Photoswitchable basicity through the use of azoheteroarenes

Electronic Supplementary Information

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Table of Contents

Synthesis
General methods
Experimental procedures
Photochemistry
pK _a titration
pH jump
pH oscillation
pK _a equation derivation
Thermal isomerisation kinetics
Geometry optimisation and TDDFT calculations1
General methods1
Energy minimised structures1
Structures and Cartesian coordinates for optimised geometry
Comparison of calculated and experimental spectra 22
GIAO ¹³ C NMR calculations
Energy minimised structures
NMR shielding tensors and chemical shifts24
Neutral and deuteronated NMR in CD ₃ OD 20
REFERENCES

Table of Figures

Figure S1:	Estimating pure Z spectrum of 1	S5
Figure S2:	Spectra for <i>E</i> - 1 and 415 nm PSS pH titration	S6
Figure S3:	Spectra for neutral, mono- and di-protonated <i>E-</i> 1	S6
Figure S4:	pH titration of <i>E</i> - 1 showing mono- and di-protonation with sigmoidal fits	S7
Figure S5:	Bromocresol purple pH titration	S7
Figure S6:	pH jump	S8
Figure S7:	pH oscillation on cycling between the <i>E</i> isomer and 405 nm PSS	S8
Figure S8:	A system involving multiple thermodynamic equilibria	S9
Figure S9:	Photoswitching involving additional equilibria	S9
Figure S10:	Thermal isomerisation of 1 in buffer	S12
Figure S11:	Calculated and experimental UV/vis spectra for neutral and protonated ${\bf 1}$	S22
Figure S12:	Difference in calculated and experimental ¹³ C NMR shifts for <i>E</i> - 1 H ⁺	S25
Figure S13:	Calculated vs. experimental 13 C chemical shifts for neutral <i>E</i> - 1	S25
Figure S14:	Proton and carbon NMR for neutral <i>E-</i> 1	S26
Figure S15:	Proton and carbon NMR for deuteronated <i>E</i> -1	S27

Table of Tables

Table S1:	Calculated data for the energy minimised structures of 1	S13
Table S2:	Calculated data for the energy minimised structures of 2	S14
Table S3:	Calculated λ_{max} and oscillator strength (f) for n- π^* and $\pi\text{-}\pi^*$ excitation of $\textbf{1}$	S14
Table S4:	Calculated data for the energy minimised structures of ${f 1}$ in methanol	S23
Table S5:	Calculated shielding tensors	S24
Table S6:	Calculated and scaled chemical shifts	S24
Table S7:	Difference in calculated and experimental 13 C NMR shifts for <i>E</i> - 1 H ⁺	S25

Synthesis

General methods

All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise indicated. All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 plates (0.25mm). TLC plates were visualized using UV light (254nm) and/or by using the appropriate TLC stain. Flash column chromatography was performed using silica gel (Sigma-Aldrich) 40-63 μ m 60 Å treated with a solvent system specified in the individual procedures. Solvents were removed by rotary evaporator at 40°C or below and the compounds further dried using high vacuum pumps. Melting points were obtained on a Reichert-Thermovar melting point apparatus and are uncorrected. Infrared spectra were recorded neat on a Perkin Elmer Frontier FT-IR Spectrometer. Reported absorptions are strong or medium strength unless stated otherwise and given in wavenumbers (cm⁻¹). ¹H and ¹³C NMR were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz. Chemical shifts (δ) are quoted in ppm (parts per million) referenced to residual solvent signals: ¹H δ = 7.27 (CDCl₃), 3.31 (CD₃OD); ¹³C δ = 77.0 (CDCl₃), 49.0 (CD₃OD). Low and high-resolution mass spectra (ESI) were recorded by the Imperial College London Department of Chemistry Mass Spectroscopy Service using a Micromass Autospec Premier and Micromass LCT Premier spectrometer.

Experimental procedures

1-Methyl-2-nitro-1H-imidazole (4)



Methyl iodide (1.5 mL, 23.6 mmol, 1.2 eq.) was added dropwise to a suspension of 2-nitroimidazole (2.23 g, 19.7 mmol, 1.0 eq.) and K₂CO₃ (4.08 g, 29.6 mmol, 1.5 eq.) in MeCN (30 mL) at 0 °C and the reaction mixture was stirred at 65 °C for 3 hours, then quenched with water (30 mL) and concentrated under reduced pressure. The resulting residue was diluted with water (20 mL) and extracted with EtOAc (4 x 50 mL), and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to afford **4** as an off-white solid (1.64 g, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, *J* = 1.0 Hz, 1H, CH), 7.07 (d, *J* = 1.0 Hz, 1H, CH), 4.09 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 128.3, 127.0, 37.5; MS (CI) *m/z* 145 (M+NH₄)⁺; HRMS (CI) *m/z* calc. for C₄H₉N₄O₂ 145.0726 found: 145.0731.

(E)-1,2-Bis(1-methyl-1H-imidazol-2-yl)diazene (1)



Nitromidazole **4** (0.74 g, 5.8 mmol, 1.0 eq.) and Zn dust (0.76 g, 11.6, 2.0 eq.) were added to a solution of 0.1 M aq. NH₄Cl (70 mL) at 45°C, resulting in the immediate formation of an orange solution which was left to stir for 1 hour. The solid was filtered off and the filtrate was extracted with CHCl₃ (2 x 50 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. Purification by column chromatography (95 : 5, DCM : MeOH) afforded **1** as an orange solid (0.27 g, 49%). Mp 224 – 225 °C (DCM); IR (neat) 1679, 1473, 1388, 1287, 1166; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 1.0 Hz, 2H, 2 x CH), 7.20 (d, *J* = 1.0 Hz, 2H, 2 x CH), 4.09 (s, 6H, 2 x CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 153.5 (2C), 131.0 (2C), 124.6 (2C), 32.9 (2C); MS (ES) *m/z* 191 (M+H)⁺; HRMS (ES) *m/z* calc. for C₈H₁₁N₆ 191.1045, found: 191.1037.



