Trans-cis isomerization energies of azopyridines: A calorimetric and computational study

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ABSTRACT. Azobenzenes undergo reversible trans-cis photo-isomerization and have been studied extensively as photo-responsive materials. Despite their similar photochemistry, azopyridines have received relatively little attention; for example, their isomerization energies are presently unknown. In comparison to azobenzenes, azopyridines offer additional opportunities for materials design through hydrogen bonding and coordination chemistry. Here we report the isomerization energies for all 3 symmetrical azopyridines (i.e. the 2,2'-, 3,3'- and 4,4'-isomers) through a combined experimental and computational study. Heat of isomerization was measured in the liquid state, with *o*-terphenyl introduced to suppress crystallization. We obtain ΔE_{iso} = 25.2±0.6 kJ mol^{-1}, 42.6±0.6 kJ mol^{-1}, and 35.0±1.8 kJ mol^{-1} for 2,2', 3,3' and 4,4'-azopyridine, respectively. For azobenzene, we obtain ΔE_{iso} = 47.0±1.3 kJ mol^{-1}, in agreement with the literature value and validating our method. Theoretical calculations yielded gas-phase ΔE_{iso} in reasonable agreement with experiment, and explain the low isomerization energy of 2,2'-azopyridine on the basis of a low-energy cis conformer. Because of the smaller van der Waals volume of the pyridine N relative to the phenyl CH, the two aromatic rings in the cis isomer can approach closer to co-planarity, leading to greater π-conjugation and lower conformational energy.

Keywords: Photochemistry, isomerization energy, DSC, ab initio

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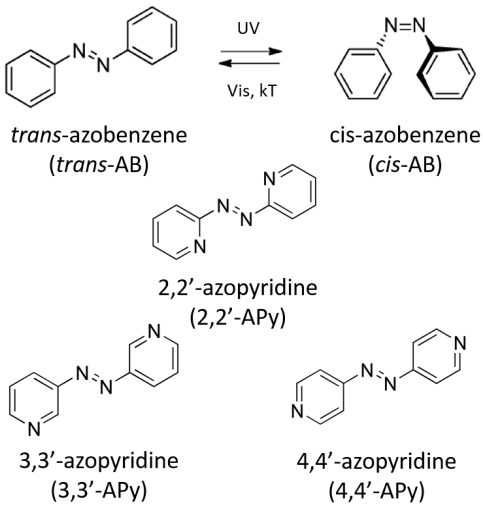
INTRODUCTION

For nearly a century, azobenzene and its derivatives have been studied because of their reversible photo-induced trans-cis isomerization and for applications as photo-responsive materials [1,2,3]. Upon irradiation, the trans isomer of azobenzene converts to the cis (Scheme 1). This reaction is reversible on storage in the dark or upon irradiation at a different wavelength. This isomerization reaction causes large changes in physical properties; for example, dipole moment (from 0 D to 3.08 D) [4] and energy (increase by 47 kJ mol^{-1}) [5]. It is possible to cycle the system many times with little fatigue and chemical decomposition, suggesting applications as durable materials. Azobenzene-based materials have been explored as molecular machines [6], data storage media [7], and protein switches [8].

Azopyridines have similar structures as azobenzenes and similar photochemistry [9], but have to date received less attention. From the standpoint of materials design, the pyridyl group offers additional control of molecular packing through hydrogen bonding and coordination chemistry. Zhao and coworkers [10] have demonstrated that azopyridine-containing polymers assemble with aliphatic and aromatic carboxylic acids to create photo-responsive liquid crystals, whose smectic/isotropic transition temperature is tunable by light. Photo-controlled swelling-shrinking are reported for the micro vesicles of an azopyridine amphiphilic polymer [11]. Similar vesicles formed by a poly(ethylene oxide)-polymethacrylate-azopyridine copolymer undergo rapid disintegration and fusion under UV irradiation, with potential use for controlled release [12]. Certain azopyridines self-assemble into nano-fibers whose length can be reduced by an order of magnitude under UV light [13]. A common ligand in coordination chemistry [14], azopyridines can be organized by metal coordination to produce MRI agents whose contrast is tunable by light [15].

