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Role of Solvent and Effect of Substituent on Azobenzene Isomerization by Using Room-Temperature Ionic Liquids as Reaction Media

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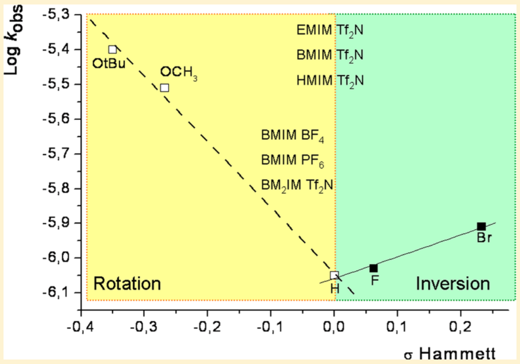
S *Supporting Information*

ABSTRACT: The effects of a *para* substituent, as the electron-donating $-OCH_3$ and $-OtBu$ groups and the electron-withdrawing $-Br$ and $-F$ atoms, on azobenzene isomerization have been investigated in a series of imidazolium ionic liquids (BMIM PF_6, BMIM BF_4, BMIM Tf_2N, EMIM Tf_2N, BM_2IM Tf_2N, and HMIM Tf_2N). The thermal *cis*−*trans* conversion tends to be improved in the presence of the substituent, as pointed out by the first-order rate constants measured at 25 °C. Both the rotation and the inversion mechanisms occur in BMIM Tf_2N, EMIM Tf_2N, and HMIM Tf_2N, as highlighted by typical V-shape Hammett plots, but only rotation takes place in BMIM PF_6, BMIM BF_4, and BM_2IM Tf_2N. The possible interactions between the cation and the anion of the solvent and both the isomers of the azobenzene derivatives have been studied by small-wide-angle X-ray scattering (SWAXS). The calculated *cis* population in the photostationary state and the hardness parameter η of the *trans* isomer show that azobenzene and F-azobenzene are the less reactive molecules for the *trans*−*cis* conversion in all the investigated ionic liquids.



1. INTRODUCTION

Since Hartley's identification[1] of the *cis* isomer in 1937, the azobenzene molecule has been widely studied and successfully employed as a component of a large variety of systems, such as molecular devices,[2,3] surface-modified materials,[4,5] and light-sensitive biomolecules.[6,7] The *trans*−*cis* isomerization can be induced by UV irradiation[8] and electrostatic[9] and mechanical stress[10] leading to typical changes in the spectroscopic properties of azobenzene.[11] The thermal *cis*−*trans* conversion takes place spontaneously in the dark due to the higher stability of the *trans* isomer.[12] The mechanism by which the reaction occurs is not yet unequivocally established since competition between rotation and inversion has been proposed.[13−15] Generally, the solvent properties, including polarity and viscosity, and the presence of substituents could promote one mechanism over the other[16−19] so that azobenzene and derivatives find many applications as kinetic or spectroscopic probes in organic solvents[20−22] and aqueous solutions.[23−25] Room-temperature ionic liquids (RTILs) have attracted much attention in the last years for their unique properties[26] and their potential high recyclability.[27,28] RTILs can be considered as designer solvents due to the possibility to change the cation or the anion in a wide range of combinations to induce strong changes in density, viscosity, melting point, and water miscibility.[29] Furthermore, different solute−solvent interactions take place by using RTILs as reaction media since both the cation and the anion can be involved.[30] The effect of the solvent on the kinetics and the dynamics of azobenzene isomerization has been widely investigated,[31−33] but to the best of our knowledge, the most recent studies in ionic liquids have concerned push−pull derivatives or a functionalized azobenzene moiety.[34−36] The aim of this work has been the evaluation of the effect induced by one electron-donating or -withdrawing substituent ($-OCH_3$, $-OtBu$, $-Br$, and $-F$) in the *para* position on the azobenzene isomerization by using a $BMIM^+/Tf_2N^-$-based RTIL as solvent to highlight the role of the cation and the anion in the reaction. The structure of the investigated azobenzenes and RTILs are reported in Figure 1.

2. RESULTS AND DISCUSSION

It was assumed that the thermodynamically stable *trans* was the dominant isomer in the azobenzene solution before irradiation.[37,38] The spectral changes induced by the exposition to UV light in BMIM Tf_2N are shown in Figure 2 as an example.