Photochemistry

Irradiation at 532 nm or 355 nm was performed using the 2nd or 3rd harmonic of a Nd:YAG (Continuum Surelite I) laser. Irradiation at 408 nm was performed using a 408 nm laser diode at 3.5 mW. 415 nm irradiation was generated using a Lambda Physik tuneable dye laser, pumped by the suitable Nd:YAG harmonic. For the pH jump experiments a 405 nm laser diode was used (~20 mW). UV/vis spectra were recorded on a Agilent 8453 photodiode array spectrophotometer, with samples held in a 4 window 1 cm x 1 cm (or 1mm x 1 cm for the pH jump experiment) quartz Suprasil cuvette, thermostatted with a Peltier temperature controller. The sample was irradiated in the UV/vis spectrometer sample chamber with the light entering at ~90 ° to the spectrometer probe light. Irradiation was continued during acquisition of the UV/vis spectrum when determining photostationary states (PSSs).¹ For light sources with tunable power, the PSS was measured at increasing power in order to ensure that the fast thermal isomerisation of **1** was not preventing the actual PSS being reached under a given set of conditions.

The E/Z compositions of the photostationary states were determined as follows. The authentic UV/vis spectrum of neutral E-**1** was obtained by leaving the sample in the dark for over 5 half-lives after a similarly prepared NMR sample showed no presence of Z isomer. As none of the wavelengths surveyed showed quantitative photoswitching to the Z isomer and the thermal isomerisation of this sample was too fast to allow analysis by NMR or other quantitative methods such as HPLC, the spectrum of the Z isomer was estimated based on the PSS with the highest concentration of Z isomer (408 nm) using the following equation:

$$Z = \frac{PSS_{408nm} - E \times f}{1 - f}$$
 where $f = E$ isomer fraction in PSS

The value of *f* was varied until a range of values were obtained that predicted a sensible UV/vis spectrum for the pure *Z* isomer (Figure S1). The maximum fraction of residual *E* isomer was taken as the highest value that ensured that the absorbance remained positive at all wavelengths. The minimum fraction of residual *E* isomer was taken as the lowest value that ensured that no obvious π - π * absorbance from the *E* isomer remained in the spectrum. The centre point of this range was used to assign the sample at (90 ± 3)% *Z*-1 and used to extrapolate the authentic *Z* isomer UV/vis spectrum with an approximate 3% uncertainty in absorbance. The other PSS ratios were assigned by interpolating between this value and the pure *E* isomer, with an estimated absolute uncertainty of about 5%.



Figure S1: Estimating pure Z spectrum of 1

ⁱ Due to limited access to the various light sources during the course of this work, several of the PSSs had to be obtained on separate occasions. The spectra for the different PSSs were combined (Figure 3A, main text), with adjustments made to account for slight variations in concentration.

pK_a titration

A 1 x 10^{-2} M stock solution of **1** in MeOH was prepared and diluted 1000-fold into 10 mM phosphate-citrate buffer (~pH 3) to 100 mL volume.ⁱⁱ This solution was kept in the dark and the pH was measured using a pH meter. The UV/vis spectrum of a 4 mL aliquot was recorded for both the *E* isomer and the PSS, following 15 seconds irradiation with 415 nm light. This aliquot was then returned to the main sample and given time to thermally isomerise back to the *E* isomer. Aqueous NaOH was then added to increase the pH and the process was repeated.

A rough pH titration was also carried out on the *E*-isomer from pH 0 to 10, in order to observe the 1st and 2nd protonation event.



Figure S2: Spectra for E-1 and 415 nm PSS pH titration (mono-protonation of the azobisimidazole).



Figure S3: Spectra for neutral, mono- and di-protonated E-1

ⁱⁱ This large volume (relative to the cuvette volume) was required so that small increases in pH could be achieved more easily with each addition of aq. NaOH.



Figure S4: pH titration of E-1 showing mono- and di-protonation with sigmoidal fits

pH jump

Initially a pH titration was carried out on the pH indicator (bromocresol purple) in buffer to check the pK_a value obtained (Figure S5). For the pH jump experiments a stock solution of bromocresol purple (BCP) sodium salt $(1.1 \times 10^{-3} \text{ M})$ and $1 (1.1 \times 10^{-3} \text{ M})$ in MeOH was prepared. The pH titration was carried out in buffer (40-fold dilution to 2.7 x 10⁻⁵ M) on both the *E* isomer and the PSS (using the 405 nm laser diode). The absorbance at 590 nm was the same for the *E* isomer and the PSS at all pHs, showing that the indicator is not affected by irradiation. A graph was plotted of the ratio of absorbance at 440 nm (π - π^* *E*-1) and absorbance at 590 nm (BCP) versus pH (Figure S6) and the exponential fit was obtained (for both *E*-1 and the PSS). The pH jump experiment was carried out using the same stock solution, but diluted into water (4-fold dilution to 2.7 x 10⁻⁴ M) in a 1 mm path length cuvette and pH values for the *E* isomer and the PSS were extracted using the exponential equation obtained from the graph (Figure S6).



Figure S5: Bromocresol purple pH titration.



Figure S6: pH jump Left) exponential fit of 440 nm / 590 nm absorbance against pH. At 590 nm only BCP absorbs and at 440 nm both BCP and **1** absorb; Right) obtaining the pH of the *E*-isomer and PSS of **1** in water, using the values obtained from the graph.

pH oscillation

The pH oscillation was carried out in a 10 mm path length cuvette at 2.7×10^{-5} M concentration by irradiating with 405 nm light and then allowing the sample to thermally isomerise back to the *E* isomer (~ 3 minutes). The pH jump achieved was considerably less than at 10^{-4} M, as expected, however the reversibility is clearly demonstrated.



Figure S7: pH oscillation upon cycling between the E isomer and 405 nm PSS

pK_a equation derivation

To measure the pK_a of the *Z* isomer directly in these species was not possible, given the thermal isomerisation rate and the large similarity between the UV/vis spectra for three of the four species under study. Stolow¹ investigated the effect of 4-substitution on the pK_a of cyclohexanecarboxylic acids by treating a system (akin to that in Figure S8) involving multiple thermodynamic equilibria where eq and ax are the conformers with the axial and equatorial carboxylate groups.



