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Kinetic analysis of the thermal isomerisation pathways in an asymmetric double azobenzene switch†

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Here we report a photochemical and kinetic study of the thermal relaxation reaction of a double azobenzene system, in which two azobenzene photochromic units are connected via a phenyl ring. Upon UV irradiation, three thermally unstable isomers are formed. Kinetic studies using arrayed 1H-NMR spectroscopy revealed four distinct barriers for the thermal reversion to the stable isomer. The double isomerised Z,Z-2 can revert thermally to the E,E-2 isomer via either of two isomerisation pathways. The thermal Z to E isomerisations are not significantly affected by the state of the neighbouring azo-switching unit in the meta position. These findings are supported by quantum chemical calculations on the thermal Z to E isomerisation.

1. Introduction

Recently organic multi-component materials based on photochromic switches1,2 (such as stilbenes, azobenzenes, diarylethenes, spiropyran, and overcrowded alkenes) have attracted increasing attention due to their possible use in data storage devices3 and sensors.4 Addressable multi-component systems based on several photochromic components are of interest to the fields of optical computing, such as in logic gates, field-effect transistors, and high density data storage.1

Single molecule systems have potential advantages over systems derived from mixtures in solution, polymer matrices, or single crystals.5 These advantages include high resolution and multi-frequency single molecular memories.6 Many examples of systems containing one5 or several7 addressable diarylethene units have been reported. Other examples include overcrowded alkenes,8 dihydropyrenes,9 bisnaphthopyrans,10 stilbenes,11 spiropyran,12 and azobenzene.12

Double azobenzenes (Scheme 1) are systems with a discrete number of azobenzene units connected in a meta orientation relative to one another and are generally used as dyes in the textile and colour industry. Azobenzene oligomers containing two13–15 or three16,17 azobenzene switching units that share a central phenyl ring have been reported; however, their switching behaviour has only scarcely been studied.

The proximity of two or more photochromic components in a multi-component system can lead to unexpected interactions that enhance their function or render the nano-scaled system inoperative. These interactions include photochemical quenching, energy transfer, steric interactions and dipole–dipole interactions. Some examples of changes to the photochemical and thermal behaviour of meta substituted bis-azobenzenes have been reported.12 For instance, Spada and co-workers18 have shown that irradiation (λ = 345 nm) of a (E,E)-m-bis-azobenzene leads to a mixture of three isomers E,E, E,Z and Z,Z at the photo-stationary state (PSS). Analysis of the quantum yield of the E to Z photo-isomerisations revealed that the isomerisation of the first azo-unit quenches the photo-isomerisation of the second azo-unit.

An open question, however, is how the individual units interact in the thermal reversion, i.e. does the switching of one unit

ESI available: Synthesis, characterisation, calculated 1H-NMR spectra, ESP maps, temperature controlled NMR experiments and fitting model for the kinetic analysis. See DOI: 10.1039/c2cp23756c
influence the second unit’s ability to switch. In the development of complex multicomponent systems it is important to understand whether the large dipole change that accompanies switching is in fact sufficient to control switching pathways.

Herein we describe the thermal relaxation mechanism of a photochromic double switch, based upon an asymmetric meta-bis-azobenzene (Scheme 1), observed after photochemical isomerisation. The asymmetry in the bis-azobenzene switch is due to the phenol ester moiety, which is either in the ortho or para position relative to the azo switching units. In contrast to bis-azobenzene systems described previously the asymmetry allows for distinguishing between the two switching units and for studying them individually. Bis-azobenzene switch 2 exhibits photochromic behaviour similar to mono-azobenzene switch 1 upon irradiation with UV light. Upon photochemical formation of the thermally unstable $Z,Z$ isomer there are two possible thermal isomerisation pathways back to the stable $E,E$ isomer. Pathway (A) goes from the $Z,Z$ isomer to ortho-$Z,E$ (relative to the butanoate moiety), followed by a final isomerisation to the $E,E$ isomer, while in pathway (B) the $Z,Z$ isomer thermally isomerises to the para-$Z,E$ (relative to the butanoate moiety) isomer first (Fig. 1).

