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Photochromism of 2-(Phenylazo)imidazoles

Joe Otsuki,*,† Kazuya Suwa,† Koichi Narutaki,† Chittaranjan Sinha,‡ Isao Yoshikawa,§ and Koji Araki§

College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan, Department of Chemistry, Jadavpur University, Kolkata 700032 India, and Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

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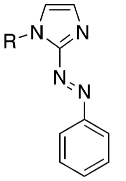
The isomerization behaviors of 2-(phenylazo)imidazole (Pai-H) and 1-*N*-methyl-2-(phenylazo)imidazole (Pai-Me) have been investigated. The crystal structure of *trans*-Pai-Me was determined, revealing that key structures around the azo group are nearly identical among azobenzene, Pai-H, and Pai-Me. Pai-Me undergoes reversible cis/trans photoisomerization, whereas Pai-H responds poorly to irradiation. The quantum yields of trans-to-cis isomerization of Pai-Me on 454 and 355 nm excitation are 0.35 ± 0.03 and 0.25 ± 0.03, respectively, in toluene. The wavelength-dependent isomerization quantum yield is well-known for azobenzene, but these values are substantially higher than those of azobenzene. The activation energy of thermal cis-to-trans isomerization of Pai-Me in toluene is 79.0 ± 3.5 kJ mol^{-1}, which is lower than that of azobenzene by 15 kJ mol^{-1}. The thermal cis-to-trans isomerization of Pai-H is even faster. Density functional theory calculations were performed, revealing that the energy gaps between the azo n-orbital and the highest π-orbital of azoimidazoles are much narrower than that of azobenzene. Finally, a preliminary study suggested that metal ions can modulate the absorption spectrum of Pai-Me without a loss of the gross photochromic behavior.

Introduction

Azobenzene is a textbook example of photoisomerization.[1] Theoretical[2−9] and experimental[10−18] studies on the isomerization mechanism are still actively being carried out, while a huge number of its derivatives have been prepared as switching components in application-oriented research projects.[19−23] Most of the derivatives have substituents on the parent azobenzene scaffold, whereas less attention has been paid to its analogues having a heterocyclic ring in place of the phenyl group. Basic properties of the isomerization of azopyridines, in which one (or both) of the phenyl groups of azobenzene is replaced by a pyridyl group, have been reported.[5,24,25] Azopyridine derivatives can participate in coordination to a metal ion and hydrogen bonding through the pyridyl-*N* and the azo group itself. Hence, it is anticipated that azopyridines can be used to modulate or switch the properties of coordination complexes or hydrogen-bonded supramolecules. This idea has been verified experimentally for both metal complexes[26−29] and hydrogen bonded liquid crystals[30] containing azopyridine units.

Phenylazoimidazoles constitute another interesting class of compounds as a potential switching group in biological applications and in coordination chemistry, since imidazole is a ubiquitous and essential group in biology, especially as a metal coordinating site. This family of compounds has been extensively used as ligands for metal ions by C.S.[31−40] and others.[41−43] However, little is known about the photochromic and thermal isomerization behaviors of phenylazoimidazoles. Indeed, a literature survey by us showed only one recent report by Majima et al. on the aspect of photoisomerization of azoimidazole derivatives.[44] In the report, they prepared (deoxy)ribofuranosyl derivatives of 2-(phenylazo)imidazole (Pai-H) and observed that these compounds undertake reversible cis/trans isomerization with photoisomerization quantum efficiencies lower than those for azobenzene. It is not clear, however, whether these properties are intrinsic to the azoimidazole chromophore or being significantly perturbed by the (deoxy)ribofuranosyl substituents. Herein we report an investigation of the isomerization of azoimidazole without (Pai-H) or with a minimum substituent (1-*N*-methyl-2-(phenylazo)imidazole; Pai-Me) to elucidate the isomerization behaviors intrinsic to the parent compound.



