

Arylazopyrazoles: Azoheteroarene Photoswitches Offering Quantitative Isomerization and Long Thermal Half-Lives

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S Supporting Information

ABSTRACT: Arylazopyrazoles, a novel class of five-membered azo photoswitches, offer quantitative photo-switching and high thermal stability of the *Z* isomer (half-lives of 10 and ~1000 days). The conformation of the *Z* isomers of these compounds, and also the arylazopyrroles, is highly dependent on the substitution pattern on the heteroarene, allowing a twisted or planar geometry, which in turn has a significant impact on the electronic spectral properties of the compounds.

Photoswitchable compounds have diverse applications, from photopharmacology and optochemical genetics to data storage.^{1–8} Azobenzenes are easily synthesized, highly versatile photoswitches. They have high extinction coefficients and quantum yields, allowing photoswitching with low-intensity light, and are stable to repeated switching.⁹ Photochemical *E–Z* isomerization induces a large change in the shape of these molecules, including a significant difference in the end-to-end distance.⁹ This has been exploited, for example, in the direct conversion of light to mechanical energy.^{10–12} Generally, the *E* isomers are more thermodynamically stable than the *Z* isomers, the notable exception being Temps and co-workers' tricyclic ethylene-bridged azobenzene, which has reversed stability due to ring strain in the *E* isomer.¹³

A large array of azobenzenes have been reported, with an assortment of applications; however there are still a number of drawbacks that limit their use for certain purposes. First, incomplete photoswitching is often observed due to overlapping absorbances in the irradiation regions of interest.³ Second, the *Z* isomer often rapidly thermally converts back to the *E* isomer. High thermal stability is particularly required in ultrahigh-density optical data storage, an area currently dominated by diarylethylenes.^{7,8} Since the properties of azobenzenes can be varied substantially by altering the substituents on the aromatic rings, a number of specific azobenzenes have been recently reported that address such limitations.^{14–17} For example, Hecht and co-workers recently reported that 2,2',6,6'-tetrafluoroazobenzene shows near-quantitative photoswitching and the longest thermal half-life reported for an azobenzene molecule (~700 days at 25 °C in DMSO).¹⁶

Five-membered azoheteroarenes (and their photochromism) are far less studied. Much of the work on azoheteroarenes has concentrated on developing donor–acceptor systems with strong nonlinear optic and solvatochromic properties.^{18–24} Of the photochromic compounds studied, generally, these

heteroaromatic compounds have incomplete *E–Z* conversion and fast thermal half-lives (usually under 1 min).^{19,20,22} Velasco and co-workers recently exploited this property to develop extremely fast photoswitches ($t_{1/2}$ values of microseconds to nanoseconds) that tolerate thousands of switching cycles without decomposition.^{25,26} Conversely, for applications requiring long half-lives and high *E–Z* conversion, the arylazoimidazoles are the only five-membered azoheteroarenes to show promise,^{27–29} with Herges and co-workers demonstrating the ability to photoswitch 1-methyl-5-phenylazoimidazole to a photostationary state (PSS) containing 98% *Z* isomer, which possesses a thermal half-life of 528 h.²⁷ However, the best PSS for the backswitching only contained 55% *E* isomer.

We report a new class of highly promising photoswitchable azoheteroarenes, the arylazopyrazoles (Figure 1),³⁰ which we have directly compared to the related arylazopyrroles. Our arylazopyrazoles show high thermal stability in solution at room temperature ($t_{1/2}$ up to 1000 days), comparable to the highest known value for an azobenzene. A large separation of the λ_{\max} values of the *E* and *Z* isomers allows good to quantitative two-way photoswitching. By virtue of their five-membered rather than six-membered aromatic ring, we find that such compounds can access a *Z* isomer conformation not accessible to azobenzenes, a conformation that can be sterically tuned by substitution on the heterocyclic ring. Such conformational properties significantly affect the intensity of the $n-\pi^*$ absorbance, thus azoheteroarenes offer photophysical and photochemical properties not achievable with azobenzenes.

