH, C_6H_{12} and a mixed solution of the two solvents

Binding energy of hydrogen-bonded dimers

Several schematic structures for the *trans–trans* (*tt*), *cis–trans* (*ct*) and *cis–cis* (*cc*) hydrogen-bonded dimers of HOAB are shown in Fig. 1. In order to confirm the possibility of dimerization for HOAB, we performed *ab initio* MO calculations to obtain the binding energy (*BE*) and the stable structures of the dimers, as can be seen in Table 2. The *BE* values are evaluated from the difference in the total energy of dimers and component monomers. For *tt* dimer A, formed by an intermolecular hydrogen bond between a hydroxyl group and a nitrogen atom, *BE* is calculated to be 9.5 kcal mol^{-1} (1 kcal mol^{-1} = 4.186 kJ mol^{-1}). For the *tt* dimer B it is calculated to be 9.3 kcal mol^{-1}, which is due not only to the stacking interaction between the benzene rings but also to the two hydrogen bonds between the hydroxyl groups and the nitrogen atoms. Catalan *et al.* reported that *trans*-stilbene aggregated in solution to form dimers and trimers.[24] Using the same method, we calculate *BE* for *trans*-stilbene to be 3.3 kcal mol^{-1}, which is a much

Table 1. Half-lifes ($\tau_{1/2}$) of *c*-HOAB and absorption maxima for $\pi\pi^*$ and $n\pi^*$ of *t*-HOAB in various solvents

					Solvent parameters			
Solvent	λ_{max}[a](nm)	λ_{max}[b](nm)	ε_{440}[c]	$\tau_{1/2}$[d](min)	DC[e]	Acidity[f]	Basicity[f]	Viscosity[g]
MeOH	348	440	1240	<1	32.66[h]	0.76	0.71	0.593
MeCN	344	425	1130	<1	35.94[h]	0.47	0.23	0.345[h]
C_6H_{12}	338	433	780	6	2.023	0.01	0.00	0.975
PhH	344	432	1110	125	2.284	0.11	0.09	0.649

[a] Absorption maximum of $\pi\pi^*$ band for the *trans* isomer.
[b] Absorption maximum of $n\pi^*$ band for the *trans* isomer.
[c] Molar absorptivity at 440 nm.
[d] Half-life of the *cis* isomer at 293 ± 1 K.
[e] Dielectric constant at 293 K unless noted otherwise (Ref. 29).
[f] Solvent Lewis acidity and basicity parameters estimated by Krygowski *et al.*[26]
[g] Viscosity at 293 K unless noted otherwise (Ref. 29).
[h] Measured at 298 K.

Table 2. Binding energy (*BE*) and bond lengths of N═N and O—H of HOAB and intermolecular bonds (N···H, CH-π) calculated using *ab initio* MO methods for hydrogen-bonded HOAB dimers and HOAB–solvent complexes

		Bond length (Å)		
Dimer or complex	*BE* (kcal mol^{-1})	N═N	O—H	N···H[a]
tt dimer A	9.5	1.28/1.28	1.01/0.98	1.79
tt dimer B	9.3	1.28/1.28	1.01	1.82
ct dimer	12.4	1.27 (*c*)/1.28 (*t*)	0.98 (*c*)/1.01 (*t*)	1.75
cc dimer	12.5	1.27/1.27	0.98/1.01	1.75
t-HOAB–MeOH	8.8	1.28	0.98	1.89
c-HOAB–MeOH	9.8	1.27	0.98	1.88
t-HOAB–MeCN	8.3	1.28	0.99	1.88[b]
c-HOAB–MeCN	8.8	1.27	0.99	1.89[b]
t-HOAB–C_6H_{12}	1.3	1.28	0.98	3.37/3.21[c]
c-HOAB–C_6H_{12}	1.3	1.26	0.98	2.88
t-HOAB–PhH	1.6	1.27	0.98	4.12/3.09[c]
c-HOAB–PhH	2.3	1.27	0.98	2.86