Figure S8: A system involving multiple thermodynamic equilibria

Where in that case, an apparent acidity constant K_a of the rapidly equilibrating system (that is measured by pH titration) is a weighted average of the K_a values, K_a^{ax} and K_a^{eq} of a conformationally locked cyclohexanecarboxylic acid where the weighting depends on the equilibration ratio (e.g., K_{base}^{conf}) of the equatorial and axial conformers.

Naively extending this approach to photochemistry by replacing the conformer equilibrium constants with PSS ratios could lead to problems given the fundamentally different nature of such a photochemical switching regarding the non-applicability of the principles of microscopic reversibility and detailed balance to the photoswitchable base. For the system in Figure S9, we repeat the derivation by Stolow and address the limitations of such an approach.



Figure S9: Photoswitching involving additional equilibria

Where the acidity constants for the isomers, *E* and *Z*, are pH and irradiation independent and defined as:

$$K_a^E = \frac{[E][H]}{[EH^+]}$$

$$K_a^Z = \frac{[Z][H]}{[ZH^+]}$$
 2

and the ratios present in the photostationary state, R, in both the acidic and basic forms are given by:

$$R^{acid} = \frac{[ZH^+]}{[EH^+]}$$

$$R^{base} = \frac{[Z]}{[E]}$$

and are not (yet) assumed to be pH independent. We assume that:

- The rate of proton exchange in the acid/base reactions is much faster than rate of the bulk photochemistry² so the relative concentrations of acidic and basic forms of either isomer is determined only by the K_a and the pH of the medium.
- 2. The thermal isomerisation of Z and ZH⁺ is not significant compared to the equivalent photochemical step (both should show first-order kinetics provided that the solution absorbance is low)². This was demonstrated for the high and low pH cases by increasing the laser power until the UV/vis spectrum of the steady state solution is unchanged.

From equations (1), (2), (3) and (4), we see that:

$$\frac{R^{base}}{R^{acid}} = \frac{[Z]}{[E]} \times \frac{[EH^+]}{[ZH^+]} = \frac{[Z][H^+]}{[ZH^+]} \times \frac{[EH^+]}{[E][H^+]} = \frac{K_a^Z}{K_a^E}$$
(5)

hence that R_{base} / R_{acid} must be independent of pH (even if the individual ratios are pH dependant) and determined by the relative pK_a values present. In our system at high pH we measure $R^{base} = 3.76$ at pH 10. Given we know that $pK_a^Z > pK_a^E$ (hence $K_a^Z << K_a^E$) this must mean that $R^{acid} >> 3.76$ at pH 10, hence $[ZH^+]/[EH^+] >> 1$ at pH 10.

If we can assume that R^{base} (and hence, from equation (5) R^{acid}) is independent of pH, this leads to the (perhaps counter-intuitive) result that the low pH PSS is essentially pure ZH⁺. The reliability of this is discussed later.

We define the apparent K_a of the interconverting system akin to Stolow that can be determined by a titration under irraditing conditions:

$$K_{a}' = \frac{\left([E] + [Z]\right)[H^{+}]}{[EH^{+}] + [ZH^{+}]}$$
(6)

As the acid/base equilibria are fully established, we can substituted for [EH⁺] and [ZH⁺] using equations (1) and (2):

$$K_{a}' = \frac{\left([E] + [Z]\right)[H^{+}]}{\frac{[E][H^{+}]}{K_{a}^{E}} + \frac{[Z][H^{+}]}{K_{a}^{Z}}} = \frac{K_{a}^{E}K_{a}^{Z}\left([E] + [Z]\right)}{K_{a}^{Z}[E] + K_{a}^{E}[Z]}$$
(7)

Then, substituting for [Z] using equation (4):

$$K_{a}' = \frac{K_{a}^{E}K_{a}^{Z}([E] + [E]R^{base})}{K_{a}^{Z}[E] + K_{a}^{E}[E]R^{base}} = \frac{K_{a}^{E}K_{a}^{Z}(1 + R^{base})}{K_{a}^{Z} + K_{a}^{E}R^{base}}$$
(8)

If we can assume that R^{base} (and hence, from equation (5) R^{acid}) is independent of pH, then we can used $R^{\text{base}} = 3.76$ (as determined at pH 9) along with $pK_a^{E} = 4.7$, $pK_a' = 5.9$ from the dark and light titrations to give $pK_a^{Z} = 6.0$. The reliability of this assumption is discussed later.

Unlike in the equilibrium situation in Figure S8, where the equilbrium ratios are determined only by the energies of the various species and not by the mechanisms through which they are formed, this may not apply to the photochemistry situation in which extra mechanisms may be possible for forwards and back reactions at different pH.

For example, excitation of EH⁺ could be followed by an excited state proton transfer from EH^{+*} to the medium to generate E* that can then undergo further photochemical reactions, the quantum yield of forming ZH⁺ from exciting EH⁺ may depend on pH and buffer concentration affecting the rates in one direction only (microscopic reversibility does not apply here). This could lead to different ratios of R^{base} and R^{acid} although a full quantitative assessment of this affect would be complicated. However, the isomerisation reaction of these species are typically ultrafast with excited state lifetimes well under 1 ns,³ so the significance of any diffusion controlled proton transfer with buffers in millimolar concentrations is likely to be negligible.

According to equation (8), if R^{base} in pH dependant, K_a' must also be pH dependant given that the individual K_a values are pH independent. This would suggest that the pH titration curve (main text, Figure 3B) may differ in shape (i.e., it may be be flatter or sharper than the one for titration in the dark). This appears not to be the case, so the conclusions presented here are likely to be good estimates.

Thermal isomerisation kinetics

The kinetics were obtained by UV/vis spectroscopy.



Figure S10: Thermal isomerisation of **1** at 25 °C in phosphate/citrate buffer, at pH 12.8 (neutral **1**) and pH 3 (mono-protonated **1**).

Geometry optimisation and TDDFT calculations

General methods

DFT calculations were performed in Gaussian09.⁴ Geometry optimisations and frequency calculations (unscaled) were performed at the B3LYP/6–31G(d,p) level^{5,6} using a PCM continuum solvent model⁷ as implemented in G09 for water, as shown to give good results by Jones and co-workers.⁸ TDDFT calculations were performed at the CAM-B3LYP/6–311G(2df,2p) level,⁹ using the same solvent model. TDDFT calculated excitation energies are unscaled.

