

# *Trans–cis* isomerization energies of azopyridines: a calorimetric and computational study

Men Zhu<sup>1</sup> · Lian Yu<sup>1</sup>

Received: 8 August 2017 / Accepted: 7 December 2017 © Akadémiai Kiadó, Budapest, Hungary 2018

#### 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 with azobenzenes, azopyridines offer additional opportunities for materials design through hydrogen bonding and coordination chemistry. Here we report the isomerization energies for all three 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  $\Delta E_{iso} = 25.2 \pm 0.6$ ,  $42.6 \pm 0.6$ , and  $35.0 \pm 1.8$  kJ mol<sup>-1</sup> for 2,2', 3,3', and 4,4'-azopyridine, respectively. For azobenzene, we obtain  $\Delta E_{iso} = 47.0 \pm 1.3$  kJ mol<sup>-1</sup>, in agreement with the literature value and validating our method. Theoretical calculations yielded gas-phase  $\Delta E_{iso}$  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 coplanarity, leading to greater  $\pi$ -conjugation and lower conformational energy.

Keywords Photochemistry · Isomerization energy · DSC · Ab initio

## Introduction

For nearly a century, azobenzene and its derivatives have been studied for their reversible photo-induced *trans-cis* isomerization and applications as photo-responsive materials [1–3]. 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 to 3.08 D) [4] and energy (increase by 47 kJ mol<sup>-1</sup>) [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], azopyridine can be organized by metal coordination to

Lian Yu lian.yu@wisc.edu

<sup>&</sup>lt;sup>1</sup> Department of Chemistry and School of Pharmacy, University of Wisconsin-Madison, Madison, WI 53705, USA



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

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 symmetrical 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.

## **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) was performed in  $CDCl_3$  with a Varian Unity-Inova 400 MHz NMR spectrometer for assessment of chemical purity. UV–visible 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<sub>2</sub>O<sub>3</sub>). 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 UVtransmitting quartz slides (2.5 cm  $\times$  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 then transferred into a preweighed 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 provided accurate results for azobenzene [18]. Molecular geometries were visualized with VMD 1.9.2 [19].



**Fig. 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 sample was dissolved in ethanol and the rest in hexane. The y-axis is extinction coefficient based on azobenzene or azopyridine concentration. OTP has no absorbance at  $\lambda > 300$  nm. (Color figure online)

# **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



**Fig. 2** DSC curves (exo up) 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<sup>-1</sup>. During the 1st heating (red) the cis isomers transform to the *trans* near 110 °C releasing heat. The exo- and endothermic events at 20–70 °C for **c** and **d** result from crystallization and melting. (Color figure online)

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 be 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].



**Fig. 3** Isomerization energy per gram vs *cis* isomer fraction for azobenzene and 2,2'-, 3,3'-, and 4,4'-azopyridines. (Color figure online)

Our method requires that prior to heating, the degree of photo-isomerization be known. Figure 1 shows the UV-visible spectra collected for this purpose. For each system, the lower curve corresponds to the non-irradiated sample (*trans* isomers only) and the upper curve to the irradiated sample (containing 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  $n - \pi^*$  transition [20], which is nearly forbidden in the *trans* isomer and significantly stronger in the *cis* isomer. From the spectra in Fig. 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 Fig. 1 for the various samples.

Figure 2 shows the DSC heating traces of the azobenzene/OTP and azopyridine/OTP mixtures (the same samples in Fig. 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 has been converted to the cis. For both samples, the first thermal event is the glass transition  $T_g$ .