[a] The shortest bond length between a nitrogen atom of the N═N bond and a hydrogen in *c*- and *t*-HOAB or solvents.
[b] The hydrogen bond length between a nitrogen atom of MeCN and a hydrogen in an OH group of HOAB.
[c] The shortest distance between carbon atoms of the PhOH part and H atoms of PhH or C_6H_{12}.

smaller value than that obtained for the *tt* dimers. This lends strong support to the hypothesis that *t*-HOAB forms dimers or aggregates in the ground state. For the *ct* and *cc* dimers, which have only one hydrogen-bonded interaction similar to *tt* dimer A, BE is calculated to be 12.4 and 12.5 kcal mol^{-1}, respectively. This indicates that, in the case of the *tt* dimer B, repulsion between the two benzene rings causes instability. There are other possible hydrogen-bonded dimers of HOAB in addition to those shown in Fig. 1, and we will report in another paper on the stability and the stable structures of all the dimers calculated by the present method.[25] However, the *BE* values calculated for the dimers illustrated in Fig. 1 clearly show that the dimers or aggregates formed by HOAB are more stable than those for *trans*-stilbene.

Binding energy of solvent–HOAB complexes

In order to understand the effect of solvent on the formation of the hydrogen-bonded dimers or aggregates of HOAB, we also calculated *BE* for the complexes of *t*- and *c*-HOAB with MeOH, MeCN, C_6H_{12} and PhH. As can be seen in Table 2, the *BE* values (8.3–9.8 kcal mol^{-1}) for MeOH and MeCN with *t*- and *c*-HOAB are sufficiently large to suggest the formation of stable HOAB–solvent complexes in the ground state. Accordingly, the formation of the hydrogen-bonded dimers or aggregates must be suppressed in MeOH and MeCN, but not in C_6H_{12} ($BE = 1.3$ kcal mol^{-1}). Optimum structures of *c*-HOAB with MeOH and MeCN are shown in Fig. 5(a) and (b), respectively. In the case of MeOH, the hydrogen atom in a hydroxyl group interacts with a nitrogen atom in *c*-HOAB (N···H = 1.88 Å). For MeCN, on the other hand, the nitrogen atom in a nitrile group interacts with the hydrogen atom in a hydroxyl group in *c*-HOAB (N···H = 1.89 Å). As described above, in both solvents *cis*-to-*trans* thermal isomerization at 293 K proceeds much faster ($\tau_{1/2} < 1$ min) than in benzene ($\tau_{1/2} =$ 125 min). Therefore, it seems likely that the rate for the thermal isomerization is accelerated owing to tautomerization assisted by the solvents, as illustrated in Scheme 1. In contrast, for C_6H_{12} the solvent cannot effectively

