Electronic Decoupling Approach to Quantitative Photoswitching in Linear Multiazobenzene Architectures

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Supporting Information

ABSTRACT: A strategy to optimize the photoswitching efficiency of rigid, linear multiazobenzene constructs is presented. It consists of introducing large dihedral angles between azobenzene moieties linked via aryl-aryl connections in their para positions. Four bisazobenzenes exhibiting different dihedral angles as well as three single azobenzene reference compounds have been synthesized, and their switching behavior has been studied as well as experimentally and theoretically analyzed. As the dihedral angle between the two azobenzene units increases



and consequently the electronic conjugation decreases, the photochromic characteristics improve, finally leading to individual azobenzene switches operating independently in the case of the perpendicular ortho, ortho', ortho', ortho'-tetramethyl biphenyl linker. The electronic decoupling leads to efficient separation of the absorption spectra of the involved switching states and hence by choosing the appropriate irradiation wavelength, an almost quantitative $E \rightarrow Z$ photoisomerization up to 97% overall Z-content can be achieved. In addition, thermal $Z \rightarrow E$ isomerization processes become independent of each other with increasing decoupling. The electronic decoupling could furthermore be proven by electrochemistry. The experimental data are supported by theory, and calculations additionally provide mechanistic insight into the preferred pathway for the thermal $Z, Z \rightarrow Z, E \rightarrow E, E$ isomerization via inversion on the inner N-atoms. Our decoupling approach outlined herein provides the basis for constructing rigid rod architectures composed of multiple azobenzene photochromes, which display practically quantitative photoswitching properties, a necessary prerequisite to achieve highly efficient transduction of light energy directly into motion.

INTRODUCTION

Molecular switches¹ have lately attracted a tremendous interest in the area of nanochemistry as bistable objects capable of performing tasks on demand, for example store data² or perform mechanical work,³ at the molecular level. This class of responsive molecules additionally allows, when ingeniously incorporated into an adequate matrix, for reversibly inducing dramatic changes in various physicochemical properties of bulk materials and surfaces (through self-assembled monolayers⁴ or thin films⁵) transferring effects from the molecular level to the macroscopic scale.⁶ Light, as an attractive stimulus offering high spatial resolution and good compatibility with most materials, has been widely used to trigger the isomerization of molecular switches, azobenzene photochromes being among the most frequently employed.⁷ This success can mainly be explained by the large geometrical change that azobenzenes undergo, from an extended and flat *E* isomer to a three-dimensional and compact *Z* isomer, upon irradiation with UV-light. Azobenzenes are therefore suitable for the photocontrolled deformation of a vast range of soft materials⁸ such as liquid crystals, liquid crystalline elastomers, colloidal spheres, or polymer gels, whereas their use in the deformation of molecular crystals has been reported only recently.9 It is interesting to note that diarylethenes, 10 another class of popular photochromes, exhibit the opposite trend: due to

the small geometrical difference between the close and open forms, diarylethenes have been successfully utilized for the photocontrolled deformation of molecular crystals,¹¹ but their use for the deformation of soft materials has thus far been rather limited.

In order to exploit this feature, we have recently investigated the utilization of azobenzene-containing rigid rods as candidates for light-gated molecular actuators undergoing substantial and reversible structural changes upon UV and visible light irradiation.¹² The construction of such photoresponsive rigid rods requires the linking of several azobenzene units via π -conjugated para connections to ensure both rigidity and linearity, while retaining the photoswitching efficiency. However, direct para connection extends electronic conjugation and leads to a dramatically decreased photoreactivity of azobenzenes.¹³ One solution to attenuate the electronic coupling consists of linking azobenzenes through meta connections.¹³ However, such kinked meta connections are not suitable for the design of rod-type macromolecules, which constitute linear objects.

Herein, we present a straightforward strategy to realize electronically decoupled and hence photoswitchable azobenzenes

Received:	May 11, 2011
Revised:	June 29, 2011
Published:	July 12, 2011



Figure 1. Molecular structures of the bisazobenzenes compounds 1-4 connected by increasing torsion angles (ϕ).

Table 1. Composition of the Photostationary State (PSS) in Cyclohexane upon Irradiation with UV Light (at 368 nm for 1 and 2 and 357 nm for a, b, c, 3, and 4)

			PSS composition $(\%)^a$					
	dihedral angle $\phi (^{\circ})^{b}$	E,E	Z,E	Z,Z	total Z			
a, b, c ^c					97			
1		72	25	3	16			
2	36.7	53	22	25	64			
3	89.9	2	10	88	93			
4	90.0	1	4	95	97			

^{*a*} As determined by UPLC analyses using integration of UV signal at wavelengths of the isosbestic points. ^{*b*} DFT-calculated dihedral angles (see Table S2). ^{*c*} The PSS compositions are identical (\pm 1%) for reference compounds **a**-**c**.

connected in a linear fashion, providing the structural basis for our photoresponsive rigid rods.¹² Our approach relies on connected azobenzenes joined via ortho substituted biphenyl linkages to enforce large dihedral angles and therefore electronic decoupling between the photochromes.¹⁴ A series of bisazobenzenes connected by a single benzene ring (compound 1) or biphenyls (compounds 2–4), exhibiting different dihedral angles (ϕ), have been synthesized (Figure 1).¹⁵ As the dihedral angle increases and consequently the electronic conjugation decreases,¹⁶ the photoswitching characteristics (amount of isomerized moieties in the photostationary state (PSS), thermal stability of the *Z* isomer) improve, finally leading to azobenzenes operating independently for the essentially perpendicular biphenyl linker in bisazobenzene 4 (Table 1).