Despite the potential of azopyridine-based materials, the current understanding of their photochemistry remains limited. To our knowledge, there has been no report on the isomerization energies of azopyridines, a fundamental parameter for materials design. This missing information is in contrast to the detailed characterization of azobenzene systems. In this study, we report the isomerization energies of all three symmetric azopyridines (the 2,2'-, 3,3'- and 4,4'-isomers, Scheme 1). Isomerization energy was obtained from the heat of isomerization measured in the liquid state using a method validated against the literature value on azobenzene. Theoretical calculations yielded results in reasonable agreement with experiment and explained the surprisingly low isomerization energy of 2,2'-azopyridine on the basis of its closer approach to planarity in the cis state.



Scheme 1. Molecular structures of azobenzene (AB) and azopyridines (APy). The cis-trans isomerization is indicated for azobenzene as an example.

EXPERIMENTAL METHODS

Azobenzene (> 99 % pure), 4,4'-azopyridine (NMR purity 96 %), 2-aminopyridine (> 99 % pure), 3-aminopyridine (99 % pure), NaClO (10-15% w/w solution), and *o*-terphenyl (OTP, 99 % pure) were purchased from Sigma-Aldrich and used as received.

Differential Scanning Calorimetry (DSC) was conducted with a TA DSC Q2000 instrument with a typical sample size of 5 mg. Nuclear Magnetic Resonance (NMR) were performed in $CDCl_3$ with a Varian Unity-Inova 400 MHz NMR Spectrometer for assessment of chemical purity. UV-Vis spectra were collected with a Hitachi U-3000 Spectrophotometer.

2,2'- and 3,3'-azopyridine were synthesized according to a literature method [16]. 1 g of 2-aminopyridine or 3-aminopyridine was dissolved in 20 mL of deionized water, and the solution was added dropwise into 60 mL NaClO solution (10-15 % w/w) in an ice-water batch under constant stirring in the dark. After one hour, the product was extracted with ethyl ether (3 times, each time 50 mL). The solvent was removed with a rotary evaporator and the product was further separated by column chromatography (mobile phase: acetone/hexane (1:10); column: basic Al_2O_3). After solvent removal by rotary evaporation, the product was recrystallized from hexane to obtain 2,2'-azopyridine or 3,3'-azopyridine. Purities by NMR: 92 % for 2,2'-azopyridine, >99 % for 3,3'-azopyridine.

The mixture of azobenzene or an azopyridine with OTP was prepared by weighing the two components into a capped glass vial and heating the vial to obtain a homogeneous solution. For photo-isomerization, an azobenzene/azopyridine-OTP solution was placed between two UV-transmitting quartz slides (2.5 cm × 2.5 cm) to form a liquid film approximately 10 μm thick. This liquid film was irradiated at room temperature with the 365 nm light from a Spectroline ENF-240C UV Lamp for a few minutes to several hours to obtain different cis isomer contents, and the longest irradiation time used was enough to reach the photo-stationary state. During irradiation, the sample was placed on a large aluminum block, which provided efficient heat dissipation and maintained the sample at the room temperature. The sample remained fully liquid throughout irradiation. The liquid was transferred into a pre-weighed Tzero Hermetic DSC pan with a capillary tube under dim light. The filled DSC pan was weighed again (to obtain the sample mass), sealed, and scanned to determine the heat of isomerization. Before each heating scan, the sample was cooled to approximately -70 °C. A portion of the sample was dissolved in ethanol or hexane and the solution's UV-visible spectrum was recorded to calculate the fraction of cis- isomer based on the known extinction coefficients of the isomers [12].

Ab initio calculations were performed with Gaussian 09 [17]. Isomerization energies were computed using G3MP2, which Cammenga *et al.* have shown provided accurate results for azobenzene [18]. Molecular geometries were illustrated with VMD 1.9.2 [19].

RESULTS AND DISCUSSION

Experimental isomerization energies. In this work, an azopyridine liquid was irradiated to convert a fraction of the trans isomers to the cis and the product was heated to measure the heat of thermal conversion from the cis isomer to the trans. In order to maintain azopyridine in the liquid state during irradiation, its crystallization must be inhibited (crystals scatter light, reducing the efficiency of the photochemical process). This was accomplished by mixing azopyridine with *o*-terphenyl (OTP), a non-crystallizing component. The amount of OTP was chosen to the smallest amount possible to suppress crystallization. In this method, the irradiated sample was measured by DSC directly, without first separating the cis isomer by chromatography [5].