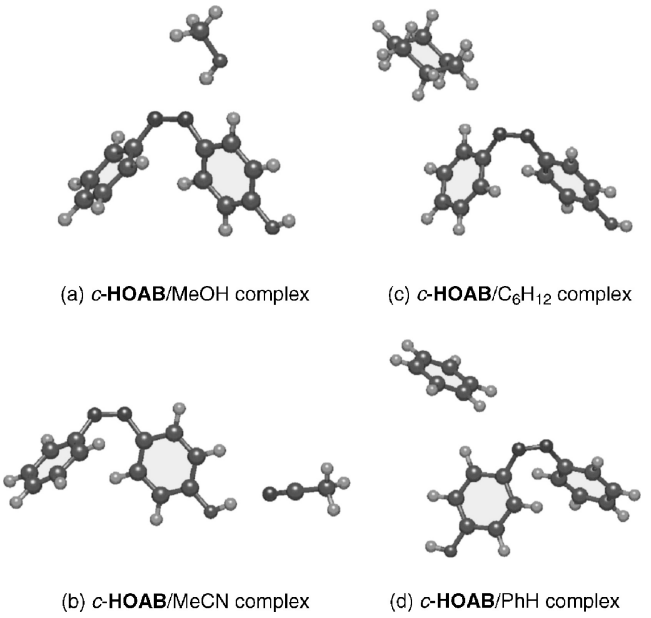
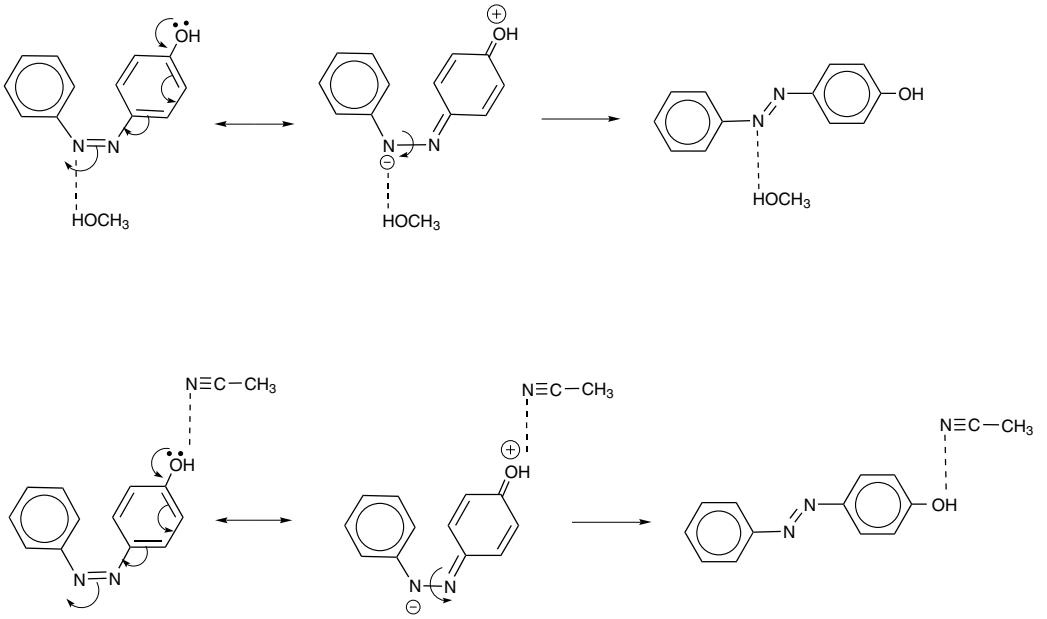
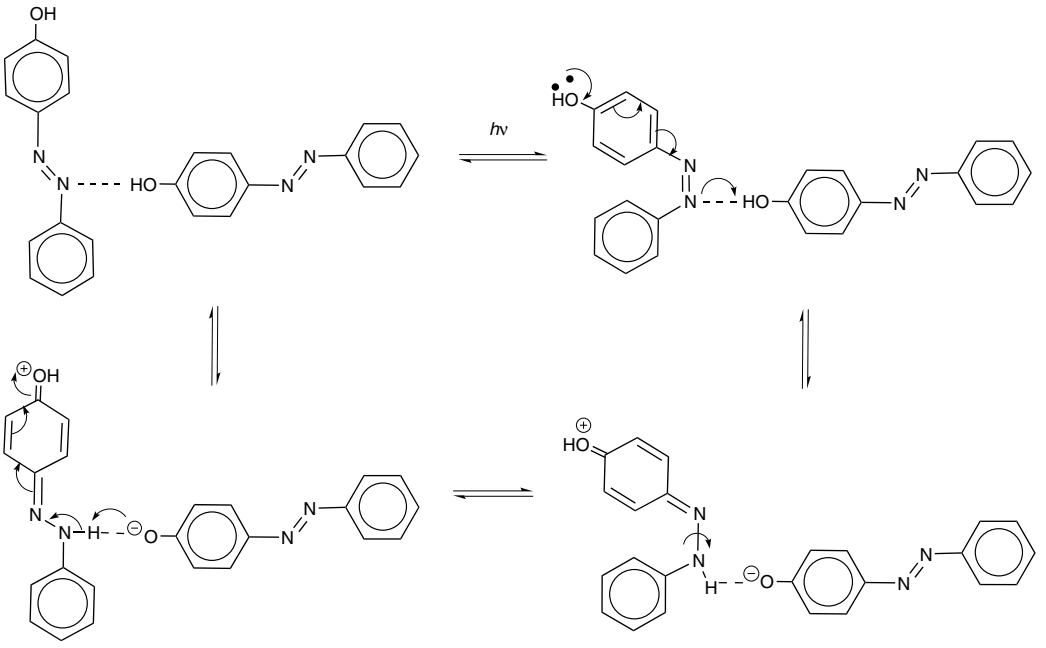


