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

Jort Robertus,a Siebren F. Reker,b Thomas C. Pijper,c Albert Deuzeman,b Wesley R. Browneac and Ben L. Feringaac

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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 photo-
chromic switches1,2 (such as stilbenes, azobenzenes, diarylethenes,
spiropyrans, 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 one6 or several7 addressable diarylethene
units have been reported. Other examples include overcrowded
alkenes,8 dihydropyrenes,9 bisnaphthopyrans,10 stilbenes,10
spiropyrans,11 and azobenzenes.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

† Electronic supplementary information (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 (λexc 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 azo-bond 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 1H-NMR spectroscopy (Fig. 12).

Upon irradiation at λexc 365 nm the UV/Vis absorption spectrum of 1 undergoes a hypsochromic shift with the band at λmax = 332 nm decreasing and a new band appearing at λmax = 261 nm (Fig. 4). Additionally new bands appear up-field from the E-2 isomer in the 1H-NMR spectrum (Fig. 5). At the photostationary state (PSS) the signal of proton b shifts from 2.581 ppm (b⁶) to 2.495 ppm (b⁶). 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 1H-NMR and UV/Vis absorption spectroscopy in order to gain an understanding of its photochemical and thermal behaviour. E,E-2 was irradiated at λexc 365 nm, in CH₂Cl₂ (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 (λmax = 331 nm) and a new band appeared at λmax = 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 (λexc 365 nm at 20 °C). E-3 (——), E-3 irradiated at λexc 355 nm (-----).
azobenzene systems (Fig. 6). The initial isosbestic point at 284 nm was not retained upon irradiation, indicating that several photochemical processes take place (Fig. 6 inset).

Irradiation (λ_{exc} 355 nm) of E,E-2 in C_2D_4Cl_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-1} (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-Z,E-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. The four isomers were isolated and studied by 1H-NMR and NOE-spectroscopy. 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^{o-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 $1\text{-b}^E$ and $1\text{-b}^Z$ 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 para-$Z, E\text{-2}$ isomer while the signal at 2.56 ppm corresponds to the ortho-$Z, E\text{-2}$ isomer.

The second method for the identification of the para-$Z, E$ and ortho-$Z, E$ isomers involved the calculation of the $^1H$-NMR chemical shifts of the four isomers of 2 with the Gaussian 09 QC package 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 $^1H$-NMR simulation was then performed with the GIAO method, using the IEFPCM solvation model (solvent: dichloroethane). The relative chemical shifts in the calculated $^1H$-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 $o-Z, E\text{-2}$ and $p-Z, E\text{-2}$ 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.

This allows for more interaction with the silica gel phase. 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). 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 $Z, Z\text{-2}$ isomer, which contains two Z-azo groups, displayed the lowest $R_t$ value of the four isomers. The stable $E, E\text{-2}$ isomer on the other hand displayed the highest $R_t$ value.

The significant difference in $R_t$ between ortho-$Z, E\text{-2}$ and para-$Z, E\text{-2}$ (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 ortho-$Z, E\text{-2}$ isomer the carbonyl group of the butanoate moiety is more exposed than in the case with the para-$Z, E\text{-2}$ 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 ortho-$Z, E\text{-2}$ isomer while the $R_t$ of 0.33 is of the para-$Z, E\text{-2}$. This conclusion is in full agreement with the experimentally obtained and calculated $^1H$-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 CH$_2$Cl$_2$, could be reverted to the $E, E\text{-2}$ isomer upon irradiation with visible light ($\lambda_{exc}$ 450 nm), confirming the photo-reversibility of switch 2 with isosbestic 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 $^1$H-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 $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the thermal isomerisation are shown in Table 1 and were calculated using the Eyring equation.

$$k = \frac{k_B T}{h} e^{-\frac{\Delta H^\ddagger}{RT}}$$  \hspace{1cm} (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.\textsuperscript{33} However, using thermal array $^1$H-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 ($k_1$ to $k_4$) 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 ($Z,Z$, $ortho-Z,E$, $para-Z,E$ and $E,E$) as a function of time (eqn (2)–(5)). These functions depend on the rate constants $k_i$,