Our method requires that prior to heating, the degree of photo-isomerization be known. Figure 1 shows the UV-visible spectra collected for this

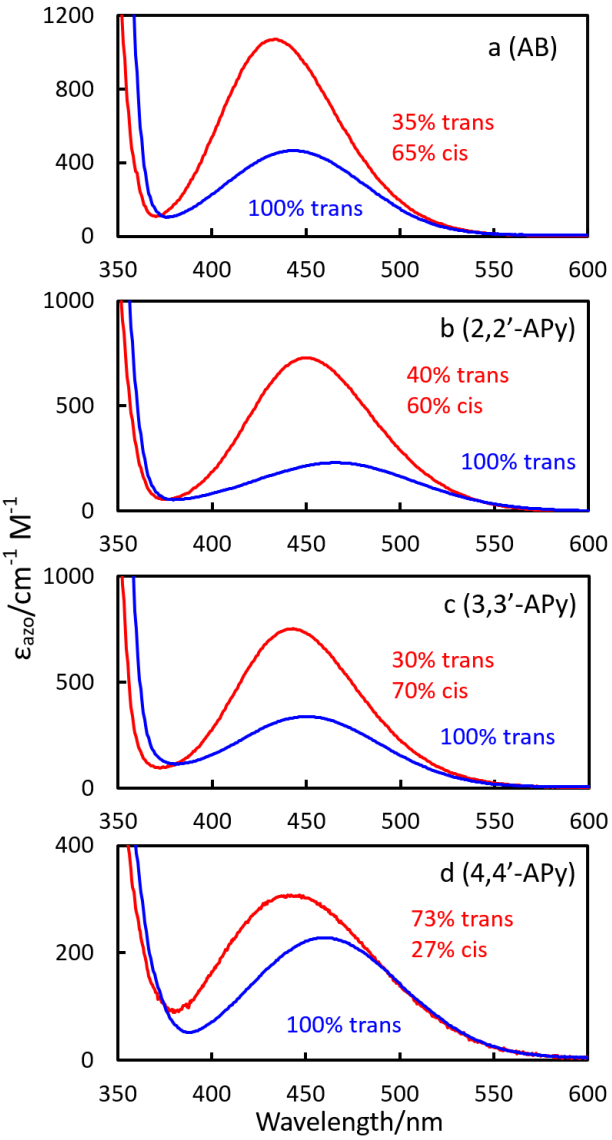


Figure 1. UV-vis spectra of azobenzene/OTP (1:2 w/w), 2,2'-azopyridine/OTP (1:2), 3,3'-azopyridine/OTP (7:93) and 4,4'-azopyridine/OTP (1:4). The first was dissolved in ethanol and rest in hexane. The y-axis is extinction coefficient based on azobenzene or azopyridine concentration. OTP has no absorbance at $\lambda > 300$ nm.

purpose. For each system, the lower curve corresponds to the non-irradiated sample (trans isomers only) and the upper curve for the irradiated sample (both trans and cis isomers). In this spectral region, azopyridine molecules account for all the absorbance, since OTP does not absorb in this region. The peak near 450 nm is the n - π* transition [20], which is nearly forbidden in the trans isomer and significantly stronger in the cis isomer. From the spectra in Figure 1 and the known extinction coefficients of the isomers [16], the fractions of the cis- and trans-isomers in a solution can be calculated. These values are indicated in Figure 1 for the respective samples.

Figure 2 shows the DSC heating traces of the azobenzene/OTP and azopyridine/OTP mixtures (the same pairs of samples in Figure 1). For each system, two curves are shown, corresponding to the sample in the 100 % trans state and the sample in which a fraction of the trans isomers have been converted to the cis. For both samples, the first thermal event is the glass transition T_g.