Energy minimised structures

SCF energies, enthalpies and free energies are calculated relative to the lowest energy conformer of the *E* isomer of the compound, using water as the solvent model. Two or three conformers were located for each compound. K_{eq} is determined as the equilibrium constant between both calculated isomers. The enthalpy, free energy and K_{eq} are given at 25 °C.

	compound		Dihedr	al angles	SCF energy	Enthalpy	Free Energy	K _{eq}
			/ ° (N=	C-N=N)	/ kJ mol ⁻¹	/ kJ mol ^{−1}	/ kJ mol ^{−1}	
	<i>E</i> - 1	1	0.0	0.0	0.0	0.0	0.0	1
tral		2	0.0	180.0	7.3	4.9	14.3	3.1 x 10 ⁻³
nen	Z- 1	1	-28.8	-28.8	51.4	50.2	52.0	7.7 x 10 ⁻¹⁰
		2	-11.9	134.0	61.2	60.4	65.5	3.3 x 10 ⁻¹²
		1	0.0	0.0	0.0	0.0	0.0	1
	<i>E-</i> 1 H ⁺ (imidazolium)	2	0.0	180.0	10.8	10.5	12.0	7.9 x 10 ⁻³
ted		3	0.0	180.0	5.4	5.3	9.4	2.3 x 10 ⁻²
ona	<i>E-</i> 1H ⁺	1	0.0	0.0	49.7	50.0	51.0	1.1 x 10 ⁻⁹
prot	(azolium)	2	0.0	180.0	42.1	42.9	44.4	1.7 x 10 ⁻⁸
		3	4.4	-178.0	89.2	89.1	95.4	1.9 x 10 ⁻¹⁷
	<i>Z</i> - 1 H⁺	1	-1.1	1.1	16.3	13.7	16.0	1.6 x 10 ⁻³
		2	-2.8	117.9	53.5	52.7	52.4	6.4 x 10 ⁻¹⁰
<i>E</i> -1 (1) relative to 1204.4 1168.1 1167.4								

Table S1: Calculated data for the energy minimised structures of **1**. For each isomer, the lowest energy conformer is in bold.

From the calculated data we can see that

- *E*-**1** is 52.0 kJ mol⁻¹ more stable than *Z*-**1**, whereas *E*-**1**H⁺ is only 16.0 kJ mol⁻¹ than *Z*-**1**H⁺, due to the additional stabilisation caused by hydrogen bonding between the proton and basic imidazole nitrogen in *Z*-**1**H⁺.
- There is a very strong preference to protonate *E*-1 on the imidazole, rather than the azo (44.4 kJ mol⁻¹)

Z-1 is much more basic than E-1 (ΔG(Z-1H⁺ + E-1 - Z-1 - E-1H⁺) = 36.0 kJ mol⁻¹) This can be estimated as 6.3 pK_a units difference, using the following derivation:

Gibbs free energy equation for a system at equilibrium: $\Delta G = -RT ln K_a$

which rearranges to: $K_a = e^{\frac{\Delta G}{-RT}}$

substituting in $pK = -log_{10}K_a$ gives $pK_a = \frac{\Delta G}{\ln(10)RT}$

	compound		Dihed	ral angle	SCF energy	Enthalpy	Free Energy	K _{eq}
			/ ° (N-	C-N=N)	/ kJ mol ⁻¹	/ kJ mol ^{−1}	/ kJ mol ⁻¹	
	E- 2	1	0.0	0.0	0.0	0.0	0.0	1
tral		2	0.0	180.0	1.1	1.4	2.8	3.2 x 10 ⁻¹
nen	Z- 2	1	-31.7	-31.7	56.0	55.0	54.2	3.2 x 10 ⁻¹⁰
		2	0.0	180.0	49.5	48.7	44.7	1.5 x 10⁻ ⁸

Table S2: Calculated data for the energy minimised structures of **2**. For each isomer, the lowest energy conformer is in bold.

Cmpd no.	n-π* $λ_{max}$	n-π* f	π –π* $λ_{max}$ / nm	π –π* f	λ_{max} separation
	/ nm				/ nm
E- 1	430	0	381	0.96	49
Z-1	493	0.17	338	0.44	155
<i>E</i> - 1 H ⁺ (imidazolium)	427	0	400	0.96	27
<i>E</i> - 1 H⁺ (azolium)	-	-	484	0.90	-
<i>Z</i> -1H⁺	453	0.002	383	0.72	70

Table S3: Calculated λ_{max} and oscillator strength (f) for n- π^* and π - π^* excitation (for the energy minimised structures). These are quoted for the lowest energy conformers (as highlighted in table S1). The differences in values for each conformer of an isomer are less than the predicted error of the method.

Structures and Cartesian coordinates for optimised geometry



Ν	-1.190727	-1.482699	1.645622
С	-2.167682	-0.924858	0.924677
Ν	-3.352582	-0.875743	1.630590
С	-3.103483	-1.429786	2.851870
С	-1.766867	-1.795741	2.837656
Ν	-2.158711	-0.419104	-0.355971
Ν	-1.036698	-0.492219	-0.956841
С	-1.027736	0.013418	-2.237534
Ν	-2.004846	0.570618	-2.958767
С	-1.428671	0.883636	-4.150792
С	-0.091865	0.518342	-4.164694
Ν	0.157280	-0.035378	-2.943284
С	1.434774	-0.572807	-2.481363
С	-4.629814	-0.337359	1.169087
Н	0.673334	0.605909	-4.920825
н	-1.209039	-2.267556	3.635317
н	-3.868601	-1.517197	3.608094
н	-1.986628	1.354965	-4.948649
Н	1.750708	-1.392436	-3.130440
Н	2.195037	0.211268	-2.493315
Н	1.302108	-0.939481	-1.465856
Н	-5.390829	-1.120678	1.182060
Н	-4.944560	0.483056	1.817760
Н	-4.497419	0.028521	0.153256