Pai-H: R = H
Pai-Me: R = Me

Results and Discussion

Crystal Structures. The crystal structure of Pai-H has been reported,[45] whereas the crystal structure of Pai-Me has only been known within metal complexes so far.[31−34] Single crystals of *trans*-Pai-Me suitable for X-ray analysis were obtained from a hexane solution by allowing the solvent to evaporate. Pai-Me crystallized in monoclinic space group $P2_1/c$ with four molecules per unit cell. Crystallography data and bond lengths and angles are reported in Tables 1 and 2, respectively, while the molecular structure is shown in Figure 1 (see Supporting Information for the CIF file). The bond lengths for C(phenyl)−N(azo) and N═N in azobenzene,[46] Pai-H,[45] and Pai-Me agree within 0.02 Å with each other. The bond angles for C(phenyl)−N═N are

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* To whom correspondence should be addressed. E-mail: otsuki@chem.cst.nihon-u.ac.jp.

† Nihon University.

‡ Jadavpur University.

§ University of Tokyo.

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TABLE 1: Crystallographic Data for Pai-Me

formula	$C_{10}H_{10}N_4$
fw	186.22
cryst size/mm	0.23_0.09_0.08
crystal system	monoclinic
space group	$P2_1/c$
a/Å	6.670(1)
b/Å	11.506(2)
c/Å	12.975(2)
α/deg	90
β/deg	114.56(5)
γ/deg	90
V/Å^3	905.7(3)
Z	4
D_{calcd}/g cm^{-1}	1.366
temp/K	120 K
μ (Cu Kα)/cm^{-1}	0.706
diffractometer	MacScience DIP-Labo
radiation	Cu Kα (λ = 1.54180 Å)
monochromator	graphite
$2\theta_{max}$/deg	146.44
no. of rflns collcd	7914
no. of indep rflns	1654
no. of rflns obsd (> 2σ)	1510
$R1$ ($I > 2\sigma(I)$)	0.0598
$wR2$ ($I > 2\sigma(I)$)	0.1828
$R1$ (all data)	0.0660
$wR2$ (all data)	0.1990
no. of params	128
GOF	1.114
max and min peaks in final diff map/e$^-$ Å^{-3}	0.337; −0.498

TABLE 2: Crystal Structure Data for Pai-Me

Bond Lengths[a]/Å			
N1−N2	1.261(2)	C6−C12	1.383(3)
N1−C3	1.424(3)	N3−C8	1.358(3)
N2−C15	1.388(3)	N3−C13	1.465(3)
C3−C6	1.394(3)	C8−C14	1.364(3)
C3−C4	1.396(3)	N4−C14	1.365(3)
C4−C11	1.388(3)	C10−C11	1.381(3)
C15−N4	1.331(3)	C10−C12	1.394(3)
C15−N3	1.367(3)		

Bond Angles[a]/deg			
N2−N1−C3	113.47(18)	C8−N3−C15	106.71(17)
N1−N2−C15	114.28(18)	C8−N3−C13	126.13(18)
C6−C3−C4	119.96(19)	C15−N3−C13	127.12(17)
C6−C3−N1	124.43(18)	N3−C8−C14	105.97(19)
C4−C3−N1	115.58(18)	C15−N4−C14	104.11(17)
C11−C4−C3	120.0(2)	C11−C10−C12	120.2(2)
N4−C15−N3	111.87(17)	C10−C11−C4	119.9(2)
N4−C15−N2	130.01(18)	C6−C12−C10	120.3(2)
N3−C15−N2	118.10(18)	C8−C14−N4	111.34(19)
C12−C6−C3	119.64(19)		

[a] Estimated standard deviations are in parentheses.

within 0.8° in these compounds. The dihedral angle for C−N═N−C is exactly 180° in azobenzene, whereas the angles are slightly deviated from planarity in Pai-H (177.81°) and in Pai-Me (177.48°). Although the two phenyl rings in azobenzene are parallel with one another,[46] the dihedral angle between the mean planes of the phenyl and imidazole rings in Pai-Me is 18.3°. This value is incidentally comparable with that of Pai-H (18.4°),[45] but the imidazole ring flips the opposite way about the C(imidazole)−N(azo) bond, most probably to avoid steric congestion around the methyl group. In the crystal of Pai-H,[45] imidazole-*N* and imidazole-*NH* participate in intermolecular hydrogen bond chains. An intramolecular hydrogen bond between imidazole-*NH* and one of the azo-*N*'s, which would form a five-membered ring, is not formed.