**Table 1** Thermodynamic data for the thermal $Z$ to $E$ isomerisation of $I$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta G^\ddagger$/kcal mol$^{-1}$</th>
<th>$\Delta H^\ddagger$/kcal mol$^{-1}$</th>
<th>$\Delta S^\ddagger$/cal K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloroethane-$d_4$</td>
<td>24.9</td>
<td>22.5</td>
<td>$-$8.1</td>
</tr>
<tr>
<td>DMSO-$d_6$</td>
<td>25.5</td>
<td>25.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Fig. 11 Changes in the UV-Vis spectrum of $E,E$-2 in CH$_2$Cl$_2$ (4.0 $\times$ 10$^{-5}$ M at 20 °C) as a result of irradiation with UV light ($\lambda_{exc}$ 355 nm). $E,E$-2 in CH$_2$Cl$_2$ (----), irradiation to PSS $\lambda_{exc}$ 355 nm (---) and subsequent irradiation $\lambda_{exc}$ 450 nm (----).

Fig. 12 $^1$H-NMR spectroscopic thermal array of unstable isomers $Z,Z$-2, $para-Z,E$-2 and $ortho-Z,E$-2 at 55 °C.

Fig. 13 Kinetic traces of thermal reversion of a PSS mixture at 55 °C, by $^1$H-NMR spectroscopy. $E,E$-2 (□), $ortho-Z,E$-2 (○), $para-Z,E$-2 (Δ) and $Z,Z$-2 (○).\textsuperscript{34}

as well as the initial concentrations $A(0) = A_0$, $B(0) = B_0$, etc. (eqn (6)–(9)).

$$\frac{dA(t)}{dt} = A'(t) = -k_1 A(t) - k_2 A(t)$$  \hspace{1cm} (2)

$$\frac{dB(t)}{dt} = B'(t) = k_1 A(t) - k_3 B(t)$$  \hspace{1cm} (3)

$$\frac{dC(t)}{dt} = C'(t) = k_2 A(t) - k_4 C(t)$$  \hspace{1cm} (4)

$$\frac{dD(t)}{dt} = D'(t) = k_3 B(t) + k_4 C(t)$$  \hspace{1cm} (5)

$$A(t) = A_0 e^{-(k_1 + k_2)t}$$  \hspace{1cm} (6)

$$B(t) = (B_0 + K_1 A_0) e^{-(k_1 + k_2)t} - K_1 A_0 e^{-(k_1 + k_2)t}$$  \hspace{1cm} (7)

$$C(t) = (C_0 + K_2 A_0) e^{-(k_1 + k_2)t} - K_2 A_0 e^{-(k_1 + k_2)t}$$  \hspace{1cm} (8)

$$D(t) = A_0 + B_0 + C_0 + D_0 - (B_0 + K_1 A_0) e^{-(k_1 + k_2)t}$$  \hspace{1cm} (9)

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Thermodynamic data for the thermal isomerisation of Z,Z-2 to E,E-2 at 20 °C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG°/kcal mol⁻¹</th>
<th>ΔH°/kcal mol⁻¹</th>
<th>ΔS°/cal K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁(Z,Z→E,E)</td>
<td>24.8±4.9</td>
<td>22.2±3.7</td>
<td>-9.0±11.2</td>
</tr>
<tr>
<td>k₂(Z,E→E,E)</td>
<td>25.6±4.8</td>
<td>24.9±3.6</td>
<td>-2.5±10.9</td>
</tr>
<tr>
<td>k₃(Z,Z→Z,E)</td>
<td>25.1±6.3</td>
<td>21.1±4.7</td>
<td>-13.6±14.3</td>
</tr>
<tr>
<td>k₄(Z,E→E,E)</td>
<td>25.2±2.2</td>
<td>22.9±1.7</td>
<td>-7.8±5.0</td>
</tr>
</tbody>
</table>

where

\[ K_1 = \frac{k_1}{k_4 + k_2 + k_3} \quad \text{and} \quad K_2 = \frac{k_2}{k_1 + k_3} \]

From the fitted data, the rate constant for thermal Z to E isomerisation of each of the thermally unstable isomers can be determined. The activation barrier (ΔG°, Table 2) for each thermal isomerisation can be calculated using the Eyring equation (1).

**Quantum chemical study of thermal Z to E isomerisation of switch 2**

Quantum chemical calculations were carried out on the E,E-2, para-Z,E-2, ortho-Z,E-2, and Z,Z-2 isomers, with the Firefly QC package, which is based partially on the GAMESS (US) source code. Geometry optimisations and energy calculations were performed using the B3LYP hybrid functional (using VWN formula 1 RPA correlation) and a 6-31G(d,p) basis set. The validity of the transition state geometries found during this study was verified by both a vibrational analysis and an IRC analysis.