Figure 2. Molecular structures of the single azobenzene reference compounds $\mathbf{a} - \mathbf{c}$ (detailed synthesis in the Supporting Information).

The photophysical, electronic, and photochemical properties have been investigated by means of UV–vis spectroscopy, cyclic voltammetry, and kinetic analyses. For the sake of comparison, the properties of the bisazobenzenes have been systematically compared to the properties of single azobenzene reference compounds ($\mathbf{a}-\mathbf{c}$, see Figure 2). The experimental observations for compounds $\mathbf{1}-\mathbf{4}$ and $\mathbf{a}-\mathbf{c}$ were complemented by quantum chemical calculations based on hybrid density functional theory.

METHODS

Synthetic Methodology. Bisazobenzene 1 has been synthesized by a three-step procedure starting from 1,4-diiodobenzene and involving a Pd-catalyzed N-arylation protocol.¹⁷ In a different approach, bisazobenzenes 2-4 have been prepared either by assembling suitably functionalized azobenzenes through Suzuki coupling (compounds 2 and 3) or by forming the N=N double





bonds on the corresponding diaminobiphenyl moiety (compound 4). Scheme 1 summarizes the detailed syntheses of bisazobenzenes 1-4.

For the preparation of compound 1, 1,4-diiodobenzene was converted to the corresponding NBoc-protected phenyl hydrazide 5^{18} that was subsequently coupled to 3,5-di-*tert*-Bu-bromobenzene via a Pd-catalyzed cross-coupling reaction to yield **6**. After subsequent deprotection/oxidation, **1** was obtained in 27% yield over three steps. For bisazobenzenes **2** and **3**, the N=N azo linkage was formed by condensation between nitrosoarene and aniline derivatives.¹⁹ Starting from the nitroso 7,²⁰ azobenzenes **8** and **9** functionalized at the para positions by halogen atoms were obtained in good yield and subsequently borylated with pinacolborane PinBH via a Pd(0)-catalyzed coupling reaction.²¹ This method was preferred to standard halogen/lithium exchange with *n*-BuLi followed by transmetalation with alkoxyboron compounds, which mainly results in the addition of the organo-lithium compound to the azo group, as previously reported in the literature.²² Bisazobenzenes **2** and **3** were finally obtained via Suzuki coupling between **8** and **10** and **9** and **11**, respectively. The sterically hindered biaryl **3** was formed in good yield thanks to the use of Buchwald's 2-(2',6'-dimethoxybiphenyl)-dicyclohexylphosphine (SPhos) ligand.²³

Another synthetic pathway, allowing for larger scale synthesis, has been used for the preparation of compound **4**. The diaminobiphenyl **13** was obtained with 55% yield over two steps involving first the formation of the hydrazine **12** by reductive homocoupling of 3,5-dimethylnitrobenzene, followed by benzidine



Figure 3. Time evolution of the absorption spectra of 2×10^{-5} M solutions of *E*,*E*-1 (ε = 46 070 M⁻¹ cm⁻¹), *E*,*E*-2 (ε = 67 280 M⁻¹ cm⁻¹), *E*,*E*-3 (ε = 65 260 M⁻¹ cm⁻¹), and *E*,*E*-4 (ε = 67 010 M⁻¹ cm⁻¹) in acetonitrile at 25 °C upon irradiation at 368 nm for 1 and 2 and 357 nm for 3 and 4, until the photostationary state (PSS) is reached (in 40 s for 1, 110 s for 2, 50 s for 3, and 40 s for 4). Molar extinction coefficients (ε) were measured at the $\lambda_{max}(\pi - \pi^*)$ of each of the compounds.

rearrangement of **12**. In a last step, **12** was converted to the bisazobenzene **13** via Mills condensation reaction with the nitroso 7.

Three single azobenzenes (a-c in Figure 2) have also been prepared as reference compounds (a and b as references for)bisazobenzene 2 and c for bisazobenzene 4) following similar synthetic strategies (see Supporting Information).

Computational Methodology. All calculations were carried out with the Gaussian 03 program package,²⁴ using hybrid density functional theory with the B3LYP exchange-correlation functional.²⁵ For neutral and doubly negatively charges species, singlets were calculated. Doublets were considered in the case of singly negatively charged species with unrestricted DFT (UB3LYP). In most cases, the 6-311G* basis set was used, in selected cases (kinetics), a smaller basis set, 6-31G*, was used.²⁶ Differences between both basis sets are small (see, for example, Table S2). Reactant (e.g., *E* or *E*,*E*) and product minima (e.g., *Z* or *E*,*Z* and *Z*,*Z*) for compounds **1**–**4** and **a**–**c**, were determined and the minimum character was verified by normal-mode analysis.

Transition states connecting reactants and products were found by the synchronous transit-guided quasi-Newton method (QST2 and QST3).^{27,28} From reactant and transition states and normal-mode analyses of stationary points, activation free energies $\Delta G^{\dagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ were determined. From the ΔG^{\ddagger} values, reaction rate constants k(T) were computed with Eyring's transition state theory as

$$k(T) = \frac{k_{\rm B}T}{h} e^{-\Delta G^{\ddagger}/RT} \tag{1}$$

Further details of the rate calculations are outlined below.