The kinetic profile of the thermal *cis*−*trans* isomerization follows a first-order decay, and the first-order rate constants k_{obs} determined at 25 ± 0.1 °C for the investigated azobenzenes in

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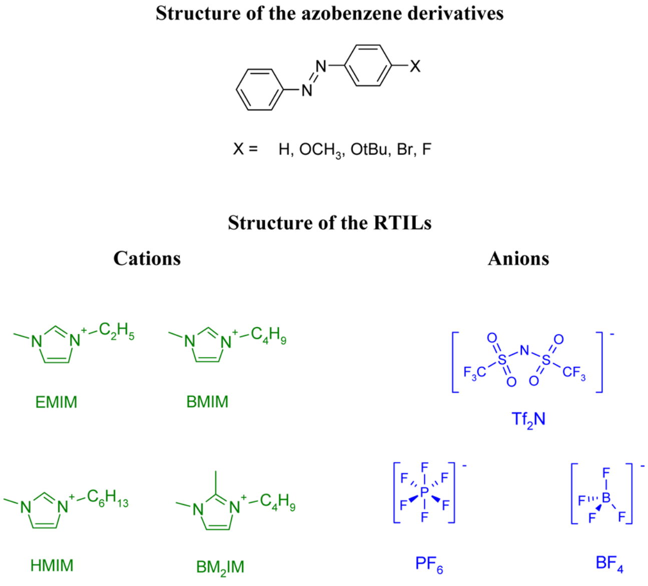

Figure 1. Structures of the investigated azobenzenes and RTILs.

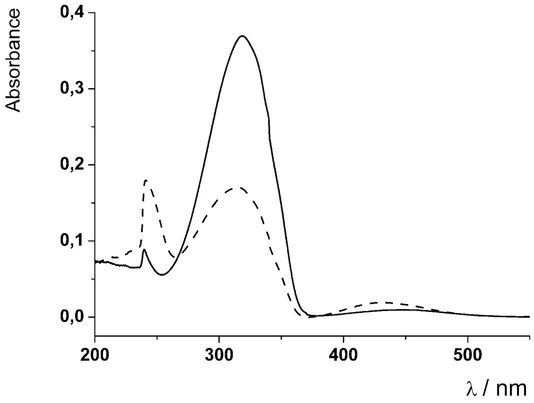

Figure 2. UV−vis spectra of azobenzene in BMIM Tf_2N before (solid line) and after (dash line) UV irradiation.

the ionic liquids are reported in Table 1. Each value corresponds to the mean between at least three different determinations.

The presence of a substituent and its position in the molecule can strongly influence kinetically and thermodynamically a large variety of reactions.[39−45] The electronic properties of an atom or a group are quantified by the Hammett constant σ values.[46] It is well-known[47−49] that the electron-donating groups promote the rotation mechanism for the *cis*−*trans* azobenzene isomerization, while the electron-withdrawing groups favor the inversion pathway. Typical V-shaped Hammett plots have been obtained in EMIM Tf_2N, HMIM Tf_2N, and BMIM Tf_2N, suggesting the coexistence of both the mechanisms, but linear plots have been determined in BMIM BF_4, BMIM PF_6, and BM_2IM Tf_2N, showing that only rotation takes place. The Hammett plots in EMIM Tf_2N and BMIM BF_4 are reported in Figure 3 as examples.

Cimiraglia and co-workers[13] have highlighted that in the case of 4-monosubstitued azobenzenes with an electron-withdrawing substituent the nitrogen atom connected with the substituted phenyl ring is involved in the rehybridation and the inversion occurs by a perpendicular displacement of the substituted ring to the azo bond. In the *cis* isomer the phenyl rings are twisted of about 53° because of steric reasons, but the electron-withdrawing substituents increase the torsion angle by the conjugation between the nitrogen lone-pair and the substituted phenyl ring. Since translational movements are limited in ionic liquids[50] rotation becomes the dominant pathway for the *cis*−*trans* isomerization.[34,36] The high viscosity[51] of BMIM BF_4, BMIM PF_6, and BM_2IM Tf_2N (103.8, 273.0, and 115.2 mPa·s, respectively) in comparison to BMIM Tf_2N (50.9 mPa·s), EMIM Tf_2N (32.0 mPa·s), and HMIM Tf_2N (68.0 mPa·s) may explain the change of mechanism from inversion to rotation in the case of Br- and F-azobenzene. Moreover, higher k_{obs} values for F-azobenzene than Br-azobenzene have been measured in the RTILs in which only the rotation mechanism occurs (Table 1), suggesting a higher efficacy for the more electronegative atom to stabilize the dipolar transition state of the reaction. Since rotation is the prevalent mechanism in polar solvents, while inversion generally occurs in nonpolar media,[52−54] BMIM BF_4, BMIM PF_6, and BM_2IM Tf_2N seem to act as polar solvents in comparison to BMIM Tf_2N, EMIM Tf_2N, and HMIM Tf_2N.