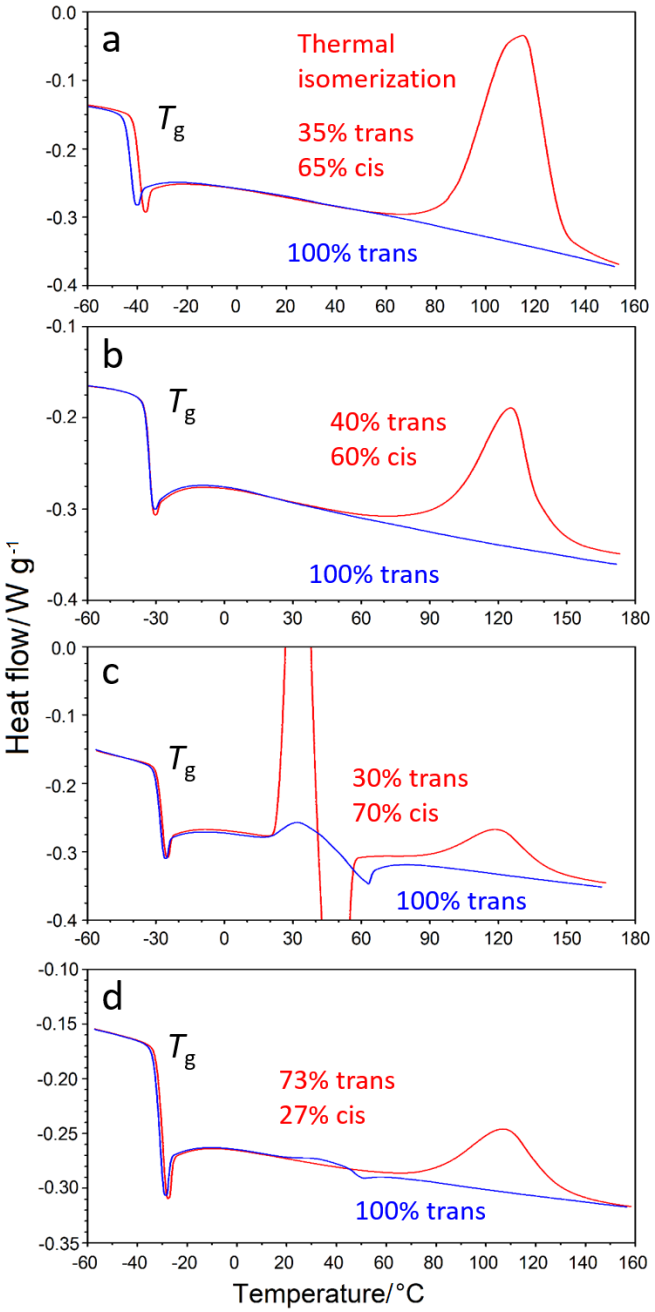


Figure 2. DSC curves of (a) azobenzene/OTP (1:2); (b) 2,2'-azopyridine/OTP (1:2); (c) 3,3'-azopyridine/OTP (7:93); (d) 4,4'-azopyridine/OTP (1:4). Heating rate = 10 °C min^{-1}. During the 1st heating (red) the cis- isomers transform to the trans near 110 °C releasing heat. The exo- and endo-thermic events at 20-70 °C for (c) and (d) result from crystallization and melting.

In the case of azobenzene (Figure 2a), the sample containing the cis isomers shows a broad exothermic peak at 110 °C, whereas the 100% trans sample does not. This event corresponds to the thermal conversion from the cis to the trans isomer [5]. Integrating this peak gives the thermal isomerization enthalpy, which under ambient pressure is approximately the same as the isomerization energy, ΔE_{iso}. In Figure 3 (solid circles), we plot the ΔE_{iso} value against the cis fraction in the sample. The samples with different cis fractions were obtained by varying the irradiation time. A linear relation is seen between the two quantities, the slope of which yields the isomerization energy: ΔE_{iso} = 258±7 J g^{-1} = 47.0±1.3 kJ mol^{-1} for azobenzene. This value agrees with the literature value of 48.2±0.3 kJ mol^{-1}, also obtained by DSC for samples of pure cis-azobenzene [5]. There are additional reports on the azobenzene isomerization energy from other methods; these values appear to be nearly independent of the physical state of the sample (gas, solution, or crystal), falling in the range 47±3 kJ mol^{-1} [5,18,21,22]. The consistency between our result and the literature results validates our method.

A noteworthy feature in Figure 2a is the small but real difference of T_g between the two traces. This difference indicates that the liquid enriched in the cis isomer has a slightly higher T_g. The effect is also observed with the azopyridines (see below). The cause for this effect is still unclear.

For 2,2'-azopyridine (Figure 2b), we observe essentially the same features as azobenzene (Figure 2a). Figure 3 (red squares) shows how the heat of isomerization changes with the fraction of the cis isomer. By the same procedure, we obtain ΔE_{iso} = 137±3 J g^{-1} = 25.2±0.6 kJ mol^{-1} for 2,2'-azopyridine.