Vertical UV/vis absorption spectra for reactant and product molecules were calculated from linear-response time-dependent density functional theory (TD-B3LYP).²⁹ To make closer contact with experiment and to account for line broadening, the stick spectrum was broadened by normalized Gaussians. Accordingly, the extinction coefficients were calculated as

$$\varepsilon(\tilde{\nu}) = \sum_{i} \frac{f_{i}}{\kappa_{\sigma}\sqrt{2\pi}} e^{-1/2\left(\frac{\tilde{\nu}-\tilde{\nu}_{i}}{\sigma}\right)^{2}}$$
(2)

Here, $\tilde{\nu} = 1/\lambda$ is the wavenumber, $\kappa = 4.319 \times 10^{-10} \text{ mol m}^{-1}$, f_i is the oscillator strength for transition *i*, and $\tilde{\nu}_i$ is the corresponding transition wavenumber, and σ is an empirical broadening factor.

All calculations were carried out with gas phase models. For similar azobenzenes,³⁰ also solvent effects on computed kinetic and spectral data were considered using polarizable continuum models. It was found that rates and optical absorption behavior do somewhat depend on a polarizable solvent. However, the differences between both theoretical treatments are at most in the order of a few percent. Larger, remaining differences to experiment for certain properties (e.g., activation entropies), can probably only be reduced by using explicit solvation models.

RESULTS AND DISCUSSION

 $E \rightarrow Z$ Photoisomerization. The absorption spectra of pure *E*,*E*-1 to *E*,*E*-4 compounds were measured in acetonitrile (Figure 3). As the electronic conjugation decreases, the absorption maxima $(\pi - \pi^* \text{ transition})$ are continuously blue-shifted, from $\lambda_{\max}(\pi - \pi^*) = 368$ nm for *E*,*E*-1 to $\lambda_{\max}(\pi - \pi^*) = 348$ nm for *E*,*E*-4. Upon UV irradiation at either 357 or 368 nm (depending on the absorption maximum: PSSs with larger *Z*-content were obtained by irradiating at the absorption maximum), the intense band corresponding to the $\pi - \pi^*$ transition decreases and the band attributed to the $n - \pi^*$ transition

(centered at around 450 nm) increases for the four compounds. This typical photochromic behavior is the consequence of the stepwise $E,E \rightarrow Z,E \rightarrow Z,Z$ isomerization process. However, the decrease in the $\pi-\pi^*$ transition band of 1 is unusually small, indicative of a *Z*-poor PSS. The relative decrease of the $\pi-\pi^*$ transition band becomes continuously stronger when going from 1 to 4, consistent with an increasing amount of *Z* forms in the PSS (as confirmed by analysis of the PSS using ultraperformance liquid chromatography coupled to a mass spectrometry detector, UPLC-MS, see Table 1).

The presence of well-defined isosbestic points at 290 nm in the absorption spectra of **3** and **4** as well as the possible reconstruction of the intermediate E_rZ isomer's spectrum by simple addition of the spectra of the E_rE and Z_rZ isomers both indicate that the two para-connected azobenzene chromophores are decoupled. However, in the absorption spectra of **1** and **2**, such well-defined isosbestic points do not exist, most clearly seen in the crossing region around 320-330 nm for **2**. The absence of sharp isosbestic points for **1** and **2** hence points to a high degree of electronic coupling between the two azobenzene moieties in these compounds. To obtain insight into the composition of the solution in the PSS, the ratios of the three isomers ($Z_rZ_rZ_rE_r$, and E_rE) were analyzed by UPLC of the irradiated solutions (Table 1).

As indicated by the change in the UV/vis spectra of 1-4 upon UV irradiation, the total amount of Z isomer in the PSS continuously increases going from 1 to 4 as the dihedral angle increases. It is worth noting the dramatic difference between the PSS composition of 1 (16% of total Z isomer) and 4 (97% of total Z isomer), the latter exhibiting the same PSS composition compared to single azobenzene reference compounds $\mathbf{a}-\mathbf{c}$. To the best of our knowledge, such a high content of Z form in the PSS of multiazobenzene chromophores has not been reported thus far.³¹

The experimental findings detailed above are generally supported by theory. Initial geometry optimization for the E,E isomers on the B3LYP/6-311G* level of theory provides the dihedral angles ϕ , which amount to 36.7° for compound 2, 89.9° for compound 3, and 90.0° for compound 4. These dihedral angles do not vary substantially if one or two azo units have been switched from the *E* to the *Z* isomer, giving E_{z} and Z_{z} isomers, respectively (see Table S2). Furthermore, the barriers for rotation about ϕ were calculated by determining the energy difference between fully geometry-optimized structures and those in which the molecules are forced to coplanarity (i.e., $\phi = 0^{\circ}$, while reoptimizing all other parameters). For rotation in compound 2, 0.07 eV (6.8 kJ/mol) are required, whereas 0.64 eV (61.7 kJ/ mol) are necessary in 3 and 1.65 eV (159 kJ/mol) in 4. Thus, the two azobenzene units of 3 and 4 are expected to be well separated electronically and coupling by twisting about ϕ is associated with high energetic penalty, while in compound 2 the azobenzene units are significantly coupled and flexible. Although the computed φ angles are very similar and close to 90° for both compounds 3 and 4, the former will appear less decoupled than the latter in finite-temperature experiments, since the energy to planarize 3 (0.64 eV) is much lower than the energy to planarize 4 (1.65 eV). Also, in the nonbiphenylic compound 1 with paraconnected diazo moieties, the electronic coupling is expected to be strong, because the molecule is flat, and the frontier orbitals have large coefficients at para positions of the benzene rings.^{30,32}