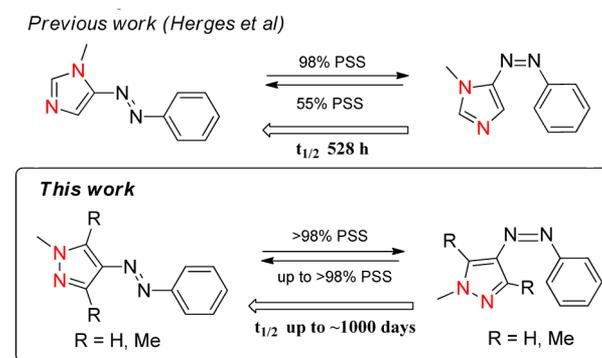
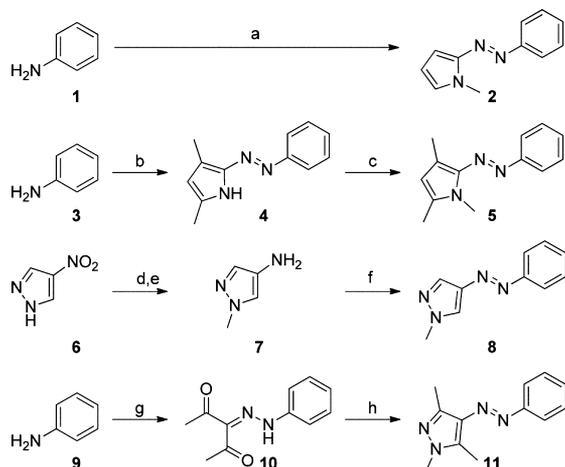


Figure 1. Azoheteroarenes with extended thermal half-lives and good photoswitching.

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Scheme 1. Synthesis of Photoswitches



Reagents and conditions. (a) concentrated HCl, aqueous NaNO₂, acetone/H₂O, 0 °C, then add to Na₂CO₃, *N*-methylpyrrole, acetone/H₂O, 0 °C to room temperature, 52%; (b) concentrated HCl, aqueous NaNO₂, H₂O, 0 °C, then 2,4-dimethylpyrrole, MeOH/pyridine, 0 °C, 71%; (c) NaH, MeI, THF, 0–60 °C, 58%; (d) K₂CO₃, MeI, MeCN, room temperature; (e) Pd/C, H₂, MeOH, room temperature, 58% from **6**; (f) nitrosobenzene, 40% aqueous NaOH/pyridine, 80 °C, 33%; (g) concentrated HCl, aqueous NaNO₂, AcOH, 0 °C, then add to NaOAc, acetylacetone, EtOH/H₂O, 0 °C to room temperature, quantitative; (h) NH₂NHMe, EtOH, reflux, quantitative.

Four heterocyclic compounds were chosen based on CAM-B3LYP/6-311G(2df,2p) TDDFT predictions of their photo-physics. All were *N*-methylated to prevent rapid *Z*–*E* thermal isomerization.^{29,31} Arylazopyrroles **2** and **5** and arylazopyrazole **11** were prepared using standard diazo couplings. Arylazopyrrole **8** was prepared from 4-amino-1-methylpyrrole and nitrosobenzene via a modified Mills reaction (Scheme 1) in a modest unoptimized yield, in line with highly substrate dependent literature yields.³² The scope for this method has previously included various aminopyridines and aminoquinolines;^{32,33} however, our study demonstrates it is also suitable for the preparation of azo compounds containing five-membered heteroarenes, of which few syntheses exist.^{25,27,34}

The UV/vis spectra of azoheteroarenes **2**, **5**, **8**, and **11** are shown in Figure 2. The pyrroles in **2** and **5** are better π donors to the electron-withdrawing azo function ($\sigma_p = +0.39$),³⁵ resulting in a red-shifted π – π^* λ_{\max} . This is consistent with π -

deficient azopyridines, having a blue-shifted π – π^* λ_{\max} in comparison to azobenzene.³⁶ *E*-pyrazoles (**8** and **11**) showed a weak n – π^* absorbance, well separated from the π – π^* band, whereas *E*-**2** and *E*-**5** had a slight shoulder on their π – π^* band, due to a weak n – π^* absorbance, poorly separated from the π – π^* absorbance. The separation of the n – π^* and π – π^* λ_{\max} bands is qualitatively consistent with the TDDFT calculations (Figure S21).