Even if the reaction mechanism can be influenced by viscosity and polarity, the solvent properties seem to have no effect on the thermal isomerization rate.[55] The conversion of the *cis* into the *trans* isomer of the investigated azobenzenes is faster in the ionic liquids in comparison to methanol and ethanol.[25] High values of k_{obs} have been obtained in the presence of $-OCH_3$ and −OtBu (Table 1), in agreement with the higher stabilization of the polar transition state generated in the rotation mechanism.[20,56] Furthermore, this charged transition state is promoted in BMIM BF_4, as suggested by the increasing of the k_{obs} values of the alkoxy derivatives from 3 up to 14 times in comparison to BMIM Tf_2N and BMIM PF_6. This effect is probably due to the properties of the BF_4^- anion, as the lower dispersion charge, the higher Kamlet−Taft β value,[57] and the smaller van der Waals radius[58] than Tf_2N^- and PF_6^-.

Previous studies[59] about the structural organization of imidazolium ionic liquids have demonstrated an extended connection between anions and cations through the formation of hydrogen bonds. SWAXS spectra of EMIM Tf_2N and BMIM BF_4 in the presence of Br- and OCH_3-azobenzene before and after UV irradiation show that the *q* position of the peaks seems

Table 1. First-Order Rate Constants for the *Cis*−*Trans* Isomerization of the Investigated Azobenzenes at 25 ± 0.1 °C

	k_{obs} (10^{-6} s^{-1})					
para-substituent	HMIM Tf_2N	BM_2IM Tf_2N	EMIM Tf_2N	BMIM Tf_2N	BMIM PF_6	BMIM BF_4
H	2.75 ± 0.1	2.76 ± 0.3	0.89 ± 0.2	3.02 ± 1.2	0.98 ± 0.1	14.2 ± 0.2
OCH_3	4.16 ± 0.3	3.12 ± 1.2	3.08 ± 0.3	4.19 ± 0.7	6.83 ± 0.1	22.7 ± 0.1
OtBu	3.54 ± 0.1	3.89 ± 0.1	3.98 ± 0.1	3.70 ± 0.1	4.78 ± 0.1	35.7 ± 0.3
Br	2.69 ± 0.1	1.61 ± 0.1	1.23 ± 0.1	3.36 ± 0.1	1.37 ± 0.1	5.55 ± 0.1
F	0.72 ± 0.3	1.70 ± 0.1	0.93 ± 0.9	1.99 ± 0.1	2.00 ± 0.1	11.0 ± 0.1

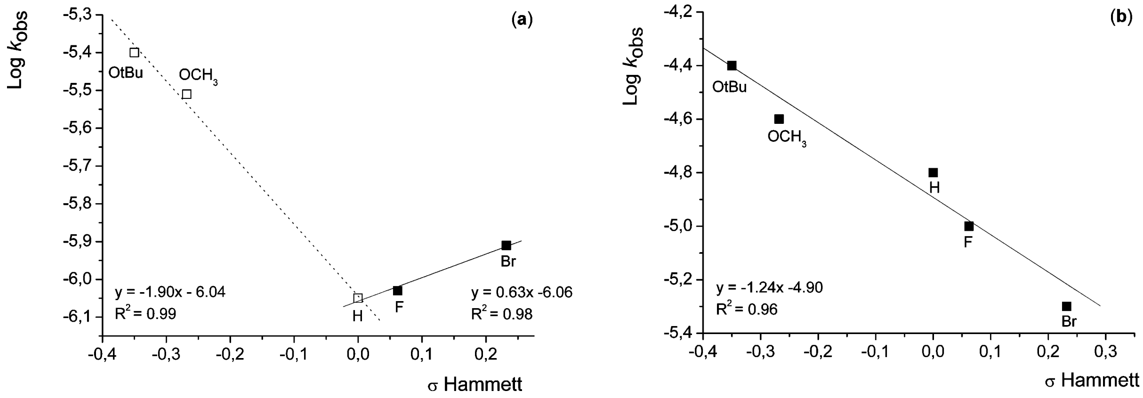

Figure 3. Hammett plots in EMIM Tf_2N (a) and BMIM BF_4 (b).