All of these expectations based on geometry considerations are born out by the calculations, which fully support the optical spectroscopy data. For instance in compound E_iE^{-1} the theoretical



Figure 4. Comparison of computed UV/vis spectra of species 1-4 in their optimized *E*,*E* (a), *E*,*Z* (b), and *Z*,*Z* (c) geometries. In all cases, TD-B3LYP/6-311G* calculations were performed, and the stick spectrum was broadened with Gaussians of 1300 cm⁻¹ in width to obtain extinction coefficients.

UV/vis spectrum (Figure 4a) is dominated by a $\pi \rightarrow \pi^*$ transition at $\lambda_{\max}(\pi - \pi^*) = 422$ nm. Similarly we find $\lambda_{\max}(\pi - \pi^*) = 419$ nm for compound *E,E*-2. Both values are strongly red-shifted in comparison to the signals of compounds *E,E*-3 and *E,E*-4, with peaks at $\lambda_{\max}(\pi - \pi^*) = 359$ nm and $\lambda_{\max}(\pi - \pi^*) = 361$ nm, respectively. The latter signals are close to the absorption maximum of reference compound **a** with a single azo unit only $(\lambda_{\max}(\pi - \pi^*) = 345$ nm, see Table S3). Thus, the two azobenzene subunits of **1** and **2** are π -conjugated and red-shifted, while the two π -subsystems of each of the compounds **3** and **4** are electronically decoupled.

When switching one unit in the compounds 1-4 to form the E,Z species, we note that, for compounds 3 and 4, an $n \rightarrow \pi^*$ band appears at around 491 nm, and a high-energy shoulder at around 300 nm, which overlaps with the lowest-energy $\pi \rightarrow \pi^*$ transition (Figure 4b). The new signals of 3 and 4 are at identical positions to those of reference compound a, which has, for example, its $n \rightarrow \pi^*$ peak at 493 nm (see Table S3). We also find that the $\pi \rightarrow \pi^*$ signal around 350 nm becomes weaker by a factor of about two relative to the E,E case, but does not shift much. This nicely shows conversion of one-half of the *E*-azobenzene chromophores and indicates again that here the two azo units are independent of each other. In contrast for compounds 1 and 2, we observe a large blue shift of the $\pi \rightarrow \pi^*$ transition at the *E*-portion of the molecule, when the other azo unit is switched to *Z*.

When switching both units to Z, calculated spectra of the Z,Z species were obtained (Figure 4c). These reflect, for compounds 3 and 4, in very good approximation the added spectra of two independent molecules a in their Z form (see Figure S11). In fact, also the E,Z and E,E spectra of 3 and 4 can be very well represented by adding the E and Z spectra of a, and two E spectra of a, respectively (see Figure S11). In contrast the Z,Z absorption spectra of compounds 1 and 2 are more complicated and shifted and cannot be reconstructed by simply adding the spectra of independent subunits. Due to the spectral shifts of signals of individual subunits in the cases of 1 and 2, but not for 3 and 4, the former cannot show a sharp isosbestic point during



Figure 5. Cyclic voltammograms of bisazobenzenes 1–4; conditions: 1 mM in dimethylformamide (DMF) containing 0.1 M (n-Bu)₄NPF₆, 1 V/s, vs ferrocene/ferrocenium (fc/fc⁺) couple. The difference of potential between the two reduction processes (ΔE) decreases from 1 to 4 as a result of the increasing electronic decoupling.

switching in contrast to the latter. This is in agreement with the experimental observations. Note that the computed spectra of all azobenzenes considered here are shifted somewhat to the red when compared to experiment, but overall features are reproduced. Furthermore, upon switching, the dipole moments of compounds 1-4 change, from zero or low values for *E*,*E* isomers, to values of around 5 D for *Z*,*Z* isomers (see Table S2). There it is

also seen that switching of each single azo unit from *E* to *Z* costs about 0.7 eV of energy, largely independent of the connection geometry, i.e., 1-4.

In summary, the high Z-content in the PSS can be correlated with the degree of decoupling leading to largely altered absorption spectra of the Z,Z isomer. As the extent of switching, i.e., the PSS composition, is governed by the ratio of the extinction coefficients at the irradiation wavelength (assuming constant quantum yields), spectral separation of both isomers is the essential parameter to attain a Z-rich PSS. As it can be seen from the calculated UV/vis spectra (Figure 4), such spectral separation of both isomers at the irradiation wavelength can be achieved for compound 3 and 4, but not for compound 1 and 2. Please note that in addition, the coupling of an electron-accepting group, such as the N=N moiety, in general seems to cause lower Zcontent in the PSS as observed in our laboratory for various azobenzene derivatives.^{13b}

Electrochemical Behavior. The degree of electronic communication between the two azobenzenes in compounds 1-4 was also investigated by cyclic voltammetry (Figure 5). While electrochemical behavior of E-azobenzenes is well described in the literature,³³ here we focus on the reduction processes consisting of the addition of one electron per azobenzene unit.³⁴ Compound E,E-1 exhibits a first reversible reduction process at -1.1 V, corresponding to the addition of one electron in one of the two N=N azo fragments,³⁵ and a second quasireversible process at -1.6 V relative to the addition of one electron in the second azo unit. Hence, there is a difference of potentials $\Delta E(1) = 0.5$ V between the two reduction processes. Compounds E,E-2 and E,E-3 also exhibit two distinguishable reversible reduction processes associated with the values $\Delta E(2) = 0.2$ V and $\Delta E(3) = 0.1$ V, respectively. Finally, the two reduction processes occur at roughly the same potential in *E*,*E*-4, i.e., $\Delta E(4) \approx 0$ V.