Exciting the π – π^* transition of azopyrazoles *E*-**8** and *E*-**11** at 355 nm resulted in complete photoswitching (>98% *Z* isomer in both cases). Near-quantitative switching was also achieved with broad-band 330–400 nm light (Figures S8,9). To our knowledge, the only azo compound for which ~100% *E*–*Z* photoswitching has been achieved is the ethylene-bridged azobenzene reported by Temps and co-workers.¹³ *Z*-**11** has a stronger n – π^* absorbance than *E*-**11**, while the n – π^* absorbance of *Z*-**8** was similar to that of *E*-**8** (Table 1). Irradiating the tail of the n – π^* absorbance of azopyrazole *Z*-**11** at 532 nm switched it back to >98% *E* isomer. Thus, **11** can be quantitatively switched in both directions, a result which surpasses the state-of-the-art ethylene-bridged azobenzene¹³ and the 2,2',6,6'-tetrafluoroazobenzene reported by Hecht and co-workers.¹⁶

Varying the substitution pattern or heterocycle resulted in less complete photoswitching. Azopyrazole *Z*-**8** only reached a 532 nm PSS containing 70 ± 3% *E* isomer, due to overlap of the *Z* and *E* isomer n – π^* absorbances. Irradiation of azopyrroles *E*-**2** and *E*-**5** at 415 nm led to PSSs containing 84 ± 2% and 85 ± 3% *Z* isomer, respectively (Figure 2). Similar to the case for the azopyrazoles, azopyrrole *Z*-**5** had a relatively intense n – π^* absorbance in comparison to *Z*-**2** and *E*-**5** (Table 1). Excitation of the n – π^* transition of azopyrrole *Z*-**5** at 532 nm led to quantitative (>98%) photoswitching to the *E* isomer. Prolonged irradiation of the tail of the n – π^* absorbance of *Z*-**2** at 532 nm led to a PSS containing 82 ± 3% *E* isomer. Quantum yields were determined where possible (Table 1). All compounds were photoswitched 20 times in each direction, and no significant degradation was observed, demonstrating high fatigue resistance (Figure S7).

For the arylazoimidazoles, Herges and co-workers reported that both isomers have a weak n – π^* absorbance and are calculated to adopt a conformation in which the heteroarene and azo function are coplanar.²⁷ In our calculations, all *E* isomers are predicted to be planar. For azopyrazole *Z*-**8** and azopyrrole *Z*-**2** (without two “ortho” methyl groups on the

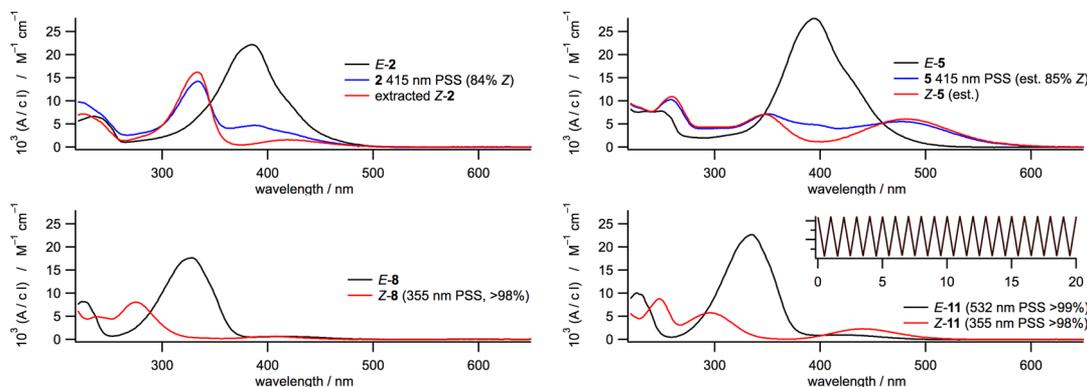


Figure 2. UV/vis spectra of azoheteroarenes in acetonitrile. Inset: repeated photoswitching cycles of azopyrazole **11**. The *Z*-**2** and *Z*-**5** spectra are determined as described in the Supporting Information.