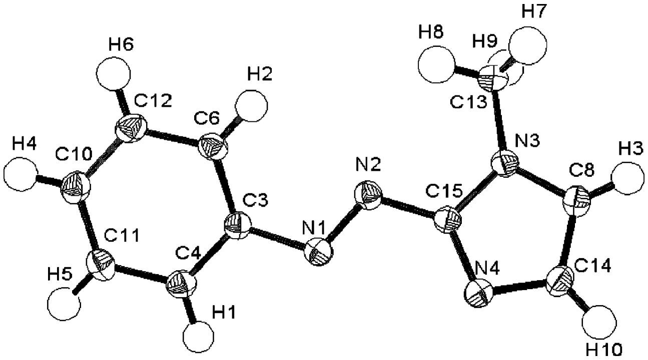

Figure 1. Crystal structure of Pai-Me, showing 50% probability ellipsoids.

TABLE 3: Absorption Features of Trans-Isomers in Toluene

	λ_{max}/nm (ϵ/M^{-1} cm^{-1})
azobenzene	320 (20700), 435 (490)
Pai-H	362 (18000), ∼450[a] (960)
Pai-Me	363 (17000), ∼450[a] (1260)

[a] Tail of the $\pi\pi^*$ band.

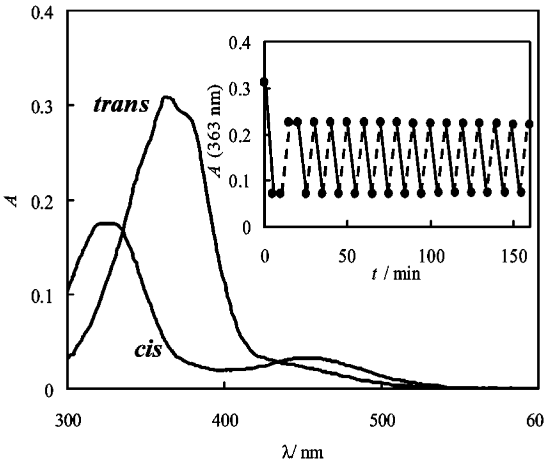

Figure 2. Absorption spectra for *cis*- and *trans*-Pai-Me (16.7 μM) in toluene at 25 °C. Inset: Absorbance changes at 363 nm upon repeated irradiation at 363 (solid lines) and 454 nm (dashed lines).

Absorption Spectra and Photochromism. Absorption spectrum for *trans*-azobenzene is characterized by a large $\pi\pi^*$ absorption band peaking at 320 nm and a small nπ^* band around 435 nm (see Table 3).[1] These bands correspond to the S2 and S1 excitations, respectively. Absorption spectra for Pai-H and Pai-Me are quite similar. The large absorption band appears at ∼360 nm, red-shifted by 40 nm from that of azobenzene. There is a low intensity tail to the lower energy side of this main band, which may well be attributed to the nπ^* transition. This is in contrast to the case of azobenzene for which the $\pi\pi^*$ and nπ^* bands are well-separated. Indeed, molecular orbital calculations by density functional theory (DFT) show that the energies of the highest π-orbital and azo n-orbital are much closer than those of azobenzene, as will be discussed in a later section.

As shown in Figure 2, the absorption spectrum of *trans*-Pai-Me in toluene changed with isosbestic points (333 and 431 nm) upon 363 nm excitation in the characteristic manner for the trans-to-cis isomerization of azo compounds,[1] indicating that excitation into the $\pi\pi^*$ band by light resulted in a clean conversion into the cis-isomer, reaching a cis-rich photostationary state. ^{1}H NMR was used to measure the content of trans and cis isomers in an irradiated $CDCl_3$ solution of Pai-Me. Then, an aliquot was taken, diluted by toluene, and its absorption spectrum was recorded. It was found from these data that a

TABLE 4: Activation Parameters for Cis-to-Trans Thermal Isomerization in Toluene

	E_a/kJ mol^{-1}	log A^c	ΔG^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
azobenzene[a]	94.2	10.9	105	−44.6
Pai-Me[b]	79.0(3.5)	9.2(0.6)	100(5)	−77.1(11.6)

[a] Reference 24. [b] Standard deviations are given in parentheses. [c] A is given in s^{-1}.

nearly complete conversion to the cis form (>98%) was attained under the photostationary state with 363 nm light irradiation. Subsequent 454 nm irradiation reversed the course of the reaction and another trans-rich photostationary state was established. Repeated irradiation showed little sign of degradation at least up to 15 cycles (trans contents between 10 and 70%), as shown in the inset of Figure 2. Similar spectral changes were also observed in hexane, acetonitrile, and ethanol.