For this study, we presumed that Z to E isomerisation would take place via the inversion mechanism. In this mechanism the lowest energy pathway passes through a virtually linear N–N–C transition state. Thermal relaxation of Z,Z-2 can take place through four distinct inversion pathways. Inversion can take place over either of the four nitrogen atoms contained in the diazo-double bonds N₁, N₂, N₃ or N₄. The thermal barrier over each of the four nitrogen atoms was calculated to determine the lowest energy pathway over the barrier to the thermal Z to E isomerisation (Tables 3 and 4).

### Table 3 Calculated electronic E°ₐ energy of activation for Z to E isomerisation via pathway A (Fig. 1)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Inversion over</th>
<th>kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z,Z-2 → ortho-Z,E-2</td>
<td>N¹</td>
<td>26.8</td>
</tr>
<tr>
<td>Z,Z-2 → ortho-Z,E-2</td>
<td>N²</td>
<td>25.6</td>
</tr>
<tr>
<td>ortho-Z,E-2 → E,E-2</td>
<td>N¹</td>
<td>26.2</td>
</tr>
<tr>
<td>ortho-Z,E-2 → E,E-2</td>
<td>N²</td>
<td>22.2</td>
</tr>
</tbody>
</table>

### Table 4 Calculated electronic E°ₐ energy of activation for Z to E isomerisation via pathway B (Fig. 1)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Inversion over</th>
<th>kcal mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z,Z-2 → para-Z,E-2</td>
<td>N³</td>
<td>25.5</td>
</tr>
<tr>
<td>Z,Z-2 → para-Z,E-2</td>
<td>N⁴</td>
<td>22.6</td>
</tr>
<tr>
<td>para-Z,E-2 → E,E-2</td>
<td>N¹</td>
<td>26.9</td>
</tr>
<tr>
<td>para-Z,E-2 → E,E-2</td>
<td>N²</td>
<td>25.1</td>
</tr>
</tbody>
</table>

3. Discussion

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). Quantum mechanical and experimental investigations suggest that substitution on the phenyl rings determines the pathway taken.

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.

Experimental and quantum mechanical calculations have shown that in unsubstituted, neutral substituted azobenzenes and sterically constrained azobenzenes 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. 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.

![Fig. 14 Mechanism of thermal relaxation via in plane inversion (upper) and out of plane rotation (lower).](image-url)
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 \(-NO_2\) and \(-NH_2\), respectively. Therefore smaller changes to the barrier are to be expected compared to 4-((4-nitrophenyl)-diazenyl)aniline 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 azobenzenes (\( \Delta H^i = \beta \Delta S^i + \Delta H^i \)),\(^{39,41}\) wherein \( \beta \) is the constant of proportionality (\( \Delta H^i \) vs. \( \Delta S^i \)) and \( \Delta H^i \) (kcal mol\(^{-1}\)) is constant regardless of the substituent.\(^{39}\)

When the determined enthalpy of activation (\( \Delta H^i \)) is plotted against the entropy of activation (\( \Delta S^i \)) 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-\( d_6 \) 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 \( \Delta S^i \) values for the thermal \( Z \) to \( E \) isomerisation (Table 2) are of the same order as reported previously.\(^{42-49}\)

The variation in \( \Delta S^i \) between isomerisations via different pathways is small as expected. The experimental uncertainty of \( \Delta S^i \) 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 \( \Delta S^i \) 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-\( Z,E-2 \) 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 \( CH_2Cl_2 \), 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-azobenzene 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.

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**Fig. 15** Representation of 2 as a push–pull system (middle) and two resonance forms. Wherein the tert-butyl ester is represented by A and the butanoate group is represented by D.

**Fig. 16** Isokinetic plots (\( \Delta H^i \) and \( \Delta S^i \)) of various azobenzenes (■), push–pull azobenzenes (●), experimentally obtained data of azobenzene-1 (▼) and bisazobenzene-2 (▲). The thermal relaxation mechanisms are indicated: inversion (—), rotation (—). Graph is reproduced in part from ref. 42.
50 This isokinetic relation originates from enthalpy/entropy compensation. When both $\Delta H^\circ$ and $\Delta S^\circ$ are positive (or negative) an increase in $\Delta H^\circ$ is compensated by a proportional increase in $\Delta S^\circ$. 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.