Table 1. Spectral and Kinetic Data for Compounds

	E isomer $\pi-\pi^*$		E isomer $n-\pi^*$		Z isomer $\pi-\pi^*$		Z isomer $n-\pi^*$		half-life ^h	$\Phi_{E-Z}^{\pi-\pi^*}$	$\Phi_{Z-E}^{n-\pi^*}$
	λ_{\max}/nm	$10^{-2}\epsilon/\text{M}^{-1}\text{cm}^{-1}$	λ_{\max}/nm	$10^{-2}\epsilon/\text{M}^{-1}\text{cm}^{-1}$	λ_{\max}/nm	$10^{-2}\epsilon/\text{M}^{-1}\text{cm}^{-1}$	λ_{\max}/nm	$10^{-2}\epsilon/\text{M}^{-1}\text{cm}^{-1}$			
2	385	221 ± 18	~413 ^a	<i>a</i>	333	157 ± 13	423	17.9 ± 1.4	2.95 ± 0.05 h	0.50 ± 0.07 ^d	0.41 ± 0.05 ^e
5	394	282 ± 23	~430 ^a	<i>a</i>	346	70.4 ± 5.7 ^b	479	60.8 ± 4.9 ^b	21.2 ± 0.5 s ^c	<i>f</i>	0.41 ± 0.05 ^e
8	328	176 ± 14	417	6.44 ± 0.51	275	80.6 ± 6.4	403	6.66 ± 0.53	~1000 days	0.61 ± 0.06 ^g	0.60 ± 0.06 ^d
11	335	227 ± 18	425	9.63 ± 0.76	296	57.7 ± 4.6	441	23.0 ± 1.8	10 ± 0.03 days	0.46 ± 0.04 ^g	0.56 ± 0.04 ^e

^a $n-\pi^*$ absorbance appears as a shoulder on the $\pi-\pi^*$ absorbance; hence, ϵ cannot be obtained. ^bThese values are for the estimated pure Z isomer (see the Supporting Information). ^cThe rate was very sensitive to water present in the sample (see the Supporting Information). ^dExcited at 415 nm. ^eExcited at 532 nm. ^fNot determined due to competing thermal reaction. ^gExcited at 355 nm. ^hAt 25 °C.

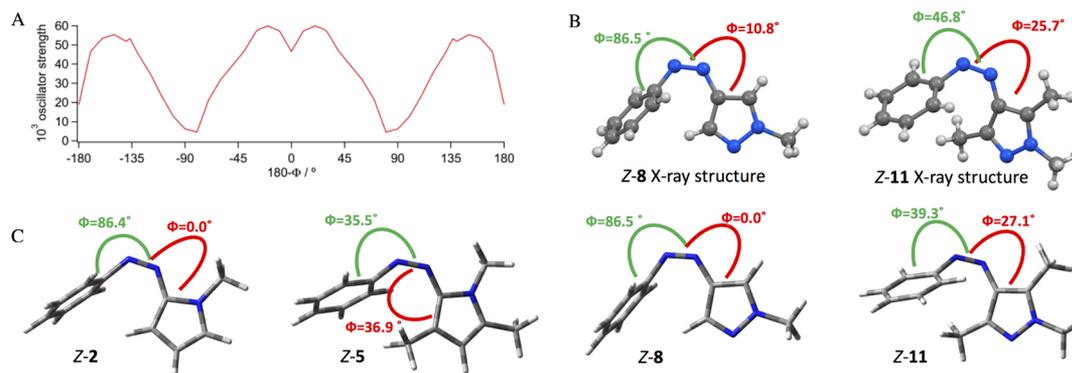


Figure 3. (A) Effect of dihedral angle on $n-\pi^*$ intensity for Z-11. (B) Crystal structures for Z-11 and Z-8. (C) Calculated conformations for Z isomers (B3LYP/6-31G(d,p)), with dihedral angles annotated. All values, except Φ_{NNhet} for Z-5, are given as $180 - \Phi$.

heterocycle) a conformation with the phenyl ring approximately orthogonal to the planar heteroarene-azo function is calculated, while the two methyl groups in azopyrazole Z-11 and azopyrrole Z-5 are predicted to force these species into a twisted conformation. TDDFT predicts low-intensity $n-\pi^*$ absorbances for all E isomers and for Z-2 and Z-8 (with the heteroarene and azo group coplanar—oscillator strengths of 0.0023 and 0.0026, respectively), as is seen in the experimental spectra. The twisted azopyrazole Z-11 and azopyrrole Z-5 are calculated and observed to have large $n-\pi^*$ absorbances.