Ν	0.112717	0.018219	-3.047517
С	-1.060956	0.056724	-2.324024
Ν	-2.051533	0.611075	-3.027050
С	-1.496128	0.933612	-4.227284
С	-0.158975	0.576616	-4.263420
Ν	-1.059833	-0.453217	-1.041193
Ν	-2.184186	-0.379383	-0.440612
С	-2.229768	-0.875246	0.841626
Ν	-1.224304	-1.455513	1.601141
С	-1.791274	-1.774857	2.802945
С	-3.115105	-1.379868	2.733313
Ν	-3.380825	-0.825873	1.522734
С	1.404454	-0.510742	-2.618577
Н	0.595055	0.671568	-5.029659
Н	-1.220412	-2.245272	3.589466
Н	-3.870453	-1.474806	3.501103
Н	-2.070071	1.405278	-5.013508
Н	1.712867	-1.322948	-3.280518
Н	2.157506	0.280025	-2.642591
Н	1.304447	-0.886965	-1.603478
С	0.174388	-1.706861	1.256115
Н	0.653042	-2.180019	2.113972
Н	0.240110	-2.366442	0.390414
Н	0.682964	-0.770932	1.023332

E-**1**H⁺ (imidazolium)



Ν	0.154504	-0.083114	-2.940424
С	-1.069947	0.012315	-2.295748
Ν	-2.001288	0.570244	-3.091624
С	-1.363947	0.829371	-4.245485
С	-0.020646	0.430749	-4.173819
Ν	-1.156732	-0.442621	-1.026326
Ν	-2.303954	-0.340639	-0.455930
С	-2.277076	-0.830241	0.822322
Ν	-1.25241	-1.373208	1.512129
С	-1.68008	-1.729062	2.768491
С	-3.00154	-1.392397	2.843353
Ν	-3.35797	-0.836819	1.630983
С	-4.68988	-0.335730	1.277241
С	1.39170	-0.635163	-2.384783
Н	0.77895	0.482406	-4.896810
Н	-1.02644	-2.183262	3.494289
Н	-3.70929	-1.500921	3.648720
Н	-1.86059	1.285669	-5.090852
Н	2.16964	-0.564227	-3.143227
Н	1.686839	-0.066858	-1.502189
Н	1.240513	-1.679732	-2.110826
Н	-5.410438	-1.150957	1.351632
Н	-4.963653	0.467576	1.962190
Н	-4.654149	0.039215	0.257159
Н	-0.324835	-1.481831	1.121462

E-1H⁺ (imidazolium) (2)

	Ŕ	\sim	X
Ν	-2.593140	0.599842	-0.031990
С	-1.586312	-0.300269	-0.021860
Ν	-2.157829	-1.532982	-0.020328
С	-3.530016	-1.378307	-0.029731
С	-3.803690	-0.040226	-0.037057
Ν	-0.293771	0.146261	-0.015376
Ν	0.594563	-0.780507	-0.005913
С	1.881968	-0.357942	0.000610
Ν	2.885029	-1.314453	0.010977
С	4.055468	-0.643580	0.015661

С	3.725582	0.718373	0.007898
Ν	2.391482	0.886814	-0.001330
С	2.705858	-2.766978	0.015971
С	-1.473216	-2.832166	-0.010636
Н	5.010083	-1.147140	0.023871
Н	-4.193920	-2.227212	-0.030407
Н	-4.741345	0.489262	-0.045237
Н	4.413563	1.552618	0.008797
Н	2.161882	-3.076967	-0.876952
Н	3.689274	-3.234043	0.024521
Н	2.150019	-3.069364	0.904180
Н	-2.238007	-3.607088	-0.012486
Н	-0.843966	-2.925467	-0.894789
Н	-0.855510	-2.918306	0.882346
Н	-2.434782	1.600064	-0.035274

 $E-\mathbf{1}H^+$ (imidazolium) (3)



Ν	0.133569	0.025471	-3.080073
С	-0.940703	-0.000126	-2.264122
Ν	-1.972216	0.552196	-2.934298
С	-1.556553	0.933993	-4.187075
С	-0.234703	0.603604	-4.279187
Ν	-0.912129	-0.512601	-0.992847
Ν	-2.062394	-0.418808	-0.424465
С	-2.187157	-0.884960	0.837133
Ν	-1.229156	-1.477474	1.659559
С	-1.858929	-1.763237	2.820043
С	-3.184540	-1.339045	2.678811
Ν	-3.377443	-0.803175	1.463813
С	1.471399	-0.476639	-2.750469
Н	0.466621	0.729608	-5.087254
Н	-1.345803	-2.233497	3.645733
Н	-3.973268	-1.411961	3.414294
Н	-2.217727	1.399862	-4.898480
Н	1.741784	-1.264585	-3.454299
Н	2.187784	0.343073	-2.815394
Н	1.450735	-0.873067	-1.738517
С	0.181477	-1.757782	1.378823
Н	0.612089	-2.227986	2.262100
Н	0.265239	-2.427366	0.522888
Н	0.708825	-0.830069	1.156937
Н	-2.896843	0.649434	-2.532566

*E-***1**H⁺ (azolium) (1)



			0
Ν	-3.405184	-0.835304	1.664380
С	-2.257610	-0.859929	0.886083
Ν	-1.216068	-1.400120	1.549862
С	-1.700699	-1.720682	2.754243
С	-3.066093	-1.376149	2.846205
Ν	-2.272023	-0.384274	-0.361867
Ν	-1.157977	-0.452186	-1.000979
С	-1.019046	-0.001052	-2.296819
Ν	0.185091	-0.087956	-2.951766
С	-0.039367	0.442486	-4.190369
С	-1.374071	0.823160	-4.216927
Ν	-1.978171	0.542988	-3.031592
С	1.454038	-0.628327	-2.454523
С	-4.720596	-0.321122	1.270703
Н	0.743553	0.504515	-4.929793
Н	-1.095647	-2.179468	3.523446
Н	-3.770687	-1.486651	3.656468
Н	-1.910280	1.281333	-5.035273
Н	2.194719	-0.534378	-3.246489
Н	1.796047	-0.061475	-1.586020
Н	1.345399	-1.684744	-2.200014
Н	-5.454299	-1.125908	1.328627
Н	-5.004976	0.491636	1.939964
Н	-4.653971	0.046412	0.249272
Н	-0.346207	-0.859041	-0.521113