As the conjugation between the two azobenzenes decreases, the two reduction processes occur at closer potential (ΔE decreases in the order $1 \rightarrow 4$). This behavior illustrates the strong electronic coupling between the two azobenzenes of *E*,*E*-1, whereas in *E*,*E*-4 the two azobenzenes are mostly decoupled. The increasing decoupling of the two azobenzenes going from 1 to 4 is additionally illustrated by the value of the reduction potentials. Indeed, the first reduction peak of 1 appears at significantly less negative potential (-1.1 V) relative to the reference single azobenzene a (-1.5 V) (see Table S1), as a result of the extended π -system, which lowers the energy of the LUMO. On the other hand, the reduction potentials of compound 4 and reference compound a are identical (-1.5 V).

The observed electrochemical behavior can also be rationalized by quantum chemical results. The tendency of species A to attach a first electron is given by the electron affinity

$$EA(A) = E(A) - E(A^{\bullet -})$$
(3)

where E(A) is the energy of the neutral species and $E(A^{\bullet-})$ that of the radical anion. To determine cyclic voltammogram peaks, free reaction energy differences, which take vibrational and finite temperature contributions and solution effects into account are needed, all of which is neglected here. Instead, nonvertical electron affinities from (U)B3LYP/6-311G* energies of the optimized structures of neutral and singly negatively charged bisazobenzenes 1–4 were calculated with this Δ -SCF method. Positive electron affinities of 1.54 eV for species *E,E*-1, 1.48 eV



Figure 6. Thermal back isomerization monitored by UPLC starting from the PSS (here for compound 4 heated at 60 °C in cyclohexane); (a) evolution of the UPLC traces upon heating (monitored at 290 nm) and (b) ratios of the three isomers $Z_{,Z}$ and $Z_{,E}$ as well as $E_{,E}$ as a function of heating time.

Table 2. Kinetic Data and Thermodynamic Parameters @ 298 K for Thermal $Z \rightarrow E$ Isomerization of Single Azobenzene Reference Compounds a-c and Bisazobenzenes 2 and 4 in Cyclohexane^{*a*}

	$ k_1 \\ (s^{-1})$	$k_2 \ (s^{-1})$	$ au_1 $ (h)	τ ₂ (h)	$\left \Delta H_1^{+} ight $ (kJ mol ⁻¹)	$\Delta {H_2}^{*}$ (kJ mol ⁻¹)	$ \Delta S_1^* $ (J mol ⁻¹ K ⁻¹)	ΔS_2^{\dagger} (J mol ⁻¹ K ⁻¹)	$ \Delta G_1^* $ (kJ mol ⁻¹)	$\Delta {G_2}^{st}$ (kJ mol ⁻¹)
a		$7.2 imes 10^{-6}$		27		91		-37		102
b		1.4×10^{-5}		14		90		-36		101
с		3.3×10^{-6}		57		95		-32		104
2	1.8×10^{-5}	1.6×10^{-5}	10	12	89	86	-37	-48	100	100
4	$4.6 imes 10^{-6}$	4.6×10^{-6}	42	42	85	85	-61	-61	103	103
${}^{a}k_{1}$ and k_{2} refer to the $Z, Z \rightarrow Z, E$ and $Z, E \rightarrow E, E$ isomerizations, respectively. Normalized data $ x $, equal to the corresponding x value divided by two were used in order to consider the statistical character of the first isomerization.										

for *E,E*-2, 1.30 eV for *E,E*-3, and 1.14 eV for *E,E*-4 were obtained (see Table S4). The trend reflects the decreasing tendency to accept an electron when going from 1 to 4 as observed experimentally in Figure 5. In fact, the electron affinity differences relative to 1, are 0.06 eV for compound 2, 0.24 eV for compound 3, and 0.40 eV for compound 4, which compares reasonably well with the experimental voltage shifts of the first reduction peak relative to compound 1, i.e. $\sim 0.1 \text{ V for } 2, \sim 0.2 \text{ V}$ for 3, and $\sim 0.4 \text{ V}$ for 4. Similar trends are obtained by estimating electron affinities more crudely from Koopmans' theorem as negative LUMO Kohn–Sham energies, i.e., $EA(A) \approx -\varepsilon_{LUMO}$. We find that from 1 to 4, ε_{LUMO} becomes continuously less negative (i.e., the electron affinity decreases), with energy shifts relative to compound 1 of 0.15 eV for 2, 0.46 eV for 3, and 0.50 eV for 4.