A similar trend is observed for the $n-\pi^*$ absorbance in planar E-azobenzene and nonplanar Z-azobenzene, the former has a lower intensity absorbance than the latter.⁹ If both arenes are coplanar with, or orthogonal to, the azo group, a mirror plane exists through the plane of the azo function and the $n-\pi^*$ transition becomes symmetry-forbidden at the equilibrium geometry. Vibrational and rotational motion results in the molecule existing in conformations with weakly allowed $n-\pi^*$ transitions, resulting in a small absorbance. The spectroscopic findings suggest azopyrazole Z-8 and azopyrrole Z-2 exist in planar (or near-planar) conformations, and the more sterically congested bis(o-methylated) azopyrazole Z-11 and azopyrrole Z-5 adopt twisted conformations. With six-membered rings, Z-azobenzenes are *always* twisted,⁹ so these five-membered heteroarenes allow steric tuning of the spectral properties not available to azobenzenes. TDDFT calculations were performed (on constrained-optimized structures of azopyrazole Z-11 for illustration) to predict the effect of the dihedral angle between the heteroarene and azo groups on the $n-\pi^*$ intensity. The intensity is minimum at planar ($\Phi = 0, \pm 180^\circ$) and orthogonal geometries ($\Phi = \pm 90^\circ$) (Figure 3A).

Crystal structures were obtained for pyrazoles Z-11 and Z-8. The Φ_{NNhet} dihedral angle of 25.7° for Z-11 observed in the solid-state structure matched well with the calculated value of

27.1° (Figure 3). Although the Z-8 crystal structure was found to have a Φ_{NNhet} dihedral angle of 10.8° (cf. the calculated value of 0.0°), this was still considerably smaller than the value of 25.7° for Z-11, as predicted. The difference between the calculated and X-ray structure dihedral angles is consistent with the work by Jacquemin and co-workers on E-azobenzene, which is believed to adopt a planar structure in solution and a twisted structure in the solid state.³⁷

Thermal isomerization kinetics were obtained for all compounds, using UV/vis (5) or ¹H NMR (2, 8, 11) spectroscopy (Table 1), and all showed first-order isomerization. The presence of two “ortho” methyls on the heteroarene accelerates the isomerization. There is some debate as to the mechanism by which thermal isomerization of azoarenes occurs.^{38–40} However, both the inversion and the rotation transition states would relieve the steric strain in the bis(o-methylated) molecules, lowering the barrier for thermal isomerization compared to the molecules lacking the bis(o-methyls) (Figure S18). This has been studied for a range of methylated azobenzenes.⁴¹

The azopyrazoles had much slower thermal rates than the azopyrroles. An Eyring plot of the kinetics of thermal isomerization of azopyrazole Z-8 in DMSO between 80 and 120 °C gave activation parameters for this process ($\Delta H^\ddagger = +115 \pm 1 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -13 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$) that are very similar to those obtained by Hecht and co-workers for 2,2',6,6'-tetrafluoroazobenzene ($\Delta H^\ddagger = +109 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -29 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$), the azobenzene having the slowest isomerization to date.¹⁶ Using these, we estimate a half-life of ~1000 days at 25 °C. This compares highly favorably to those observed for diarylethenes and suggests that azoheteroarenes may hold potential for optical data storage.⁷ Substituted azopyrazole 11 was found to have a half-life of 10 days at 25 °C in acetonitrile. Azopyrrole 5 had a very fast thermal rate in

acetonitrile, $\sim 10^3$ faster than that for 4-aminoazobenzene in a similar polar aprotic solvent.⁴² By substitution of the phenyl ring of **5** with a para-electron-withdrawing group, push–pull azopyrrole systems can be generated with rapid thermal isomerization rates.²⁵

We have demonstrated that the five-membered azoheteroarenes hold significant potential in comparison to their more common azobenzene counterparts. For example, azopyrazole **11** can be quantitatively photoswitched in both directions; to the best of our knowledge, this ability is superior to that of all other azobenzenes reported to date.^{13,16} Furthermore, azopyrazole **8** has a very long thermal half-life (~ 1000 days), which is comparable to some of the slowest azo photoswitches reported, and positions this compound class excellently with respect to photochromic compounds used in optical storage devices.^{16,43}

The *Z* isomers of such five-membered azoheteroarenes can access a conformation with a coplanar heteroarene-azo function approximately orthogonal to the phenyl group resulting in a reduction of the $n-\pi^*$ absorbance intensity, on symmetry grounds. The *Z* isomer of a corresponding azobenzene photoswitch cannot access such a conformation due to the increased ring size. This effect for five-membered azoheteroarenes is readily tuned, using steric interactions alone, by choice of the substituents on the heteroaromatic ring. We believe that the azoheteroarene photoswitches will provide unique applications of these molecules, through access to photo-physical and photochemical properties not achievable in the more commonly used azobenzenes.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving synthetic methods, NMR and crystallographic data, photochemical methods including additional spectra and kinetics, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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