 $E-\mathbf{1}H^+$ (azolium) (2)

4	J.	X	Ĺ
Ν	0.154269	0.035634	-3.120069
С	-0.968873	0.025848	-2.309803
Ν	-2.035873	0.566934	-2.926665
С	-1.591521	0.924500	-4.138450
С	-0.227769	0.601868	-4.279437
Ν	-0.917243	-0.480499	-1.070214
Ν	-2.015372	-0.439273	-0.405880
С	-2.189636	-0.899713	0.876017
Ν	-1.241539	-1.480895	1.676812

С	-1.891055	-1.764656	2.846144
С	-3.202958	-1.338253	2.689889
Ν	-3.381441	-0.799572	1.457555
С	1.489128	-0.468552	-2.783218
Н	0.452484	0.741043	-5.105903
Н	-1.381189	-2.234426	3.672881
Н	-4.005801	-1.401006	3.409762
Н	-2.226741	1.393708	-4.876338
Н	1.763615	-1.259464	-3.482138
Н	2.209536	0.348035	-2.843062
Н	1.464349	-0.864173	-1.770799
С	0.169946	-1.760272	1.393043
Н	0.598853	-2.230109	2.276471
Н	0.254839	-2.434849	0.540723
Н	0.699935	-0.832314	1.176907
Н	-2.856873	-0.034405	-0.837210





Ν	-2.738797	0.587156	-0.044876
С	-1.728835	-0.339717	0.012870
Ν	-2.163435	-1.585725	0.098220
С	-3.520456	-1.469076	0.095884
С	-3.897518	-0.138691	0.009372
Ν	-0.395052	0.044925	-0.013309
Ν	0.541011	-0.836153	-0.038028
С	1.838882	-0.547427	-0.028293
Ν	2.517623	0.682387	0.045490
С	3.827003	0.386588	0.017926
С	3.933253	-1.015293	-0.075333
Ν	2.725814	-1.573256	-0.098263
С	-2.637009	2.045222	-0.148902
Н	-4.864237	0.339273	-0.017027
Н	4.587126	1.152352	0.068902
Н	4.846010	-1.592223	-0.121499
Н	-4.165274	-2.333568	0.158660
Н	-3.641890	2.445965	-0.268385
Н	-2.196302	2.466129	0.757491
Н	-2.045956	2.323652	-1.023758
С	1.970186	2.038495	0.157986
Н	2.800880	2.736554	0.244342
Н	1.402116	2.294885	-0.739405
Н	1.355397	2.125103	1.057364
Н	-0.201051	1.045939	-0.010380

Z-**1** (1)



С	0.282617	-0.015127	0.400565
Ν	0.475741	0.291265	1.685619
С	1.812847	0.511223	1.803723
С	2.451404	0.333866	0.587019
Ν	1.469884	0.024950	-0.307789
С	1.645977	-0.267387	-1.726319
Н	3.490157	0.393842	0.300353
Ν	-0.881806	-0.108894	-0.343794
Ν	-2.028098	-0.418331	0.106068
С	-2.284299	-1.017447	1.328413
Ν	-3.594489	-0.988850	1.770657
С	-3.660026	-1.807476	2.859256
С	-2.388945	-2.337128	3.012179
Ν	-1.542169	-1.844520	2.068513
Н	-2.060921	-3.051097	3.755602
Н	-4.570514	-1.938639	3.423695
С	-4.681659	-0.189195	1.216280
Н	2.263437	0.791905	2.746175
Н	2.470128	0.332092	-2.114357
Н	1.865382	-1.327270	-1.880048
Н	0.723897	-0.014206	-2.248147
Н	-5.622405	-0.724008	1.351022
Н	-4.742599	0.781919	1.714623
Н	-4.490242	-0.034700	0.155090





Ν	-1.559275	-2.098675	2.017395
С	-2.195964	-1.174028	1.224506
Ν	-3.312376	-0.722958	1.783740
С	-3.362942	-1.328154	3.013839
С	-2.306681	-2.194926	3.169576
Ν	-1.888191	-0.890880	-0.121790
Ν	-0.751335	-0.497574	-0.524795
С	0.283534	-0.077238	0.287423
Ν	0.317468	0.223987	1.590683
С	1.545979	0.759596	1.802081
С	2.279719	0.783857	0.623332
Ν	1.470152	0.263490	-0.335885
С	1.811867	0.062217	-1.742511
н	3.282548	1.118988	0.407352
н	-2.038485	-2.880085	3.959347
н	-4.162896	-1.127701	3.713292
н	1.858510	1.107674	2.776923
н	2.415370	0.902657	-2.086573
н	2.374880	-0.865862	-1.867997
н	0.889395	0.005140	-2.316858
С	-0.361196	-2.873586	1.722368
н	-0.442745	-3.848087	2.205188
Н	-0.276307	-3.023859	0.645341
Н	0.529407	-2.355442	2.084640

Z-1H⁺(1)

С	0.531970	-0.309220	0.327092
Ν	0.618739	0.201467	1.576756
С	1.756395	0.943508	1.689804
С	2.393866	0.891421	0.473495
Ν	1.629258	0.119142	-0.357462
С	1.945946	-0.222107	-1.748554
Н	3.317062	1.341496	0.146757
Ν	-0.375643	-1.100067	-0.329225
Ν	-1.452499	-1.603098	0.142714
С	-1.968581	-1.489262	1.396142
Ν	-3.156064	-2.158363	1.633138
С	-3.501870	-1.921014	2.916809
С	-2.511135	-1.097752	3.451078
Ν	-1.578389	-0.838858	2.514639
Н	-2.451070	-0.697322	4.452278
Н	-4.395668	-2.332635	3.359374
С	-3.886872	-2.988586	0.672547
Н	2.030320	1.448570	2.601470
Н	2.732968	0.448182	-2.088876
Н	2.288852	-1.256063	-1.806321
Н	1.055827	-0.096480	-2.362025
Н	-4.850278	-3.245969	1.109365
Н	-4.035089	-2.432101	-0.251773
Н	-3.322350	-3.898063	0.462591
н	-0.142508	-0.017598	2,269227