2. Results

Synthesis and characterisation

Azobenzene $E$-1 and bis-azobenzene $E,E$-2 were synthesised using the procedure described below (see ESI† for details). Aminobenzoic acid tert-butyl ester 4 was diazotised in a diluted aqueous HCl solution containing NaNO₂ at 0 °C. Subsequently, the 4-diazo benzoic acid tert-butyl ester 5 was treated with phenol and KOH in MeOH at 0 °C to obtain azobenzene switch $E$-6 (see ESI†) and bis-azobenzene switch $E,E$-3 in 68% and 9% yield, respectively. The ester derivatives $E,E$-2 and $E$-1 were prepared by introducing a butyric acid moiety via N,N′-dicyclohexylcarbodiimide (DCC) and 4(dimethylamino)pyridine (DMAP) coupling providing the desired switches $E,E$-2 and $E$-1 in 93% and 97% yield, respectively (Fig. 2).22

Characterisation of photochemical and thermal isomerisation

Initially, the photochromic activity of switch 3 was investigated under neutral, acidic and basic conditions by UV/Vis spectroscopy. Irradiation ($\lambda_{\text{exc}}$ 355 nm, at 20 °C) of 3 did not result in changes in the UV/Vis spectrum under any of the conditions examined (Fig. 3 and Fig. S13 and S14, ESI†). This is ascribed to the effect of the phenol substituent on the central phenyl ring (i.e. the resonance structure to which the azobond contributes significantly).23 Further investigation of photochromic properties under acidic or basic conditions did not lead to the formation of new isomers (see Fig. S12 and S13, ESI†).22

Esterification of the phenolic group as in bis-azobenzene 2 restores the switching functionality of the bis-azobenzene. Additionally the introduction of the butanoate moiety allows for the kinetic study of the thermal isomerisation mechanisms of each of the azobenzene switching units using $^1$H-NMR spectroscopy (Fig. 12).

Upon irradiation at $\lambda_{\text{exc}}$ 365 nm the UV/Vis absorption spectrum of 1 undergoes a hypsochromic shift with the band at $\lambda_{\text{max}} = 332$ nm decreasing and a new band appearing at $\lambda_{\text{max}} = 261$ nm (Fig. 4). Additionally new bands appear up-field from the $E$-2 isomer in the $^1$H-NMR spectrum (Fig. 5). At the photostationary state (PSS) the signal of proton b shifts from 2.581 ppm (b$^6$) to 2.495 ppm (b$^6$). From the integration of these signals the $Z/E$ ratio was determined to be 81 : 19.

The switching behaviour of bis-azobenzene 2 was studied using $^1$H-NMR and UV/Vis absorption spectroscopy in order to gain an understanding of its photochemical and thermal behaviour. $E,E$-2 was irradiated at $\lambda_{\text{exc}}$ 365 nm, in CH$_2$Cl$_2$ (Scheme 1), at -20 °C to prevent the reverse thermal isomerisation from the thermally unstable isomers to a stable $E,E$ isomer. Upon irradiation, the intensity of the long wavelength band decreased ($\lambda_{\text{max}} = 331$ nm) and a new band appeared at $\lambda_{\text{max}} = 268$ nm. This hypsochromic shift is characteristic for

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Fig. 1 Schematic representation of the possible pathways for thermal relaxation from unstable isomer $Z,Z$-2 to stable isomer $E,E$-2.

Fig. 2 Synthesis of phenol substituted azobenzene switch 3 and butanoate functionalised azobenzene switch 2.

Fig. 3 Changes in the UV/Vis absorption spectra of E-3 in acetonitrile (3.87 × 10⁻⁵ M) upon irradiation ($\lambda_{\text{exc}}$ 365 nm at 20 °C). E-3 (——), E-3 irradiated at $\lambda_{\text{exc}}$ 355 nm (-----).
azobenzene systems (Fig. 6). 25 The initial isosbestic point at 284 nm was not retained upon irradiation, indicating that several photochemical processes take place (Fig. 6 inset).

Irradiation ($\lambda_{\text{exc}}$ 355 nm) of $E,E$-2 in C$_2$D$_4$Cl$_2$ at 20 °C led to an up-field shift in the signals in the aliphatic region of the 1H-NMR spectrum of 2. The signal for proton b$_{E,E}$ (Fig. 7) at approximately 2.69 ppm diminished in intensity and three new signals appeared at 2.60, 2.53 and 2.48 ppm for the para-Z,E, ortho-Z,E, and the Z,Z isomers (Fig. 8), respectively. 1H-NMR spectroscopy revealed that UV irradiation results in the formation of three thermally unstable isomers at the PSS; para-E,Z-2 (13%), ortho-Z,E-2 (15%), and Z,Z-2 (33%). Thermal-reversibility of the switching was demonstrated by 1H-NMR spectroscopy (Fig. 8); heating of the PSS mixture at 40 °C leads selectively to thermal reversion to the stable E,E isomer.