For 3,3'-azopyridine (Figure 2c), the essential features of the DSC results are still similar to those of azobenzene (Figure 2a) and 2,2'-azopyridine (Figure 2b), with the exception that crystallization occurred during the DSC analysis. This azopyridine crystallizes more rapidly than the other two compounds, necessitating a higher concentration of OTP (93 % w/w vs. 67 % w/w). Even at a higher OTP concentration, crystallization still took place during the DSC scan. In the 100% trans sample,

crystallization occurs near 30 °C and the resulting crystals melt near 60 °C. In the sample containing the cis isomer, crystallization occurs near 20 °C and crystal melting at 40 °C. All these events were confirmed by optical microscopy on a temperature-controlled stage. Despite the complications from crystallization and melting, the thermal isomerization is still clearly observed in the liquid state. This event also occurs near 110 °C, prior to which the system has entered to the liquid state (after crystallization and melting). Applying the same procedure as above, we obtain ΔE_{iso} = 231±3 J g^{-1} = 42.6±0.6 kJ mol^{-1} for 3,3'-azopyridine.

The situation for 4,4'-azopyridine (Figure 2d) is similar to that of 3,3'-azopyridine just described (Figure 2c). Here the 100% trans sample showed weak thermal events corresponding to crystallization (20 °C) and crystal melting (45 °C), whereas the cis-containing sample was free of these events. For this system, we obtain ΔE_{iso} = 190±10 J g^{-1} = 35.0±1.8 kJ mol^{-1}.

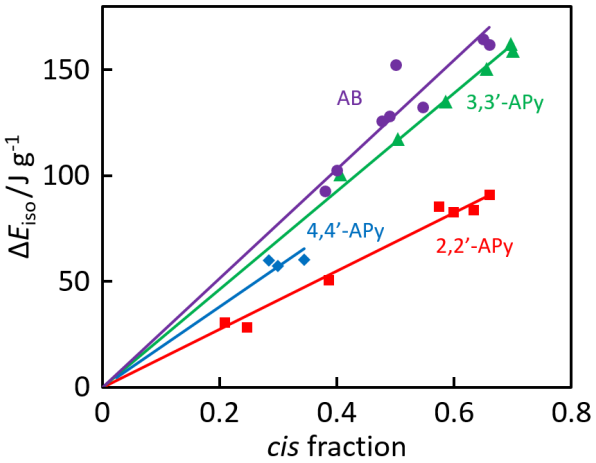


Figure 3. Isomerization energy per gram vs cis isomer fraction for azobenzene and 2,2'-, 3,3'-, and 4,4'-azopyridines.

Viewing the above results together, we note that the thermal conversions of the trans isomers to the cis all occur at approximately the same temperatures, indicating a similar kinetic barrier for isomerization. This similarity is not surprising given the similar structures of these molecules. There is a significant variation in the ΔE_{iso} values within this group of molecules; the value for 2,2'-azopyridine is almost half of other systems. This result was studied further through theoretical calculations (see below).

Quantum chemical calculations. Table 1 shows the results of G3MP2 calculations for the molecules of this study. For each azo compound, calculations were performed for both the cis and the trans isomer in the gas phase. For 2,2'- and 3,3'-azopyridines, each cis or trans configuration must be further specified depending on whether the pyridine N is close (c) or far (f) relative to the central N=N bond, resulting in the cc, fc, and ff combinations, as illustrated in Figure 4 [4]. This complexity does not arise for azobenzene or 4,4'-azopyridine because of their symmetry. In Table 1, E is the energy at 298.15 K, and ΔE is the energy of a given conformer relative to the lowest energy conformer.

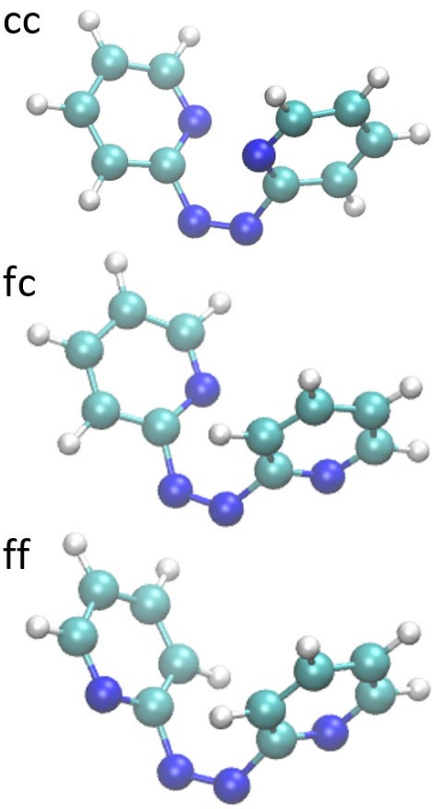


Figure 4. Illustraion of the cc, fc, and ff conformers with cis 2,2'-azopyridine as an example.