Z-**1**H⁺(2)



NI	1 (1) [1	2 205022	
IN O	-1.012551	-2.205822	2.088052
С	-2.058260	-1.352497	1.207532
Ν	-3.107734	-0.728886	1.765688
С	-3.309193	-1.210171	3.046440
С	-2.374174	-2.175538	3.246340
Ν	-1.746201	-1.259162	-0.158795
Ν	-0.657656	-0.758328	-0.585914
С	0.278083	-0.165971	0.202118
Ν	0.275434	0.075180	1.523765
С	1.418312	0.740325	1.765605
С	2.144082	0.916695	0.580051
Ν	1.416692	0.346398	-0.400244
С	1.780796	0.251851	-1.816107
Н	3.093207	1.394776	0.390980
Н	-2.185127	-2.811105	4.095565
Н	-4.089425	-0.831697	3.684831
н	1.693985	1.076524	2.755247
н	2.159846	1.217160	-2.151435
н	2.548682	-0.512759	-1.948678
н	0.892697	-0.018293	-2.382448
С	-0.462863	-3.147701	1.889158
Н	-0.620578	-4.059659	2.462785
н	-0.383126	-3.397158	0.831349
н	0.446445	-2.644866	2.223454
Н	-3.645708	-0.005544	1.305970
			-

E- 2 (1)			
>	\checkmark		\checkmark
н	4.228687	1.918811	0.190032
С	3.532600	1.093346	0.120230
Ν	2.221493	1.186595	0.117437
С	1.779819	-0.121603	0.011892
С	2.859065	-0.989793	-0.047600
Ν	3.974549	-0.201270	0.022558
Н	2.907865	-2.064252	-0.131087
С	5.363474	-0.645849	-0.001667
Н	5.563635	-1.310873	0.841369
Н	6.011144	0.227921	0.071877
Н	5.577290	-1.171496	-0.934948
Ν	0.466321	-0.575300	-0.033625
Ν	-0.421616	0.332437	0.030477
С	-1.735088	-0.121311	-0.015007
Ν	-2.176705	-1.429523	-0.120575
С	-3.487815	-1.336333	-0.123293
Н	-4.183864	-2.161830	-0.193086
С	-2.814369	0.746835	0.044567
Ν	-3.929814	-0.041738	-0.025526
Н	-2.863216	1.821287	0.128117
С	-5.318749	0.402817	-0.001442
Н	-5.966412	-0.471021	-0.074191
Н	-5.519072	1.067188	-0.844957
Н	-5.532407	0.929177	0.931462

E- 2 (2)				
ý	\mathfrak{I}		Y	
С	-2.688618	0.946364	0.006139	
С	-1.817535	-0.131945	-0.079786	
Ν	-2.526961	-1.314640	-0.153513	
С	-3.791622	-0.954512	-0.112827	
Ν	-3.943960	0.404076	-0.016198	
Ν	-0.424482	-0.190213	-0.100949	
Ν	0.136526	0.948697	-0.028706	
С	1.524689	0.936289	-0.046573	
С	2.272534	2.101915	0.025326	
Ν	3.580609	1.706534	-0.018188	
С	3.572637	0.337804	-0.113263	
Ν	2.358867	-0.165229	-0.133380	
С	4.756813	2.568281	0.027274	
С	-5.206014	1.133263	0.050187	
Н	-2.515623	2.007568	0.078050	
Н	1.977090	3.136634	0.100877	
Н	-4.645425	-1.617175	-0.148521	
Н	4.494630	-0.226201	-0.163786	
Н	-6.026762	0.417029	0.010596	
Н	-5.268372	1.697713	0.983186	
Н	-5.290459	1.821278	-0.793902	
Н	4.752393	3.260325	-0.817661	
Н	4.774348	3.136561	0.959802	
Η	5.649336	1.944745	-0.027144	

Z-**2** (1)



С	-2.368972	-1.023137	1.081328
С	-3.621732	-0.959101	1.671371
Ν	-3.532797	-1.704692	2.815684
С	-2.262992	-2.220655	2.847305
Ν	-2.124751	-0.490037	-0.192456
Ν	-0.983306	-0.169178	-0.638404
С	0.170547	-0.015128	0.143412
Ν	0.243249	0.417892	1.454863
С	1.528081	0.572658	1.684694
Ν	2.302326	0.262712	0.596536
С	1.440519	-0.086721	-0.407690
Н	1.777182	-0.362534	-1.394785
н	-4.525057	-0.447545	1.377962
С	3.757953	0.308164	0.521439
Н	-1.945074	-2.884971	3.639855
С	-4.584931	-1.918196	3.802585
Н	1.969891	0.920526	2.608985
Н	-4.211032	-2.592545	4.573323
Н	-4.870464	-0.970799	4.265594
н	-5.461534	-2.367204	3.330428
Н	4.075156	0.990368	-0.270365
Н	4.147238	0.664394	1.475451
н	4.160099	-0.687754	0.321709

*Z-***2** (2)

	\downarrow	1 1	大
m			
C	1.58/890	0.513309	-0.5/9644
C	0.615462	-0.052287	0.240479
Ν	1.196471	-0.439991	1.439412
С	2.464604	-0.114494	1.329144
Ν	2.754325	0.467505	0.122347
Ν	-0.686239	-0.126924	-0.249961
Ν	-1.738708	-0.589681	0.289926
С	-1.923885	-1.170615	1.546909
Ν	-3.242302	-1.561085	1.783469
С	-3.244574	-2.078767	2.985855
Ν	-2.000198	-2.055232	3.564338
С	-1.149591	-1.481989	2.664885
С	-1.649775	-2.548776	4.892187
С	4.062423	0.943470	-0.317663
Н	1.518135	0.925309	-1.574106
Н	-0.100926	-1.332805	2.851805
Н	-4.100663	-2.489315	3.504464
Н	3.227737	-0.269617	2.079740
Н	-2.546048	-2.953288	5.362889
Н	-0.898533	-3.338103	4.817403
Н	-1.258664	-1.736037	5.508271
Н	4.022773	2.014296	-0.527430
н	4.785890	0.760784	0.476844
Н	4.374864	0.409065	-1.217126

Comparison of calculated and experimental spectra

The calculated spectra below are the weighted averages of the energy minimised structures of each isomer. After TDDFT calculations of the excitation energies, the spectra were simulated using the Gaussview 5 program and default peak widths and unscaled excitation energies. TDDFT spectra were then scaled relative to the *E* isomer experimental spectra so that the maximum peak heights were similar for easy comparison.