In the case of azobenzene (Fig. 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,  $\Delta E_{iso}$ . In Fig. 3 (solid circles), we plot the  $\Delta E_{iso}$  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:  $\Delta E_{iso} = 258 \pm$ 7 J  $g^{-1} = 47.0 \pm 1.3$  kJ mol<sup>-1</sup> for azobenzene. This value agrees with the literature value of 48.2  $\pm$ 0.3 kJ mol<sup>-1</sup>, 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

 Table 1 Calculated gas-phase properties of azobenzene (AB) and azopyridines (APy)

	$\Delta E/kJ \text{ mol}^{-1}$	Torsion angle C–N–N–C/degree	μ/D	Calculated aver. $\mu$ /D	Exp. μ/D Ref [4]
AB-trans	0	180	0	0	0.52
AB-cis	45.8	8.60	3.45	3.45	3.08
2,2'-APy-cis-cc	26.8	10.36	4.10	4.18	4.04
2,2'-APy-cis-fc	38.2	9.39	6.19		
2,2'-APy-cis-ff	36.3	7.92	6.13		
2,2'-APy-trans-cc	10.6	180	0	0.49	1.78
2,2'-APy-trans-fc	6.06	180	3.34		
2,2'-APy-trans-ff	0	180	0		
3,3'-APy-cis-cc	49.9	9.35	0.63	2.75	2.85
3,3'-APy-cis-fc	50.9	8.88	4.20		
3,3'-APy-cis-ff	50.6	8.59	2.98		
3,3'-APy-trans-cc	6.47	180	0	1.25	2.42
3,3'-APy-trans-fc	3.52	180	4.01		
3,3'-APy-trans-ff	0	180	0		
4,4'-APy-cis	41.8	7.39	0.33	0.33	N/A
4,4'-APy-trans	0	180	0	0	0.42

Bold font indicates the lowest energy of the three conformers (cc, fc, ff) for 2,2'- or 3,3'-azopyridine



Fig. 4 Illustraion of the cc, fc, and ff conformers with *cis* 2,2'-azopyridine as an example. (Color figure online)

physical state of the sample (gas, solution, or crystal), falling in the range  $47 \pm 3 \text{ kJ mol}^{-1}$  [5, 18, 21, 22]. The consistency between our result and the literature results validates our method.

A noteworthy feature in Fig. 2a is the small but real difference of  $T_{\rm g}$  between the two traces. This difference indicates that the liquid enriched in the *cis* isomer has a slightly higher  $T_{\rm g}$ . The effect is also observed with the azopyridines (see below).

For 2,2'-azopyridine (Fig. 2b), we observe essentially the same features as azobenzene (Fig. 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  $\Delta E_{iso} = 137 \pm 3 \text{ J g}^{-1} = 25.2 \pm 0.6 \text{ kJ mol}^{-1}$  for 2,2'-azopyridine.

For 3,3'-azopyridine (Fig. 2c), the essential features of the DSC results are still similar to those of azobenzene (Fig. 2a) and 2,2'-azopyridine (Fig. 2b), with the exception that crystallization occurred during the DSC analysis. This



Fig. 5 Comparison of calculated and experimental isomerization energies. Circles are results from this work. Standard deviations of experimental  $\Delta E$  are shown or are smaller than the symbol size. Triangle indicates the literature experimental value of  $\Delta E_{\rm iso}$  [18]. (Color figure online)

azopyridine crystallizes more rapidly than the other two compounds, necessitating a higher concentration of OTP (93 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 the liquid state (after crystallization and melting). Applying the same procedure as above, we obtain  $\Delta E_{iso} = 231 \pm 3 \text{ J g}^{-1} = 42.6 \pm$  $0.6 \text{ kJ mol}^{-1}$  for 3,3'-azopyridine.

The situation for 4,4'-azopyridine (Fig. 2d) is similar to that of 3,3'-azopyridine just described (Fig. 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  $\Delta E_{iso} = 190 \pm$ 10 J g<sup>-1</sup> = 35.0 ± 1.8 kJ mol<sup>-1</sup>. Viewing the above results together, we note that the thermal conversions of the *cis* isomers to the *trans* 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  $\Delta E_{iso}$  values within this group of molecules; the value for 2,2'-azopyridine is almost half of the Table 2Torsion angles for<br/>azobenzene (AB) and<br/>azopyridines (APy)

	$\theta$ (C–N–N–C)/degree	$\varphi_1$ /degree	$\varphi_2$ /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

 $\varphi_1$  and  $\varphi_2$  are the torsion angles of the aromatic rings relative to the azo bond

values for the 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* isomer 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 Fig. 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  $\Delta E$  is the energy of a given conformer relative to the lowest energy conformer.