The isomers in the PSS mixture of $E,E$-2 were separated by preparative TLC. 26 The four isomers were isolated 27, 28 and studied by 1H-NMR and NOE-spectroscopy. 29 The $E,E$-2 (2.69 ppm, $R_f$ = 0.44) and Z,Z-2 (2.48 ppm, $R_f$ = 0.12) isomers could be identified by 1H-NMR spectroscopy (Fig. 8). The para-Z,E and ortho-Z,E isomers were identified using three methods. First, the chemical shifts in the 1H-NMR spectra of switch 1 (4,4′-substitution pattern) were compared with those in the 1H-NMR spectra of the isomers para-Z,E and ortho-Z,E. The change in chemical shift between the signal for protons 2-b$_{p-Z,E}$ and 2-b$_{E,E}$ equals 0.083 ppm while the change between protons 2-b$_{p-Z,E}$ and 2-b$_{E,E}$ equals 0.123 ppm (Fig. 8). This change corresponds well to the change in chemical
shifts observed between \( \text{I-}b^E \) and \( \text{I-}b^Z \) which is 0.086 ppm (Fig. 5). Therefore, the signal at 2.60 ppm is representative of a \( 4,4' \)-substitution pattern and corresponds to the \( \text{para-Z,E-2} \) isomer while the signal at 2.56 ppm corresponds to the \( \text{ortho-Z,E-2} \) isomer.

The second method for the identification of the \( \text{para-Z,E} \) and \( \text{ortho-Z,E} \) isomers involved the calculation of the \( ^1\text{H-NMR} \) chemical shifts of the four isomers of 2 with the Gaussian 09 QC package\(^3\) using density functional theory (Fig. 9). Each molecular geometry was first optimised in the gas-phase with the OPBE functional and a 6-311G(d,p) basis set. The subsequent \( ^1\text{H-NMR} \) simulation was then performed with the GIAO method, using the same functional and basis set, and with the IEFPCM solvation model (solvent: dichloroethane). The relative chemical shifts in the calculated \( ^1\text{H-NMR} \) spectra are in good agreement with the experimentally obtained spectra—both absolute and relative positions of the calculated signals for the aromatic protons show good correspondence. This provided further evidence for the assignment of the \( \alpha-Z,E-2 \) and \( p-Z,E-2 \) isomers.

Finally, a distinction between the different isomers could also be made based on the retention factor \( (R_t) \) of each of the isomers on silica gel TLC plates. We observed that the \( Z \)-isomers generally displayed a lower \( R_t \) than the \( E \)-isomers. A rationale for this is that, for a \( Z \)-azo group, the lone pairs on the nitrogen atoms are situated on the same side of the molecule and thereby lie relatively unexposed on the periphery of the molecule.

For an \( E \)-azo group however, the nitrogen atoms are less easily accessible due to steric hindrance from the neighbouring phenyl groups, which makes it more difficult for them to interact with the silica gel phase. The exposed \( Z \)-azo groups could be visualised by mapping the electrostatic potential (ESP) for each molecule (Fig. 10).\(^32\) In these maps, the \( Z \)-azo groups are visible while the \( E \)-azo groups are somewhat obscured.

In agreement with the above rationale, we found that the thermally unstable \( \text{Z,Z-2} \) isomer, which contains two \( Z \)-azo groups, displayed the lowest \( R_t \) value of the four isomers. The stable \( E,E-2 \) isomer on the other hand displayed the highest \( R_t \) value.

The significant difference in \( R_t \) between \( \text{ortho-Z,E-2} \) and \( \text{para-Z,E-2} \) (0.20 and 0.33) is remarkable as both isomers contain one \( Z \)-azo and one \( E \)-azo group. The sole difference between these isomers is the position of the \( Z \)-azo bond relative to the butanoate moiety on the central phenyl ring. The ESP maps indicate that with the \( \text{ortho-Z,E-2} \) isomer the carbonyl group of the butanoate moiety is more exposed than in the case with the \( \text{para-Z,E-2} \) isomer where it is shielded by one of the phenyl groups attached to the \( Z \)-azo group. This indicates that the isomer with the lower \( R_t \) of 0.20 is the \( \text{ortho-Z,E-2} \) isomer while the \( R_t \) of 0.33 is of the \( \text{para-Z,E-2} \) isomer. This conclusion is in full agreement with the experimentally obtained and calculated \( ^1\text{H-NMR} \) spectroscopic data described above.