On the other hand, Pai-H showed very sluggish changes, if at all, under the same irradiation conditions. This should be, in principle, due to a low quantum yield of the trans-to-cis photoisomerization and/or a fast thermal cis-to-trans back-reaction. Although the photoisomerization quantum yield cannot be measured, we measured the thermal cis-to-trans isomerization rate of Pai-H, and we found that this rate is indeed much faster than that of Pai-Me. Thus, the fast cis-to-trans isomerization shifts the photostationary state significantly toward a trans-rich state under our irradiation conditions, explaining, at least partially, the poor conversion to the cis isomer. The thermal reaction will be discussed in detail in the following section.

The quantum yields for the trans-to-cis photoisomerization of azobenzene through the S1 and S2 excitations differ: in nonpolar solvents, $\phi = \sim 0.25$ and ~ 0.1, respectively.[47,48] This apparent violation of Kasha's rule has been causing much controversy about its origin and the mechanism of photoisomerization. We have measured quantum yields for the trans-to-cis photoisomerization of Pai-Me in toluene on two different irradiation wavelengths, i.e., 454 and 355 nm. The yields were obtained as $\phi = 0.35 \pm 0.03$ and 0.25 ± 0.03 on 454 and 355 nm excitations, respectively. Important points in these results are that (1) the quantum yield depends on the excitation wavelength for Pai-Me, as is the case for azobenzene, and (2) these quantum yields are significantly higher than those for azobenzene. The wavelength-dependent isomerization yield implies that the excited Pai-Me is subjected to dual relaxation pathways similar to the ones that are operative for azobenzene.[2−9]

According to Majima et al.,[44] the quantum yields for the trans-to-cis photoisomerization of 1-*N*-(deoxy)ribofuranosyl derivatives of Pai-H on S2 excitation are 0.06−0.08 in methanol, and they concluded that the photoisomerization efficiency of these compounds is lower than that of azobenzene. It may be possible that the (deoxy)ribofuranosyl substituent is detrimental to the photoisomerization in some way. Another possibility of the discrepancy is the difference in the solvents used (methanol vs toluene).

Thermal Cis-to-Trans Isomerization. Thermal cis-to-trans isomerization of Pai-Me was followed by UV−vis spectroscopy in toluene at varied temperatures. At 25 °C, the rate constant was found to be $k = 2.2 \times 10^{-5}$ s^{-1}. The Arrhenius plot in the range from 10 to 50 °C gave a linear relationship, from which the activation energy was obtained as $E_a = 79.0 \pm 3.5$ kJ mol^{-1}. This value is substantially lower than that of azobenzene (94.2 kJ mol^{-1}).[24] Activation parameters are compared with those for azobenzene[24] in Table 4. It is noted that the faster cis-to-trans thermal isomerization of Pai-Me compared to azobenzene is due to a lower enthalpy factor, since the activation entropy is of a larger negative value.

The exact cis-to-trans thermal parameters for Pai-H could not be obtained, due to the low yield of cis-isomer. However, it was found that the estimated isomerization rate (1.0×10^{-2} s^{-1} at 25 °C) was 420 times larger than that of Pai-Me by following the dark reaction of a partially cis-containing solution.

A few possibilities have been considered as the reasons for the fast cis-to-trans thermal isomerization of Pai-H, although no conclusion can be drawn at present. The effect of imidazole-*NH* on isomerization was investigated, since Lewis acids significantly lowers the cis-to-trans isomerization barrier of azobenzene compounds.[5,24] We reasoned that if imidazole-*NH* worked as a Lewis acid and facilitated cis-to-trans thermal isomerization of Pai-H, the same effect would also be exerted on Pai-Me. Thus, we prepared a mixed solution of Pai-H and Pai-Me in toluene (0.1 mM each). Then, the solution was illuminated at the $\pi\pi^*$ band to see if the presence of imidazole-*NH* retards the photoisomerization of Pai-Me by facilitating thermal cis-to-trans reverse reaction. Pai-Me in the mixed solution, however, isomerized at nearly the same rate with that in a pure Pai-Me solution. Therefore, the notion that the imidazole-*NH* might be responsible through an intermolecular manner for the fast thermal isomerization of Pai-H can be excluded.