For azobenzene, our results reproduce the literature values [18]. The calculated isomerization energy  $\Delta E_{\rm iso} = 45.8$  kJ mol<sup>-1</sup> agrees with the experimental value in the gas phase (47.4 ± 3.2 kJ mol<sup>-1</sup>) [18]. The torsion angles C–N–N–C (180° for the *trans* and 8.60° for the cis) agree with those in the crystals (180° and 7.68°) [23, 24].

For each azopyridine, the *trans* isomer has planar geometry, as expected for a system attempting to optimize the delocalization of  $\pi$  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<sup>-1</sup>) is in fair agreement with the experimental value (35.0 kJ mol<sup>-1</sup>). For 2,2'- or 3,3'-azopyridine, each *trans* or *cis* isomer has multiple conformers (cc, fc, ff). Assuming Boltzmann distribution between the three conformers and noting their degeneracies (1 for cc and ff; 2 for fc), we obtain  $\Delta E_{\rm iso} = 26.1$  kJ mol<sup>-1</sup> for 2,2'-azopyridine at its

isomerization temperature 398 K, in good agreement with 25.2 kJ mol<sup>-1</sup> from experiment. For 3,3'-azopyridine, the same procedure yields  $\Delta E_{iso} = 48.7$  kJ mol<sup>-1</sup> at 393 K, compared to 42.6 kJ mol<sup>-1</sup> from experiment, a fair agreement. In Fig. 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.

It is noteworthy that G3MP2 can reproduce the surprisingly low  $\Delta E_{iso}$  for 2,2'-azopyridine. According to the calculations, the cc isomer of cis 2,2'-azopyridine has especially low energy among its three conformers (cc, fc, and ff). In this conformer, the two aromatic rings approach coplanarity 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 (2.3), suggesting the closest approach to coplanarity and the greatest extent of  $\pi$  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 closely approach coplanarity is likely a result of the smaller van der Waals volume of the pyridine N relative to the phenyl CH.

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 nonzero. This could be a result of 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 three 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 lowenergy 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 coplanarity, leading to greater  $\pi$ -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.

Acknowledgements We thank the National Science Foundation for supporting this work through Grant No. DMR-1234320 and through the University of Wisconsin—Madison MRSEC (DMR-1720415).

## References

- 1. Hartley GS. The cis-form of azobenzene. Nature. 1937;140:281.
- 2. Bandara HMD, Burdette SC. Photoisomerization in different classes of azobenzene. Chem Soc Rev. 2012;41:1809–25.
- Yager KG, Barrett CJ. Novel photo-switching using azobenzene functional materials. J Photochem Photobiol A: Chem. 2006;182:250–61.
- Bullock DJW, Cumper CWN, Vogel AI. Physical properties and chemical constitution. Part 63. The electric dipole moments of azobenzene, azopyridines, and azoquinolines. J Chem Soc. 1965;5316–23.
- Wolf E, Cammenga HK. Thermodynamic and kinetic investigation of the thermal isomerization of cis-azobenzene. Z. Phys. Chem. (Neue Folge). 1977;107:21–38.
- Yamada M, Kondo M, Mamiya JI, Yu Y, Kinoshita M, Barrett CJ, Ikeda T. Photomobile polymer materials: towards light-driven plastic motors. Angew Chem Int Ed. 2008;47:4986–8.
- Natansohn A, Rochon P. Photoinduced motions in azo-containing polymers. Chem Rev. 2002;102:4139–76.
- Banghart MR, Mourot A, Fortin DL, Yao JZ, Kramer RH, Trauner D. Photochromic blockers of voltage-gated potassium channels. Angew Chem Int Ed. 2009;48:9097–101.
- 9. Campbell N, Henderson AW, Taylor D. Geometrical Isomerism of Azo-compounds. J. Chem. Soc. 1953;1281–5.
- Cui L, Zhao Y. Azopyridine side chain polymers: an efficient way to prepare photoactive liquid crystalline materials through self-assembly. Chem Mater. 2004;16:2076–82.