**Photochemical \( Z \) to \( E \) isomerisation of switch 2**

The photo-reversibility of the switching was demonstrated by UV-Vis absorption spectroscopy (Fig. 11). A sample containing a PSS mixture of 2 (Fig. 11) in \( \text{CH}_2\text{Cl}_2 \), could be reverted to the \( E,E-2 \) isomer upon irradiation with visible light \( (\lambda_{\text{exc}} 450 \text{ nm}) \), confirming the photo-reversibility of switch 2 with isobestic points maintained.

**Thermal behaviour of \( Z \) to \( E \) isomerisation of switch 1**

The thermal \( Z \) to \( E \) isomerisation of a PSS\(_{365} \text{nm} \) mixture of switch 1 was studied at four temperatures in dichloroethane-\( d_4 \) (50, 65, 70 and 75 °C) and DMSO-\( d_6 \) (60, 70, 80 and 85 °C)
by ¹H-NMR spectroscopy using a thermal array experiment (see ESI). A first order exponential decay could be fitted to the collected traces, from which the rate constant k for the thermal Z to E isomerisation could be determined. The thermodynamic parameters ΔG°, ΔH° and ΔS° for the thermal isomerisation are shown in Table 1 and were calculated using the Eyring equation.

\[ k = \frac{k_B T}{h} e^{-\frac{\Delta H°}{RT}} \]  

(1)

**Thermal behaviour of Z to E isomerisation of switch 2**

The photochemically generated thermally unstable Z,Z-2 isomer has two possible thermal isomerisation pathways to the stable E,E-2 isomer. Pathway (A) goes from the Z,Z isomer to Z,E, followed by a final isomerisation to the E,E isomer, while in pathway (B) Z,Z-2 isomerises to the E,Z isomer followed by isomerisation to E,E-2 (Fig. 1). A kinetic study of pure Z,Z-2 proved to be experimentally inaccessible. However, using thermal array ¹H-NMR spectroscopic experiments at five temperatures (28.1, 45.0, 54.5, 64.6 and 68.7 °C) a kinetic study of the thermal reversion of Z,Z-2, ortho-Z,E-2 and para-Z,E-2 could be carried out simultaneously (Fig. 12).

**Fitting model for the kinetic analysis of thermal Z to E isomerisation of switch 2**

Our aim was to extract the four rate constants (k₁ to k₄) for Z to E isomerisation of the thermally unstable isomers of switch 2 from the kinetic traces in Fig. 13. Each of the four kinetic traces is described by two rate constants, as shown in Fig. 1. Each state is associated with a function A(t), B(t), C(t) and D(t), which describes the relative concentration of each isomer (Z,Z, o-Z,E, p-Z,E and E,E) as a function of time (eqn (2)–(5)). These functions depend on the rate constants kᵢ, as well as the initial concentrations A(0) = A₀, B(0) = B₀, etc. (eqn (6)–(9)).

\[ \frac{dA(t)}{dt} \equiv A'(t) = -k_1A(t) - k_2A(t) \]  

(2)

\[ \frac{dB(t)}{dt} \equiv B'(t) = k_1A(t) - k_3B(t) \]  

(3)

\[ \frac{dC(t)}{dt} \equiv C'(t) = k_2A(t) - k_4C(t) \]  

(4)

\[ \frac{dD(t)}{dt} \equiv D'(t) = k_3B(t) + k_4C(t) \]  

(5)

\[ A(t) = A_0e^{-k_1t} \]  

(6)

\[ B(t) = (B_0 + k_1A_0)e^{-k_2t} - k_1A_0e^{-k_1t} - k_2A_0e^{-k_3t} \]  

(7)

\[ C(t) = (C_0 + k_2A_0)e^{-k_1t} - k_2A_0e^{-k_1t} - k_3C_0e^{-k_2t} \]  

(8)

\[ D(t) = A_0 + B_0 + C_0 + D_0 - (B_0 + k_1A_0)e^{-k_2t} \]  

(9)

![Fig. 11](image1) Changes in the UV-Vis spectrum of E,E-2 in CH₂Cl₂ (4.0 × 10⁻³ M at 20 °C) as a result of irradiation with UV light (λₑcₓ 355 nm). E,E-2 in CH₂Cl₂ (---), irradiation to PSS λₑcₓ 355 nm (---) and subsequent irradiation λₑcₓ 450 nm (---).

![Fig. 12](image2) ¹H-NMR spectroscopic thermal array of unstable isomers Z,Z-2, para-Z,E-2 and ortho-Z,E-2 at 55 °C.