Pai-H could, in principle, adopt the proton-displaced hydrazone-type tautomer, in which the imidazole-N*H* is moved to one of the azo-*N*'s adjacent to the phenyl ring and the linkage between the azo nitrogens is a single bond. In this form, thermal back conversion to the trans form should be facile. At least for the trans isomer, however, the hydrazone form is unlikely, since the double bond character of the N═N linkage in Pai-H is about the same as that in Pai-Me, as revealed by the similarity in their bond lengths in the crystal.[45] In addition, spectroscopic studies in the UV−visible range indicated that *trans*-Pai-H exists in the azo form also in solution.[49] Still, the hydrazone form could play a role in the cis isomer and/or in the transition state.

DFT Calculations. DFT calculations were carried out for azobenzene, Pai-H, and Pai-Me to shed light on their properties from a theoretical point of view. Generalized gradient approximation with B88[50] and LYP[51] potentials for the exchange and correlation terms, respectively, and the DZVP basis set were used. Structure optimization was first conducted for trans and cis isomers (see Supporting Information for detailed results). The calculations tend to give an only slightly longer N═N double bond in the trans isomers than those in the crystal structures by 0.03−0.04 Å. There are two minimum energy conformations for each isomer, related by a 180°-flip about the C(imidazole)−N(azo) bond, due to the asymmetry of the imidazole ring about the axis through this bond. For *trans*-Pai-H, one of the conformers, that is, one that is found in the crystal, is more stable than the other by 12.3 kJ mol^{-1}. For the two conformations of *trans*-Pai-Me, the lowest energy conformation is the one not found in the crystal, but the two conformers are almost isoenergetic, within 0.6 kJ mol^{-1}. For the two conformations in the cis-isomer, the one with the imidazole-*NH* or imidazole-*NMe* being away from the phenyl group is more stable by 10 and 20 kJ mol^{-1}, for Pai-H and Pai-Me, respectively. This is consistent with our observation that no nuclear Overhauser effect is detected between the methyl protons and any of the phenyl protons in the ^{1}H NMR spectrum for the *cis*-Pai-Me.

The frontier molecular orbitals of Pai-H and Pai-Me are shown in Figure 3 along with the orbital energies. The orbital

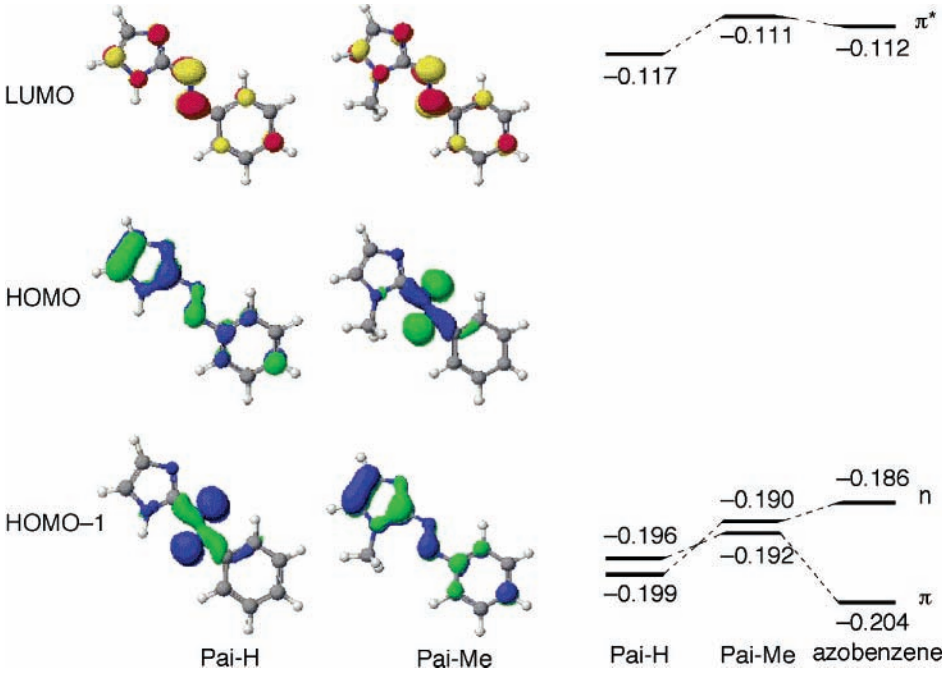

Figure 3. Frontier molecular orbitals of Pai-H and Pai-Me. The orbital energies are compared with those of azobenzene in the diagram. Orbitals of similar symmetries are related by dotted lines. Orbital energy values are given in hartrees.