For azobenzene, our results reproduce the literature values [18]. The calculated isomerization energy ΔE_{iso} = 45.8 kJ mol^{-1} agrees with the experimental value in the gas phase (47.4 ± 3.2 kJ mol^{-1}) [18]. The torsion angles C-N-N-C (180° for the trans and 8.60° for the cis) compare favorably with those in the crystals (180° and 7.68°) [23,24] as do the dipole moments (calculated: 0 D for the trans and 3.45 D for the cis; measured: 0 for the trans and 3.08 D for the cis) [4]. These consistencies indicate the validity of the computational method.

Table 1. Calculated gas-phase properties of azobenzene (AB) and azopyridines (APy). Bold font indicates the lowest-energy of the 3 conformers (cc, fc, ff) for 2,2'- or 3,3'-azopyridine.

	E/Hartree	Δ*E*/kJ mol^{-1}	Torsion angle C-N-N-C/degree	μ/D	Calculated aver. μ/D	Exp. μ/D (Ref. 4)
AB-trans	-571.78048	0	180	0	0	0.52
AB-cis	-571.79791	45.8	8.60	3.45	3.45	3.08
2,2'-APy-cis-cc	-603.86394	26.8	10.36	4.10		
2,2'-APy-cis-fc	-603.85957	38.2	9.39	6.19	4.18	4.04
2,2'-APy-cis-ff	-603.86029	36.3	7.92	6.13		
2,2'-APy-trans-cc	-603.87009	10.6	180	0		
2,2'-APy-trans-fc	-603.87182	6.06	180	3.34	0.49	1.78
2,2'-APy-trans-ff	-603.87412	0	180	0		
3,3'-APy-cis-cc	-603.85274	49.9	9.35	0.63		
3,3'-APy-cis-fc	-603.85237	50.9	8.88	4.20	2.75	2.85
3,3'-APy-cis-ff	-603.85248	50.6	8.59	2.98		
3,3'-APy-trans-cc	-603.86929	6.47	180	0		
3,3'-APy-trans-fc	-603.87041	3.52	180	4.01	1.25	2.42
3,3'-APy-trans-ff	-603.87175	0	180	0		
4,4'-APy-cis	-603.85457	41.8	7.39	0.33	0.33	N/A
4,4'-APy-trans	-603.87051	0	180	0	0	0.42

For each azopyridine, the trans isomer has planar geometry, as expected for a system attempting to optimize the delocalization of π electrons. For the trans isomers, the dipole moments are expected to vanish by symmetry except for the fc conformer of 2,2'- or 3,3'- azopyridine; this is indeed the case. For the cis isomers, the C-N-N-C torsion angles are about 9°, similar to that of azobenzene.

Concerning the isomerization energies, the calculated value for 4,4'-azopyridine (41.8 kJ mol^{-1}) can be compared with the experimental value (35.0 kJ mol^{-1}). This agreement between theory and experiment is modest, albeit worse than the agreement in the case of azobenzene. For 2,2'- or 3,3'-azopyridine, each trans or cis isomer has multiple conformers (cc, fc, ff). Assuming Boltzmann distribution between the 3 conformers and noting their degeneracies (1 for cc and ff; 2 for fc), we obtain ΔE_{iso} = 26.1 kJ mol^{-1} for 2,2'-azopyridine at its isomerization temperature 398 K, in good agreement with 25.2 kJ mol^{-1} from experiment. For 3,3'-azopyridine, the same procedure yields ΔE_{iso} = 48.7 kJ mol^{-1} at 393 K, compared to 42.6 kJ mol^{-1} from experiment, a fair agreement. In Figure 5, the foregoing comparison between theory and experiment is shown graphically. Overall, there is a broad agreement between theory and experiment. The residual difference is likely a result of the combined errors in both methods.