Figure 5. Optimum structures of *c*-HOAB–solvent complexes obtained by *ab initio* MO calculations. For MeOH another complex ($BE = 9.3$ kcal mol^{-1}) in which the solvent molecule interacts with the other nitrogen atom in *c*-HOAB is obtained



Scheme 1. Thermal *cis*-to-*trans* isomerization of *c*-HOAB accelerated by the formation of the hydrogen-bonded complexes with MeOH and MeCN



Scheme 2. Thermal *cis*-to-*trans* isomerization of *c*-HOAB through the hydrogen-bonded dimer

suppress the formation of hydrogen-bonded dimers because of the weak interaction with HOAB. The rate ($\tau_{1/2} = 6$ min) for the *cis*-to-*trans* thermal isomerization is also much faster than that for benzene. Therefore, as for MeOH, the hydrogen-bonded interaction in *ct* dimer would catalyze the *cis*-to-*trans* isomerization, as depicted in Scheme 2.

The *BE* values calculated for PhH are 1.6 kcal mol^{-1} for *t*-HOAB and 2.3 kcal mol^{-1} for *c*-HOAB. As shown in Fig. 5(d), a hydrogen atom of the solvent molecule seems to interact with a nitrogen atom of the *cis* isomer. However, the calculated N···H bond length is 2.86 Å, which is too long to be regarded as a hydrogen bond. Furthermore, on the basis of the relative acidity for organic solvents estimated by Krygowski *et al.*,[26] the acidity of cyclohexane (0.01) and benzene (0.11) is much weaker than that of methanol (0.76). Therefore, it is not the acidity of the two solvents which accelerates the thermal *cis*-to-*trans* isomerization of HOAB. On the other hand, the structure of the benzene–*c*-HOAB complex may pre-empt the formation of hydrogen-bonded dimers with another *cis* or *trans* isomer. The results reported in a previous study of benzene molecules suggest that it is also possible that π–π stacking interaction occurs between benzene molecules and aromatic rings of *c*-HOAB.[27] Accordingly, the additional solvent molecules would suppress the interaction of the *cis* isomer with another *cis* or *trans* isomer. Because of this, the *cis* isomer may have a relatively longer $\tau_{1/2}$ in PhH than in C_6H_{12}. It was found by Schulte-Frohlinde that *cis*-to-*trans* thermal isomerization of HOAB was self-catalyzed at concentrations between 10^{-4} and 10^{-2} M.[28] The concentration effect observed also seems to indicate the participation of dimers or aggregates of HOAB.

Effect of acid on the *cis*-to-*trans* isomerization

We have confirmed the effect of proton on the *cis*-to-*trans* isomerization in benzene. As suggested in Scheme 1, if MeOH interacts with a nitrogen atom, addition of HCl must cause acceleration of the isomerization rate. In fact, $\tau_{1/2}$ in PhH decreases to 71 min in the presence of 1×10^{-8} M HCl and further decreases with increase in the concentration ($\tau_{1/2} = 36$ min for 1×10^{-5} M HCl), as can be seen in Fig. 6. This result strongly supports the hypothesis that a hydrogen-bonded interaction occurs between a nitrogen atom of *c*-HOAB and a hydroxyl group of MeOH.