![Fig. 13](image3) Kinetic traces of thermal reversion of a PSS mixture at 55 °C, by ¹H-NMR spectroscopy. E,E-2 (□), o-Z,E-2 (○), p-Z,E-2 (△) and Z,Z-2 (○).
The thermal isomerisation behaviour of the individual switching units in switch 2 can be analysed by comparison with the thermal behaviour of switch 1 (Table 1) and the calculated quantum chemical data for switch 2 in Table 3. However, before considering the influence of the interactions of the neighbouring azobenzene units on the thermal Z to E isomerisation, we must determine if a change in the mechanism of the isomerisation of switches 1 and 2 occurs.

There are two known mechanisms for azobenzene Z to E isomerisation; a rotation mechanism wherein a 180° rotation takes place around the N=N double bond and the inversion mechanism, which proceeds *via* a dipolar transition state (Fig. 14). 41-43 Quantum mechanical and experimental investigations suggest that substitution on the phenyl rings determines the pathway taken. 44-46,48

It is proposed that the mechanism of thermal isomerisation in azobenzenes containing electron donating and electron withdrawing functionalities on opposite sides of the switch (known as push–pull systems) takes place *via* rotation in highly polar solvents. 47,48

Experimental 49 and quantum mechanical calculations 46 have shown that in unsubstituted, neutrally substituted azobenzenes and sterically constrained azobenzenes 49 the thermal Z to E isomerisation takes place *via* the inversion mechanism.

Calculations by Hecht, Saalfrank, and co-workers have revealed that azobenzenes containing electron withdrawing groups lower the isomerisation barrier more effectively than electron donating groups. The groups have the same effect whether in the 2-position (*ortho*) or 4-position (*para*) of the azobenzene. 46 In both cases strong electronically active groups (EDG or EWG) induce enhanced lowering of the thermal barrier than lesser donating or withdrawing groups. Substituents in the *meta* position only give rise to small changes in the barrier to isomerisation.

In push–pull azobenzenes, the *para* and *ortho* substituted positions lower the barrier to the greatest extent.

1 contains tert-butyl esters in the 4′ and the 4″ positions. The tert-butyl ester is moderately electron withdrawing (A), whereas the molecule contains a moderately electron donating (D) butanoate group in the 4-position (Fig. 15). Consequently, both switching units resemble the push–pull design. The TS of thermal isomerisation *via* the rotation mechanism has a zwitterionic character and might be stabilised by resonance
in push–pull systems. This would result in a change of mechanism for the thermal Z to E isomerisation.

However, the tert-butyl ester and the butanoate group are far weaker electron withdrawing and electron donating groups than the –NO2 and –NH2, respectively. Therefore smaller changes to the barrier are to be expected compared to 4-(4-nitrophenyl)diazenylaniline push–pull systems.39,40

An isokinetic relation has previously been reported for the thermal Z to E isomerisation for a number of variously substituted azobenzene switches (ΔH‡ = βΔS‡ + ΔH‡1),39,41 wherein β is the constant of proportionality (ΔH‡ vs. ΔS‡) and ΔH‡1 (kcal mol⁻¹) is constant regardless of the substituent.39 When the determined enthalpy of activation (ΔH‡) is plotted against the entropy of activation (ΔS‡) for each Z to E thermal isomerisation step, Tables 1 and 2 (Fig. 16), the data points fall in line with the previously reported data (unfunctionalised azobenzene, crown ether bridged azobenzene, morpholine-carbonyl azobenzenes, and azobenzene in zeolites) for the inversion mechanism.42

From the isokinetic plot, it can be concluded that there is no change in the mechanism of thermal relaxation, going from Z,Z-2 to E,E-2 regardless of which of the two pathways is taken (Fig. 16). As a consequence we can exclude that the preferred pathway of the thermal isomerisation is the result of a change in the thermal Z to E isomerisation mechanism of the azo-double bond. Kinetic measurements of the Z to E isomerisation of switch 1 in DMSO-d6 also exclude the rotation mechanism in polar solvents, indicating that the mechanisms of Z to E isomerisation of 1 and 2 are not solvent dependent. The determined ΔS‡ values for the thermal Z to E isomerisation (Table 2) are of the same order as reported previously.42-49 The variation in ΔS‡ between isomerisations via different pathways is small as expected. The experimental uncertainty of ΔS‡ is relatively large as a result of the method used for the kinetic analysis. Therefore no conclusions can be drawn on the basis of the absolute ΔS‡ values.