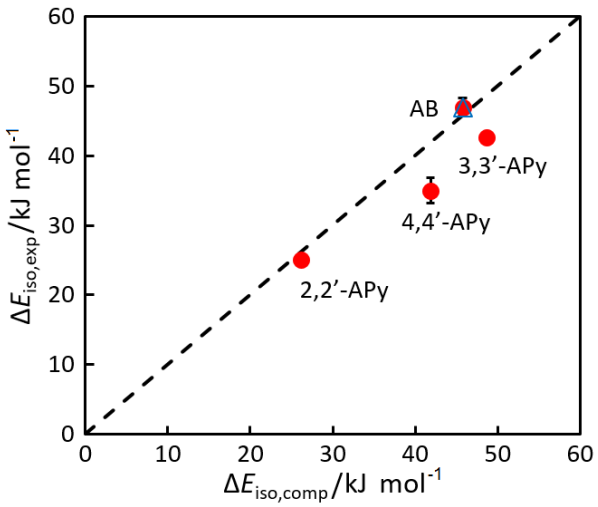


Figure 5. Comparison of calculated and experimental isomerization energies. Circles are results from this work. Standard deviations of experimental ΔE are shown or are smaller than the symbol size. Triangle indicates the literature experimental value of ΔE_{iso} [18].

It is noteworthy that G3MP2 can reproduce the surprisingly low ΔE_{iso} for 2,2'-azopyridine. According to the calculations, the cc isomer of cis 2,2'-azopyridine has especially low energy among its 3 conformers (cc, fc, and ff). In this conformer, the two aromatic rings approaches co-planarity the closest.

This can be seen by summing the cosines of the three torsional angles that describe the departure from planarity at the three sites of torsion (Table 2). For a trans isomer (planar), this sum is three. For a cis isomer, this value is between zero and three. In the cc conformer of cis-2,2'-azopyridine, this sum is the largest, indicating the closest approach to co-planarity and the greatest extent of π conjugation among all the cis isomers. This presumably leads to a lower conformational energy [25,26]. The ability for the cc conformer of cis 2,2'-azopyridine to approach co-planarity the closest is likely a result of the smaller van der Waals volume of the pyridine N relative to the phenyl CH.

Table 2. Torsion angles for azobenzene (AB) and azopyridines (APy). φ_1 and φ_2 are the torsion angles of the aromatic rings relative to the azo bond.

	θ (C-N-N-C)/degree	φ_1/degree	φ_2/degree	$\cos\theta + \cos\varphi_1 + \cos\varphi_2$
AB-cis	8.60	51.81	51.81	2.23
2,2'-APy-cis-cc	10.36	48.67	48.67	2.30
2,2'-APy-cis-fc	9.39	42.01	59.87	2.23
2,2'-APy-cis-ff	7.92	63.23	63.23	1.89
3,3'-APy-cis-cc	9.35	53.12	53.12	2.19
3,3'-APy-cis-fc	8.88	53.74	49.75	2.23
3,3'-APy-cis-ff	8.59	52.29	52.29	2.21
4,4'-APy-cis	7.39	56.21	56.21	2.10

Table 1 shows the calculated dipole moment at 298.15 K for each isomer of the 3 azopyridines. For an isomer that has multiple conformers, an average dipole moment is computed assuming Boltzmann distribution between the conformers. The results agree reasonably well with the experimental data [4]. The residual difference is likely a result of the combined errors in both techniques. Bullock *et al.* noted that the dipole moment should vanish for trans azobenzene and trans 4,4'-azopyridine, but their

experimental values are non-zero. They suggest that one possible reason is the contamination from the cis isomer, perhaps formed in solutions not in complete darkness [4].

CONCLUSIONS

In this work we obtained the isomerization energies of all 3 symmetrical azopyridines for the first time by experiment and quantum chemical calculations. Our method was validated against the literature value on azobenzene. The computational results are in reasonable agreement with experiment, and explain the low isomerization energy of 2,2'-azopyridine on the basis of a low-energy cis conformer. Because of the smaller van der Waals volume of the pyridine N relative to the phenyl CH, the two aromatic rings in the cc cis isomer can approach closer to co-planarity, leading to greater π-conjugation and lower conformational energy. Our results are relevant for developing azopyridine-based materials. Given their ability to form hydrogen bonds and metal coordination bonds, azopyridine molecules may expand the design space for photo-responsive materials.

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