- Han K, Su W, Zhong M, Yan Q, Luo Y, Zhang Q, Li Y. Reversible photocontrolled swelling-shrinking behavior of micron vesicles self-assembled from azopyridine-containing diblock copolymer. Macromol Rapid Commun. 2008;29:1866–70.
- Lin L, Yan Z, Gu J, Zhang Y, Feng Z, Yu Y. UV-responsive behavior of azopyridine-containing diblock copolymeric vesicles: photoinduced fusion, disintegration and rearrangement. Macromol Rapid Commun. 2009;30:1089–93.
- Aoki K, Nakagawa M, Ichimura K. Self-assembly of amphoteric azopyridine carboxylic acids: organized structures and macroscopic organized morphology influenced by heat, pH change, and light. J Am Chem Soc. 2000;122:10997–1004.
- Baldwin DA, Lever ABP, Parish RV. Complexes of 2,2'-azopyridine with iron(II), cobalt(II), nickel(II), copper(I), and copper(II). Infrared study. Inorg Chem. 1969;8:107–15.
- Dommaschk M, Peters M, Gutzeit F, Schütt C, Näther C, Sönnichsen FD, Tiwari S, Riedel C, Boretius S, Herges R. Photoswitchable magnetic resonance imaging contrast by improved light-driven coordination-induced spin state switch. J Am Chem Soc. 2015;137:7552–5.
- Brown EV, Granneman GR. Cis-trans isomerism in the pyridyl analogs of azobenzene. Kinetic and molecular orbital analysis. J Am Chem Soc. 1975;97:621–7.
- 17. Frisch MJ, et al. Gaussian 09, revision E.01. Wallingford: Gaussian, Inc.; 2009.
- Cammenga HK, Emel'yanenko VN, Verevkin SP. Re-investigation and data assessment of the isomerization and 2,2'-cyclization of stilbenes and azobenzenes. Ind Eng Chem Res. 2009;48:10120–8.
- Humphrey W, Dalke A, Schulten K. VMD—visual molecular dynamics. J. Molec. Graphics. 1996;14:33–8.
- 20. Cusati T, Granucci G, Persico M, Spighi G. Oscillator strength and polarization of the forbidden  $n - > \pi^*$  band of transazobenzene: a computational study. J Chem Phys. 2008;128:194312.
- Dias AR, da Piedade MEM, Simoes JAM, Simoni JA, Teixeira C, Diogo HP, Yang M, Pilcher G. Enthalpies of formation of cisazobenzene and trans-azobenzene. J Chem Thermodyn. 1992;24:439–47.
- Adamson AW, Vogler A, Kunkely H, Wachter R. Photocalorimetry. Enthalpies of photolysis of trans-azobenzene, ferrioxalate and cobaltioxalate ions, chromium hexacarbonyl, dirhenium dicarbonyl. J Am Chem Soc. 1978;100:1298–300.
- Harada J, Ogawa K. X-ray diffraction analysis of nonequilibrium states in crystals: observation of an unstable conformer in flashcooled crystals. J Am Chem Soc. 2004;126:3539–44.
- Mostad A, Rømming C. A refinement of the crystal structure of cis-azobenzene. Acta Chem Scand. 1971;25:3561–8.
- Ishikawa T, Noro T, Shoda T. Theoretical study on the photoisomerization of azobenzene. J. Chem. Phys. 2001;115:7503–12.
- 26. Cembran A, Bernardi F, Garavelli M, Gagliardi L, Orlandi G. On the mechanism of the cis – trans isomerization in the lowest electronic states of azobenzene: S0, S1, and T1. J Am Chem Soc. 2004;126:3234–43.