The TDDFT predictions of the excitation wavelengths for the neutral compounds were slightly blueshifted compared to the experimental spectra in terms of the π - π * transition. Both the calculated and experimental *E* spectra had no n- π * absorbance, while the calculated n- π * absorbance for the *Z* isomer matched the experimental spectrum well. The blue-shift in calculated π - π * absorbances compared to the experimental spectra was more apparent for the protonated compounds.

The TDDFT calculations were able to predict the general features of the spectra well, allowing visualisation of the separation between absorbances that is necessary to achieve good photoswitching.



Figure S11: Calculated (CAM-B3LYP/6-11G(2df,2p)) and experimental UV/vis spectra for neutral and protonated **1**.

GIAO ¹³C NMR calculations

Geometry optimisations were repeated for the neutral and protonated species using the PCM solvent method for methanol at the B3LYP/6–31G(d,p) level of theory.^{5,6} The GIAO method was used for NMR chemical shift calculations,^{10,11} at both the B3LYP/6-311G(2df,2p) and mPW1PW91/6-311G(2df,2p) levels to ensure that changing the functional didn't alter the results significantly. NMR shielding tensors (σ) were calculated for the lowest energy conformers and also for benzene as a reference. Chemical shifts were obtained using the calculated tensor and experimental chemical shifts for benzene.¹² The calculated chemical shifts were then scaled using the calculated and experimental values for neutral *E*-**1**, by plotting a graph of δ_{calc} vs δ_{exp} and obtaining the slope and intercept of the linear fit.¹³

$$\delta_{scaled} = \frac{\delta_{calc} - intercept}{slope}$$

Energy minimised structures

SCF energies, enthalpies and free energies are calculated relative to the lowest energy conformer of each species. Population fraction is the normalised Boltzmann factor at 25 °C.

	compound		SCF energy	Enthalpy	Free	Population
			/ kJ mol ^{−1}	/ kJ mol ⁻¹	Energy / kJ mol ⁻¹	fraction
	E- 1	1	0.0	0.0	0.0	0.978
neutral		2	7.4	7.4	9.4	0.022
	<i>Z</i> -1	1	0.0	0.0	0.0	0.996
		2	61.4	60.6	13.7	0.004
protonated	<i>E-</i> 1 H⁺ (imidazolium)	1	0.0	0.0	0.0	0.971
		2	10.8	10.6	12.1	0.007
		3	5.4	5.3	9.4	0.022
	<i>E-</i> 1 H⁺ (azolium)	1	7.6	7.2	6.7	0.062
		2	0.0	0.0	0.0	0.938
	<i>Z</i> - 1 H ⁺	1	0.0	0.0	0.0	1.000

Table S4: Calculated data for the energy minimised structures of **1** with methanol as the solvent model. For each isomer, the lowest energy conformer is in bold.

NMR shielding tensors and chemical shifts



		Shielding tensor (σ)			
		C1/C1'	C2/C2'	C3/C3'	C4/C4'
	<i>E</i> - 1 (neutral)	21.85	52.40	44.58	150.36
B3LYP	<i>E-</i> 1 imidH⁺	24.46	48.03	46.98	147.50
	<i>E-</i> 1 azoH⁺	31.69	38.87	39.62	145.38
	<i>E</i> - 1 (neutral)	27.34	56.46	49.30	154.29
mPW1PW91	<i>E-</i> 1 imidH⁺	29.87	52.58	51.27	151.51
	<i>E-</i> 1 azoH⁺	37.19	43.38	44.05	149.48

Table S5. Calculated shielding tensors.

			Scaled chemical shifts (δ)		
		C1/C1'	C2/C2'	C3/C3'	C4/C4'
	<i>E-</i> 1 (neutral)	153.49	125.56	132.71	35.98
B3LYP	<i>E-</i> 1 imidH⁺	151.10	129.55	130.51	38.60
	<i>E-</i> 1 azoH⁺	144.49	137.92	137.24	40.54
	<i>E-</i> 1 (neutral)	153.03	126.15	132.75	35.86
mPW1PW91	<i>E-</i> 1 imidH⁺	150.69	129.73	130.94	38.43
	<i>E-</i> 1 azoH⁺	143.93	138.22	137.61	40.30

Table S6. Calculated scaled chemical shifts.

	B3	LYP	mPW1PW91		
Carbon number	Δδ(azoH-exp)	Δδ(imidH-exp)	Δδ(azoH-exp)	Δδ(imidH-exp)	
1/1'	-7.07	-0.46	-7.63	-0.87	
2/2'	9.70	1.33	10.00	1.51	
3/3'	7.69	0.96	8.06	1.39	
4/4'	5.90	3.96	5.66	3.79	

Table S7. Difference in calculated and experimental ¹³C NMR shifts for *E*-**1**H⁺, with protonation on either the azo or the imidazole nitrogen. Experimental values are for the deuteronated imidazole.



Figure S12: Difference in calculated and experimental ¹³C NMR shifts for *E*-**1**H⁺, with protonation on either the azo or the imidazole nitrogen. Experimental values are for the deuteronated imidazole.



Figure S13: Calculated vs. experimental ¹³C chemical shifts for neutral *E*-**1**. Intercept and gradient values used to scale calculated chemical shifts.

Neutral and deuteronated NMR in CD₃OD

The deuteronated sample was prepared by addition of 1 equivalent of acetyl chloride to neutral *E*-**1** in CD_3OD (to form $AcOCD_3$ and D^+).



Figure S14: Proton and carbon NMR for neutral E-1 in CD₃OD.



Figure S15: Proton and carbon NMR for deuteronated *E*-**1** in CD₃OD.

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