From the data in Table 2 it is apparent that, although the azo-units share a phenyl ring, significant interaction does not occur between the azo-units in regard to the thermal Z to E isomerisations. The pathways described in Fig. 1 contribute equally to the thermal relaxation from Z,Z-2 to E,E-2. The difference in relative speed of depletion of the ortho and para-Z,Z-2 isomers, which can be seen in Fig. 12 and 13, was found not to be significant. No significant differences could be determined for any of the activation barriers to each of the four isomerisation steps described in Fig. 1. Changes in the polarity of the neighbouring azo-group do not have an effect on the thermal relaxation of meta substituted bisazobenzene switches. This is possibly due to the position of the switching units relative to one another, i.e. meta. This is also indicated by comparison of the UV/Vis spectra of switches 1 and 2 (Fig. 4 and 6) in which only minor differences are observed, indicating that the electronic structure of the azo switching units is not perturbed significantly by introducing a second azo-unit meta relative to its position. As described above, substitution in the meta position only gives rise to small changes in the barrier to the thermal Z to E relaxation. These findings correlate well with quantum mechanical modelling (vide supra). It should be noted that quantum mechanical calculations perform well considering they were performed in the gas-phase. This is most likely due to the use of CH2Cl2, which, being an apolar solvent, would result in little additional stabilization of the dipolar-like transition state.

4. Conclusions

Herein we described the kinetic behaviour of a meta bis-azobenzene system. This system serves as a model to study the effect of more complex azobenzene systems. Our results indicate that the thermal Z to E isomerisations of one of the switching units do not affect the second unit significantly. Both units in 2 function independently from each other and behave as individual switches. Furthermore, it was shown that the thermal behaviour of bis-azobenzene 2 is comparable to that of azobenzene 1. It can be expected that bis-azobenzenes containing two switches positioned meta relative to one another show similar thermal relaxation behaviour.

Additionally, we determined that the weakly electron donating group (EDG) and electron withdrawing group (EWG) do not change the mechanism of the thermal Z to E isomerisation of switches 1 and 2. This is advantageous as the tert-butyl esters are easily deprotected and can be used for further functionalisation and the introduction of bio- or photo-active groups via ester synthesis, without having major electronic effect on the mechanism of thermal helix inversion and therefore their function when incorporated into more complex systems.

Acknowledgements

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Notes and references


22. Experimental procedures and investigation using UV/Vis absorption spectroscopy can be found in the experimental section.


24. Proton b will be used throughout this manuscript to identify the individual isomers.


26. SiO$_2$ PLC plates, eluted with 1:10 ethyl acetate/pentane.

27. Para-Z-E-2 was obtained as a mixture with stable E,E-2, as a result of thermal isomerisation.

28. Ortho-Z-E-2 was obtained as a mixture with stable E,E-2, as a result of thermal isomerisation.

29. NOE-experiments of the isolated isomers were inconclusive, probably due to the high conformational freedom in the molecule.

30. Traces of ethyl acetate remain in the 1H-NMR sample of

31. NOE-experiments of the isolated isomers were inconclusive, probably due to the high conformational freedom in the molecule.

32. The organic solvents were removed in vacuo (30 °C), however due to the thermal Z to E isomerisation, the isomers cannot be heated under reduced pressure for an extended period. During removal of the organic solvent ortho-$Z$-E-2 and para-$Z$-E-2 partially revert back to the thermally stable E,E-2 isomer.


34. ESP maps for the E-E and Z-Z isomers can be found in the ESI.

35. A separation of the photochemically generated isomers using PLC, the Z,Z-2 can only be obtained as mixtures of Z,Z-2 and ortho or para-E,Z-2 as a result of the rapid thermal revision of Z,Z-2.

36. Statistical outliers were removed using Grubbs’s test.

37. We list the coefficients $k_1$, $k_2$, $k_3$ and $k_4$, as extracted from the fits at each of the temperatures (28.1, 45.0, 54.5, 64.6 and 68.7 °C respectively). We give a statistical error (1σ) as coming from the fit. The systematic error is estimated by varying the end time of the fit.

38. The data are fitted for all the isomers simultaneously.


This isokinetic relation originates from enthalpy/entropy compensation. When both $\Delta H$ and $\Delta S$ are positive (or negative) an increase in $\Delta H$ is compensated by a proportional increase in $\Delta S$. See for example: (a) J. E. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963, ch. 9; (b) E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, California, 2004, ch. 8.


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