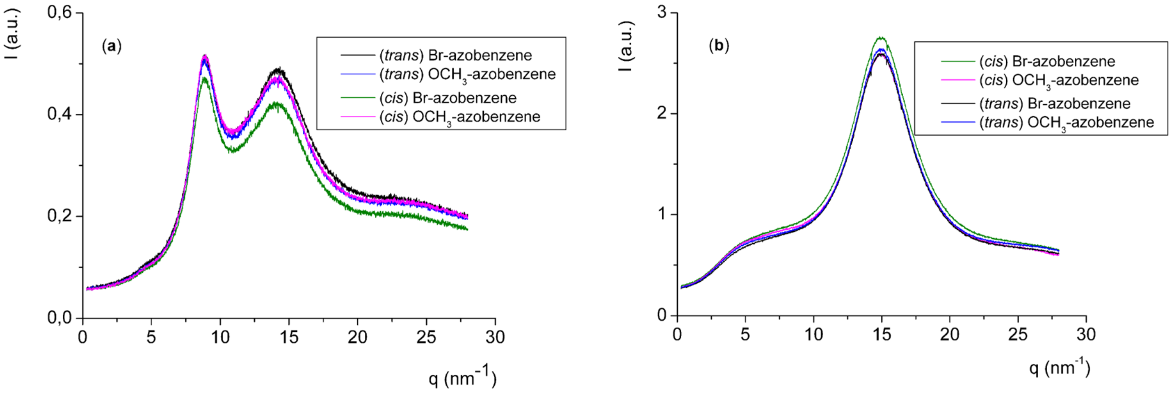

Figure 4. SWAXS spectra for Br- and OCH_3-azobenzene isomers at 3 × 10^{-5} M in EMIM Tf_2N (a) and BMIM BF_4 (b).

Table 2. Hardness Parameter (eV) of the *Trans* Isomer and *Cis* Population after UV Irradiation in the Different Ionic Liquids

		cis isomer population (%)					
η_{trans}	*para*-substituent	HMIM Tf_2N	BM_2IM Tf_2N	EMIM Tf_2N	BMIM Tf_2N	BMIM PF_6	BMIM BF_4
1.98	H	49.4 ± 2	41.2 ± 4	55.1 ± 2	53.5 ± 1	60.7 ± 4	78.8 ± 2
1.86	OCH_3	93.8 ± 1	67.8 ± 6	96.1 ± 3	84.9 ± 9	97.4 ± 2	94.8 ± 2
1.93	OtBu	62.8 ± 4	81.8 ± 1	84.6 ± 1	91.2 ± 1	91.3 ± 5	85.9 ± 2
1.93	Br	80.8 ± 1	77.4 ± 2	81.4 ± 1	76.9 ± 1	86.8 ± 1	98.1 ± 2
1.97	F	58.4 ± 2	65.3 ± 1	63.4 ± 1	60.9 ± 2	61.7 ± 2	69.9 ± 1

to be not affected by the azobenzenes at the investigated concentrations, suggesting that the structural network of cations and anions of the RTILs is retained (Figure 4).

The rate of the thermal isomerization is independent of the initial concentration of the *cis* isomer in solution,[60] but the solvent and the nature of the substituents could influence the amount of the *cis* azobenzene formed by irradiation.[19,61] The reactivity of the *trans* isomer to form the less stable *cis* by UV irradiation can be related to the η value. Generally, a higher η corresponds to a less reactive system.[62,63] The *cis* population in the photostationary state obtained by using eq 1 and the hardness parameter η of the *trans* isomer for the investigated azobenzenes are reported in Table 2.

The formation of the *cis* isomer is strongly favored in the presence of the substituent in all the RTILs. The amount of the *cis* isomer of azobenzene increases from 49.4% in HMIM Tf_2N and 60.7% in BMIM PF_6 up to 93.8% and 97.4%, respectively, in the presence of the methoxy group.

The azobenzene molecule (X = H) is the less reactive system, as confirmed by the highest η, while the OCH_3-azobenzene derivate is the most reactive between the derivatives, as confirmed by the lowest η. Interestingly, F-azobenzene is the system closer to azobenzene for *cis* population and η value, suggesting a similar low reactivity in the *trans*−*cis* conversion.