It is more difficult to describe the second reduction step, i.e. the attachment of a second electron. The electron affinity of the anion, $EA(A^{\bullet-}) = E(A^{\bullet-}) - E(A^{\bullet\bullet2-})$ is negative when gasphase molecular structures are used (see Table S4), and no clear trends emerge on this level of theory. Instead we may take the energy differences of the LUMO and LUMO+1 of the neutral molecules as a rough measure for the quantity ΔE as defined in Figure 5. In this way we get $\Delta E(1) = 1.06 \text{ eV}$, $\Delta E(2) = 0.48 \text{ eV}$, $\Delta E(3) = 0.07$ eV, and $\Delta E(4) = 0.03$ eV, compared to the experimental values of $\Delta E(1) = 0.5$ (e)V, $\Delta E(2) = 0.2$ (e)V, $\Delta E(3) = 0.1$ (e)V, and $\Delta E(4) = 0.0$ (e)V (see Table S4). Thus, despite the meaning and value of Kohn-Sham orbital energies should not be overemphasized, the computed trend shows that the LUMO π^* orbitals of individual azobenzene units remain almost intact and uncoupled in the case of compound 4 and even 3, while in 1 and 2 they are coupled and form bonding and antibonding combinations with lower and higher energies, respectively. Interestingly, the attachment of electrons leads to

geometry changes, in particular in the ϕ dihedral angles, which all become smaller the more electrons are added (see Table S4). That indicates that the degree of conjugation between the two azobenzene units increases in anionic species, with possible implications for electrochemical or electron-induced switching.

Thermal $Z \rightarrow E$ **Isomerization.** Bisazobenzenes 1–4 thermally revert from the *Z*,*Z* to the *E*,*E* isomer via the *Z*,*E* form. The process has been followed for compounds 2 and 4 by UPLC-MS monitoring. Figure 6 shows the typical evolution of the ratios of the three isomers upon heating, in that case for 4 at 60 °C, starting from the PSS (*Z*,*Z* = 95%, *Z*,*E* = 4%, *E*,*E* = 1%).

The three evolution curves (Figure 6b) perfectly fit with exponential decays of the first order for the Z,Z isomer, and of the second order for the Z,E and E,E isomers, in agreement with an apparent first order cascade reaction $Z, Z \rightarrow Z, E \rightarrow E, E$.³⁶ The rate constants k_1 and k_2 associated with the $Z, Z \rightarrow Z, E$ and $Z, E \rightarrow Z$ *E,E* reactions, respectively, were obtained by using the *Z*,*Z* and *Z*, E ratios vs time curves, respectively (see Figures S6-S9). Activation parameters for the thermal isomerization of compounds 2 and 4 (Table 2) were consequently determined via Eyring analysis³⁷ by measuring the rate constants at different temperatures (see Figure S10). In order to accurately compare the kinetics of the two consecutive thermal isomerizations, the statistical character of the first isomerization (two different azobenzene units per molecule are available for the first isomerization, $Z_1Z \rightarrow Z_2E$ or $Z_2Z \rightarrow E_2Z$) must be considered. Thus, normalized data, denoted by |x|, were introduced for the $Z, Z \rightarrow$ *Z*,*E* process. The normalized rate constant $|k_1|$ is therefore equal to the corresponding k_1 value divided by two. The normalized thermodynamic parameters (that is the parameters corresponding to the first $Z, Z \rightarrow Z, E$ or E, Z isomerization and taking into account statistics) were subsequently determined by using $|k_1|$ values determined at different temperatures. For comparison,

	$ k_1 \\ (s^{-1})$	$k_2 \ (s^{-1})$	$ \Delta H_1^* $ (kJ mol ⁻¹)	$\Delta {H_2}^{\dagger}$ (kJ mol ⁻¹)	$ \Delta S_1^{\dagger} $ (J mol ⁻¹ K ⁻¹)	ΔS_2^{\dagger} (J mol ⁻¹ K ⁻¹)	$ \Delta G_1^* $ (kJ mol ⁻¹)	$\Delta {G_2}^{st}$ (kJ mol ⁻¹)
a		4.6×10^{-5}		101.5		12.6		97.8
ь		9.4×10^{-5}		97.2		4.1		96.0
с		9.0×10^{-5}		99.9		12.6		96.1
2	6.3×10^{-4}	1.1×10^{-3}	94.1	93.6	9.5	12.5	91.3	89.9
4	1.6×10^{-4}	3.9×10^{-4}	98.9	99.1	14.2	22.3	94.6	92.5
2*	1.3×10^{-5}	1.5×10^{-5}	102.6	103.0	5.9	8.3	100.8	100.5
4*	6.6×10^{-6}	8.4×10^{-5}	103.3	101.4	-0.7	17.1	102.6	96.3

Table 3. Kinetic Data and Thermodynamic Parameters Derived from B3LYP/6-31G* Eyring Transition State Calculations for Compounds a-c As Well As 2 and 4 in the Gas Phase @ 298.15 K^a

^{*a*} Rates k_1 and k_2 refer to the $Z, Z \rightarrow Z, E$ and $Z, E \rightarrow E, E$ isomerizations, respectively. Normalized data |x|, equal to the corresponding x value divided by two, were used in order to consider the statistical character of the first isomerization. For the latter two compounds, two different entries indicate low-activation pathways (without *) and high-activation pathways (with *) respectively, for $Z, Z \rightarrow Z, E$ (index 1) and $Z, E \rightarrow E, E$ (index 2) isomerizations.

kinetic data and thermodynamic parameters of the $Z \rightarrow E$ isomerization have also been determined for the reference compounds $\mathbf{a}-\mathbf{c}$ employing UV/vis spectroscopy (see the Supporting Information).