energies of azobenzene are also included for comparison purposes. The most notable difference between the orbitals of azoimidazoles and those of azobenzene is in the energy gap between the azo n-orbital and the highest π-orbital. The energy gap for azobenzene is 0.018 hartree, whereas it is as small as 0.002−0.003 hartree for azoimidazoles. On the other hand, the symmetries of these frontier orbitals of azoimidazoles are quite similar to those of azobenzene, regardless of the replacement of a phenyl ring by an imidazole moiety. Dissymmetry is only reflected in the higher unoccupied orbitals and in the lower occupied orbitals.

The Effect of Metal Ions. Imidazole is a good Lewis base to coordinate to metal ions. Azo nitrogens can also participate in coordination. In fact, a number of coordination compounds involving phenylazoimidazole derivatives as ligands have been prepared.[31−43] To investigate possible modulation of photochromes by metal ions,[10] we carried out a preliminary investigation of the effect of added metal ions ($ZnCl_2$, $AgClO_4$, and $CuCl_2{\cdot}2H_2O$) on the photochromic behavior of Pai-Me. The absorption spectra and responses to illumination were examined for 0.1 mM Pai-Me in the presence of 0.3 mM metal ion in methanol solutions. The results are displayed in Figure 4.

In the presence of Zn(II),[31,32] the absorption spectrum of Pai-Me was only slightly modified, as shown in Figure 4a, although it is known that Pai-Me and $ZnCl_2$ form a chelate complex of the composition of $Zn(Pai\text{-}Me)Cl_2{\cdot}H_2O$.[31] The $\pi\pi^*$ band intensity is somewhat lowered, while the absorbance around 430 nm is increased. In contrast, in the presence of Ag(I)[35−37,41] and Cu(II),[33] the $\pi\pi^*$ band showed a red shift by ∼10 nm as shown in Figure 4, parts b and c. The composition of the Ag(I) complex is $Ag(Pai\text{-}Me)_2$.[35,36] The crystal structure of a related complex, bis[1-ethyl-2-(naphthyl-α-azo)imidazole]silver(I) perchlorate shows that both of the imidazole-*N* and the azo-*N* make coordination bonds to form a chelate complex, although the latter bond length (2.85 Å) is much longer than the former (2.12 Å).[37] Cu(II) also forms a chelate complex with Pai-Me.[33] These solutions of metal complexes were illuminated at the $\pi\pi^*$ peak. Pai-Me isomerized into the cis-form upon illumination in the presence of these metal ions, as shown in the figures. Subsequent illumination at 454 nm reversed the course of the reaction, and the content of trans isomer increased again. These experiments show that the modulation of absorption spectra is possible simply by adding a metal ion without a loss

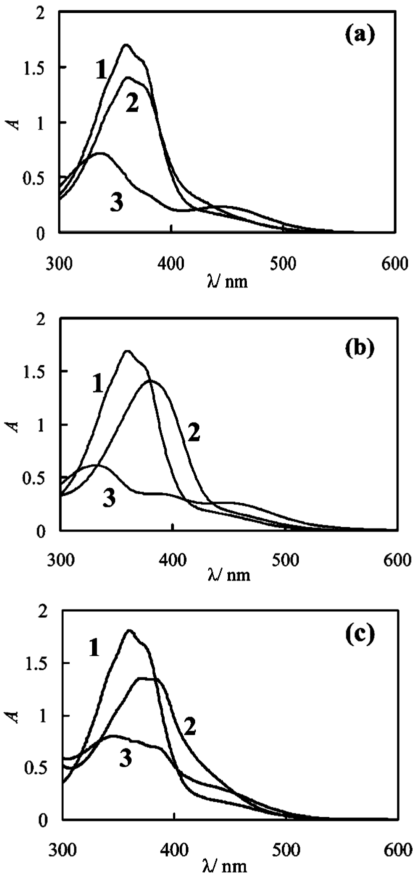

Figure 4. Effect of added metal ions (0.3 mM) on the photochromism of Pai-Me (0.1 mM) in methanol at 25 °C. Spectra for (1) Pai-Me only, (2) Pai-Me plus ion, and (3) Pai-Me plus ion illuminated at the $\pi\pi^*$ λ_{max} for 10 min: (a) $ZnCl_2$, (b) $AgClO_4$, and (c) $CuCl_2{\cdot}2H_2O$.

of the gross photochromic behavior. These preliminary data bode well for the development of photoswitches using azoimidazole derivatives in coordination chemistry.