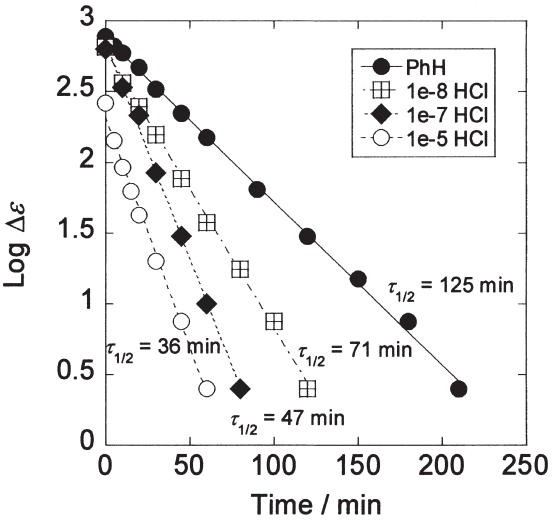


Figure 6. Effect of HCl on $\tau_{1/2}$ in PhH

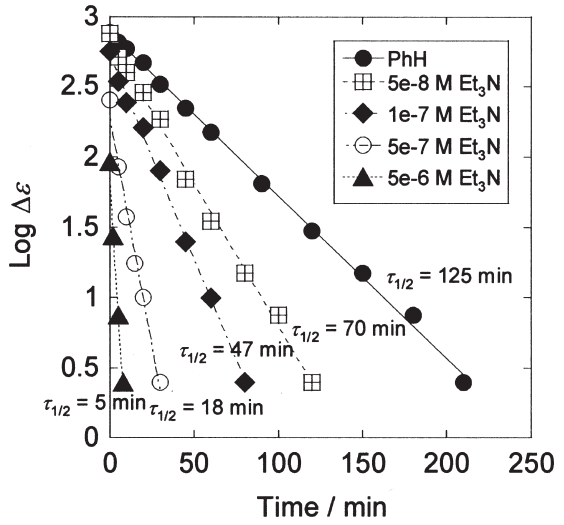


Figure 7. Effect of triethylamine (TEA) on $\tau_{1/2}$ in PhH

Effect of base on the *cis*-to-*trans* isomerization

It is also noteworthy that addition of TEA causes a decrease in $\tau_{1/2}$ in PhH. As can be seen in Fig. 7, in the presence of 5×10^{-8} M TEA $\tau_{1/2}$ in PhH is 70 min and a further decrease is observed with increase in the concentration: $\tau_{1/2} = 5$ min for 5×10^{-6} M TEA. This result also supports the proposal in Scheme 1 of a mechanism for *cis*-to-*trans* isomerization in which the nitrogen atom of MeCN acts as a base to interact with the hydroxyl group of *c*-HOAB.

CONCLUSIONS

The *cis* and *trans* isomers of HOAB form hydrogen-bonded complexes with MeOH and MeCN. Owing to the formation of these complexes, HOAB exists as a monomer in these solvents. In C_6H_{12} the intermolecular interaction between HOAB and the solvent molecule is weaker than with MeOH and MeCN; therefore, hydrogen-bonded dimers or aggregates exist together with the monomers. The thermal stability of *c*-HOAB depends on the interaction site in the isomer with the solvent and the *BE*. In the case of MeOH, it seems likely that a hydrogen atom of the hydroxyl group acts as an acid on the nitrogen atom of *c*-HOAB. For MeCN, the nitrogen atom acts as a base on the hydroxyl group of *c*-HOAB. Both interactions accelerate the rate of *cis*-to-*trans* isomerization, as suggested in Scheme 1. In the case of PhH, $\tau_{1/2}$ (125 min) is much longer than in non-aromatic solvents. This is probably because the structure of the HOAB–PhH complex suppresses the formation of dimers or aggregates of HOAB, but this solvent molecule does not act on *c*-HOAB as either an acid or a base. This interesting interaction between HOAB and solvent may provide a new approach by which to study the characteristics of azobenzenes in the excited state.[17]

Acknowledgements

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