First, it is interesting to note the difference of stability between the single azobenzenes $\mathbf{a}-\mathbf{c}$, which, at room temperature (298 K), display thermal half-lives (τ) of 27 h, 14 h, and 57 h, respectively. From these values, the two following rules of thumb can be deduced: (i) extension of the conjugation is detrimental to the stability of the Z form and (ii) meta substitution is beneficial to the stability of the Z form.³⁸

Both $Z_{1}Z$ and $Z_{1}E$ isomers of compound 2 exhibit similar stabilities, with half-lives of 10 and 12 h, respectively, the Z,E-2 isomer being slightly more stable than Z,Z-2. Both isomers display similar thermal stability as their reference isomer, i.e., Z-b (half-life of 14 h). Remarkably, both Z,Z-4 and Z,E-4 isomers were observed to thermally revert at exactly the same rate ($|\tau_1| =$ τ_2 = 42 h), indicating again that the two azobenzenes in 4 are electronically and geometrically decoupled. Interestingly, when two azobenzenes are connected into a cyclophane³⁹ or by a simple methylene CH₂ linker,^{31a} it was found that the rate constants of the $Z_1Z \rightarrow Z_2E$ and $Z_2E \rightarrow E_2E$ isomerizations are very different (sometimes up to 4 orders of magnitude^{39a}), as a consequence of either ring strain or π -stacking tendency, i.e. geometrical or electronic coupling, respectively. Half-lives of Z,Z-4 and Z,E-4 are somewhat shorter compared to the reference isomer Z-c, which observed to revert with a half-life of 57 h.

The activation enthalpies ΔH^{\dagger} , entropies ΔS^{\dagger} , and free energies ΔG^{\dagger} of reference compounds $\mathbf{a}-\mathbf{c}$ are in good agreement with parameters determined for other azobenzene derivatives.^{7b,30,40} The activation free energies ΔG^{\dagger} of bisazobenzenes 2 and 4 are practically identical to their reference compounds (around 100 kJ mol⁻¹), but ΔH^{\dagger} and ΔS^{\dagger} of bisazobenzenes 2 and 4 are lower and higher, respectively, when compared to their references **b** and **c**. According to our previous work,³⁰ electronically active substituents in para-positions of azobenzenes generally lead to lower barriers for thermal $Z \rightarrow E$ isomerization. This effect is particularly large for electron-accepting groups, i.e., displaying a (-M) effect. Because the azo moiety constitutes such an acceptor group, connecting two azobenzenes in para-positions therefore reduces the thermal $Z \rightarrow E$ isomerization barriers, as observed in our experiments.

The thermal isomerization behavior was also studied by quantum chemistry using Eyring's transition state theory according to eq 1.³⁷ The temperature dependence of ΔS^{\ddagger} was neglected,

i.e., $\Delta S^{\dagger} = \Delta S^{\dagger}(T_0)$ was assumed, where T_0 is a reference temperature, chosen as 298.15 K. The temperature dependence of ΔH^{\dagger} was approximated as $\Delta H^{\dagger} = \Delta H^{\dagger}(0) + T\Delta C_{\rm v}(T_0)$ from the zero-point corrected enthalpy $\Delta H^{\dagger}(0) = \Delta E^{\dagger} + \Delta E^{\dagger}_{\rm ZPE}$ at T = 0 K (ΔE is a difference of SCF energies), and the heat capacity at constant volume $C_{\rm v}$.

In analogy to Table 2, reaction rates and kinetic parameters as obtained from gas phase B3LYP/6-31G* Eyring transition state theory are compiled in Table 3. The meaningfulness of the calculated values with regard to experiment becomes apparent from the reference compounds $\mathbf{a}-\mathbf{c}$, for which the computed $Z \rightarrow E$ isomerization rates k_2 are in the order of the experimental values of $\sim 10^{-5}$ s⁻¹. It was also confirmed that compound b displays the highest isomerization rate. In contrast to experiment, however, the activation entropies are positive in theory, an observation which already has been made.³⁰ This failure is due to the fact that activation entropies for larger molecules are often inaccurate when calculated under the harmonic approximation, and most of all also probably due to the neglect of an explicit, viscous solvent in the present theory. However, absolute rates are in pretty good agreement because gas phase B3LYP activation enthalpies ΔH^{\dagger} are by about 5–10 kJ/mol too large when compared to experiment (see Table 2) and thus compensating the positive activation entropies.

Returning to the thermal isomerization of bisazobenzenes, theory nicely corroborates experimental findings. The rows in Table 3 labeled 2 and 4 (without *) indicate that rate constants for individual isomerization steps $Z, Z \rightarrow E, Z$ and $E, Z \rightarrow E, E$ differ by not much more than a factor of 2 (for both compounds). This is a rather small difference given the exponential sensitivity of rate calculations. Also activation free energies differ by approximately 2 kJ/mol only. Further, the activation free energies for 2 are 2-3kJ/mol smaller than those of 4, which is in good agreement with experiment and consequently rates are faster for 2 than for 4, and half-lives shorter. Absolute activation free energies and entropies, as well as rates are not in quantitative agreement with experiment, as expected: rates are too fast by a factor of up to about 100. Again, this has to do with a too large (entropy) prefactor, and with the fact that a viscous solvent can hinder the isomerization reactions, even more so for large molecules such as 2 and 4.