Conclusion

In this study, we have investigated the isomerization behaviors of 2-(phenylazo)imidazoles, i.e., Pai-H and Pai-Me. It has become clear from this study that this class of compounds are well-behaved photochromes. This is of particular interest in that these compounds have sites for coordination (imidazole-*N* in addition to azo-*N*'s) and hydrogen bonding (imidazole-*N* and -*NH*, in addition to azo-*N*'s) interactions. We anticipate that photoresponsive molecular devices will be developed from these promising materials.

This study has also produced new questions to be solved. The quantum yields for the trans-to-cis photoisomerization were found to depend on the excitation wavelength. This seems to imply an underlying mechanism common to that of azobenzene. However, the values of these quantum yields are substantially higher than those of azobenzene. The thermal cis-to-trans isomerization rate of Pai-Me was found to be substantially faster than that of azobenzene, and this is more so for Pai-H. Further experimental and theoretical studies may be required to clarify these issues.

Experimental Section

Materials. Pai-H[52] and Pai-Me[35,38] were prepared and purified according to previously published procedures. Spectroscopic grade toluene and methanol were purchased from Wako Chemical. Toluene was distilled from Na prior to use, while methanol was used as received. Metal salts were purchased from Kanto Chemical, and were used as received.

X-ray Crystallography. The single crystals of Pai-Me suitable for X-ray analysis were obtained from a hexane solution being allowed to evaporate slowly. Crystallographic data were collected by a MAC Science DIP-Labo imaging plate system using Cu Kα radiation ($\lambda = 1.54180$ Å). All structures were solved by the direct method and refined by full matrix least squares on F^2 by SHELX-97.[53] The measurement was carried out at 120 K.

Spectroscopic and Isomerization Studies. Absorption spectra were taken with a Shimadzu UV-2400PC spectrometer in a 1 × 1 cm quartz optical cell maintained at 25 °C with a Peltier thermostat. The light source of a Shimadzu RF-5300PC fluorimeter was used as an excitation light, with a slit width of 5 nm. An optical filter was used to cut off overtones when necessary. The absorption spectrum of *cis*-Pai-Me was obtained by extrapolation of the absorption spectrum of a cis-rich mixture for which the composition is known from ^{1}H NMR integration. Quantum yields (ϕ) were obtained by measuring initial trans-to-cis isomerization rates (υ) in a well-stirred solution within the above instrument using the equation,

$$\upsilon = (\phi I_0/V)(1 - 10^{-\mathrm{Abs}})$$

where I_0 is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial absorbance at the irradiation wavelength. The value of I_0 was obtained by using azobenzene ($\phi = 0.11$ and 0.24 for $\pi\pi^*$ and $n\pi^*$ excitations, respectively[47]) under the same irradiation conditions.

The thermal cis-to-trans isomerization rates were obtained by monitoring absorption changes intermittently for a cis-rich solution kept in the dark at constant temperatures in the range from 10 to 50 °C. The activation energy (E_a) and the frequency factor (A) were obtained from the Arrhenius plot,

$$\ln k = \ln A - E_a/RT$$

where k is the measured rate constant, R is the gas constant, and T is temperature. The values of activation free energy (ΔG^*) and activation entropy (ΔS^*) were obtained through the relationships,

$$\Delta G^* = E_a - R\,T - T\Delta S^*$$

and

$$\Delta S^* = [\ln A - 1 - \ln(k_B T/h)]R$$

where k_B and h are Boltzmann's and Planck's constants, respectively.[24]

DFT Calculations. DFT calculations were performed using the DGauss code[54] implemented in a commercial CAChe package. Generalized gradient approximation with B88[50] and LYP[51] potentials for exchange and correlation terms, respectively, and the DZVP basis set were used.

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Supporting Information Available: The crystallographic data for Pai-Me in CIF format and the results of DFT calculations for Pai-H and Pai-Me, including figures of optimized structures and tables of energies and selected geometric values and coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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