3. CONCLUSIONS

Both rotation and inversion take place for the *cis*−*trans* azobenzene isomerization in BMIM Tf_2N, EMIM Tf_2N, and HMIM Tf_2N, according to the electronic nature of the substituent. A change of mechanism from inversion to rotation has been observed for Br- and F-azobenzene in BMIM BF_4, BMIM PF_6, and BM_2IM Tf_2N, according to the viscosity of the solvent. The structural organization of cations and anions seems to be not affected by the presence of the azobenzene isomers as suggested by SWAXS measurements. The *cis* population of the azobenzene derivatives increases in the photostationary state and the calculated η values of the *trans* isomer suggest that OCH_3-azobenzene is the most reactive system of the investigated molecules for the *trans*−*cis* conversion. The azobenzene isomerization still represents a model reaction and the results presented herein could contribute to the understanding and the improving of RTILs as reaction media.

4. EXPERIMENTAL SECTION

General Information. Azobenzene and ethanol (99% spectroscopy grade) were purchased from Fluka and used without further purification; *p*-OCH_3-azobenzene, *p*-OtBu-azobenzene, *p*-Br-azobenzene and *p*-F-azobenzene were obtained as previously described.[64] BMIM Tf_2N (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), BMIM PF_6 (1-butyl-3-methylimidazolium hexafluorophosphate), BMIM BF_4 (1-butyl-3-methylimidazolium tetrafluoroborate), EMIM Tf_2N (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), BM_2IM Tf_2N (1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide) and HMIM Tf_2N (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) were purchased from IoLiTec and Solvionics and stirred under vacuum at 60 °C overnight before the preparation of the samples.

Sample Preparation for the Kinetics Measurements. Stock ethanol solutions from the investigated azobenzenes were prepared at a concentration of 2.6×10^{-3} M and kept in the dark at room temperature at least for 4 days before use. Then, an appropriate amount was transferred into a 1 cm light pass quartz cuvette containing 200 μL of the proper ionic liquid to obtain a final concentration of 2.6×10^{-5} M. The sample was irradiated for 45 min by using a Hg−Xe arc lamp (150 W) equipped with a band-pass interference filter centered at 365.0 +2/-0 nm wavelength and 10.0 +2/-2 nm bandwidth: the spectral changes, as the decreasing of the high-intensity absorption band centered in the wavelength range 315−349 nm (depending both on the substituent and the solvent) and the increasing of the low-intensity band at about 440 nm (due to an $n \rightarrow \pi^*$ transition) were used as evidence for the *trans*−*cis* isomerization. The first-order rate constants k_{obs} were spectrophotometrically calculated by monitoring in the dark the absorption change at or near the absorption maximum of the *trans* isomer over a period of about 24 h.

Determination of the *Cis* Population and the Hardness Parameter. The *cis* population in the photostationary state formed by UV irradiation was calculated as follows[61]

$$\%\ cis = 100(A_{trans} - A_{trans(i)})/A_{trans} \qquad (1)$$

where A_{trans} and $A_{trans(i)}$ are the absorbance of the *trans* isomer before and after the irradiation, respectively. The hardness parameter η values were calculated from the HOMO and LUMO energies[62] of the *trans* isomers by using DFT (B3LYP/6-31G**).

SWAXS Analysis. Small-wide-angle X-ray scattering (SWAXS) experiments were performed by using an instrument with a line collimation setup. The system used a Cu Kα radiation source in a sealed tube (λ = 0.1542 nm) working at 40 kV and 50 mA. The system is equipped with a translucent beam stop, which allows the determination of the $q = 0$ position by the direct measurement of an attenuated primary beam. The scattering signals were acquired on a sensitive SWAXS imaging plate slide as a detector (q range 0.28−28 nm^{-1}). In that configuration, the distance sample−detector is of 261.2 nm. The samples at 3×10^{-5} and 3×10^{-2} M azobenzene concentrations were introduced into a quartz capillary with a diameter of 1 mm and a sealed special glass capillary with a diameter of 1.5 mm, respectively. The scattering signals were collected over 30 min under vacuum at room temperature and treated with SAXSquant software. All data were corrected for the background scattering from the empty cell and for slit-smearing effects by a desmearing procedure using the Lake method.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Hammett plots in the RTILs, HOMO and LUMO energies of the *trans* isomers used for the determination of η, additional SWAXS spectra, and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00898.

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Notes

The authors declare no competing financial interest.

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