The detailed analysis of the origin of these results is complicated by the fact that an azobenzene unit with two nonequivalent ligands at the N atoms has two nonequivalent transition states with (almost) linear N–N–C units. This is indicated in Figure 7, where the isomerization from Z_z to E_z and further to E_z for



Figure 7. Schematic representation of the thermal isomerization $Z_{,}Z \rightarrow Z_{,}E \rightarrow E_{,}E$ for molecule **4**. As shown, we can define four different TSs with almost linear N–N–C units. Characteristic rates and electronic energy differences (without ZPE and temperature corrections), ΔE (in eV), between stationary states are also shown. Calculations on B3LYP/6-31G* level of theory.

compound 4 is demonstrated, with two distinct transition states for each partial reaction (labeled TS_{1a}/TS_{1b} and TS_{2a}/TS_{2b}). It can be seen that the $Z \rightarrow E$ isomerizations have their lowest activation energies when isomerizing at one of the inner N atoms. The associated activation energies are reduced by up to 10 kJ/ mol as compared to isomerizations taking place at the outer N atoms. As a consequence, the isomerization rates are faster for these lower-energy paths. In Table 3, the entries 2/4 and $2^*/4^*$ refer to the low- and high-activation energy pathways, respectively, although in experiment only the lower energy path should be relevant.

CONCLUSIONS AND OUTLOOK

Herein, we have detailed a molecular design based strategy to optimize the photoswitching efficiency of para-connected bisazobenzenes, constituting the key structural motif to realize photoresponsive rigid rod architectures. Our approach is based on introducing large dihedral angles (ϕ) between adjacent azobenzene moieties linearly linked via highly twisted aryl-aryl connections to electronically decouple the individual photochromes. In order to validate our approach, four bisazobenzenes (1-4) exhibiting different dihedral angles as well as three single azobenzene reference compounds (a-c) have been synthesized and were investigated with regard to their photochromic and thermochromic behavior as well as electrochemical properties. Experimental findings have been systematically complemented by DFT calculations.

It could be shown that as the dihedral angle increases, in the order from 1 to 4, and consequently the electronic coupling decreases, the photoswitching characteristics dramatically improve, finally leading to azobenzenes operating independently of each other for the practically perpendicular ($\phi = 90^{\circ}$) ortho, ortho, ortho', ortho'-tetramethyl biphenyl linker in bisazobenzene 4. Due to the electronic decoupling, the absorption spectra in 3 and 4 are well separated, and therefore by choosing the appropriate irradiation wavelength almost quantitative photoisomerization giving rise to a total amount of 97% Z isomer in the PSS for the latter compound. Furthermore, decoupling in bisazobenzene 4 leads to the same thermal stability of both $Z_{1}Z$ and $Z_{2}E$ isomers (half-life of 42 h), also comparable to single azobenzene reference compound a. These two findings are in stark contrast to strongly coupled azobenzenes. For example compound 1, incorporating a direct *para*-phenylene bridge, displays a very low Z content in the PSS (16% Z form overall). In the same compound (1) or when two azobenzenes are connected into a cyclophane or by a methylene CH₂ linker, the two rate constants of the Z_{2} Z,E and $Z,E \rightarrow E,E$ isomerizations (k_1 and k_2 , respectively) can differ dramatically (sometimes up to 4 orders of magnitude).^{13,39a} The general conclusion that large dihedral angles allow for efficiently decoupling azobenzene moieties (compound 4) was furthermore confirmed by the inspection of the UV-vis spectra, revealing well-defined isosbestic points, and the cyclic voltammograms, displaying a single reduction wave corresponding to the simultaneous addition of two electrons per molecule, one in each N=N double bond.

In most of this work, experiment and theory are in good agreement regarding the spectroscopic, electronic, and thermodynamic data. The theorically found additivity of fragment UV/ spectra for compounds 3 and 4, and nonadditivity for 1 and 2, is a direct proof of the decoupling of fragment π -systems in the former species, a prerequisite for restoring the switching ability. Moreover, calculations provide mechanistic insight, indicating a preferred pathway for the thermal back $Z,Z \rightarrow Z,E \rightarrow E,E$ isomerization *via* inversion on the inner N-atoms.

The above-described strategy for achieving almost quantitative photoswitching of para-connected azobenzenes can be used to build complex photoresponsive systems.^{6,7} For instance, connecting several electronically and geometrically decoupled azobenzenes in their para-position results in linear rigid rod oligomers and polymers, displaying significant changes in size and shape upon UV irradiation.¹² Integration of such shrinkable rigid rod architectures into self-assembled nanostructured soft materials to design systems, capable of efficiently converting light into molecular and eventually macroscopic motion, is currently being explored in our laboratories.

ASSOCIATED CONTENT

Supporting Information. Synthetic details and compound characterization, photochemistry, electrochemistry, spectroscopy, kinetic analyses, and computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Generous support by the German Research Foundation (DFG via SFB 658, subprojects B8 and C2) is gratefully acknowledged. Wacker Chemie AG, BASF AG, Bayer Industry Services, and Sasol Germany are thanked for generous donations of chemicals.

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