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Accepted version (Final draft)

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Please cite the original version:
Herges, R., Moorman, W., Tellkamp, T., Stadler, E., Röhricht, F., Naether, C., Puttreddy, R., Rissanen, K., & Gescheidt, G. (2020). Efficient Conversion of Light to Chemical Energy: Directional, Chiral Photoswitches with Very High Quantum Yields. Angewandte Chemie, 59(35), 15081-15086. https://doi.org/10.1002/anie.202005361
Efficient Conversion of Light to Chemical Energy: Directional, Chiral Photoswitches with Very High Quantum Yields

Widukind Moormann, Tobias Tellkamp, Eduard Stadler, Fynn Röhrich, Christian Näther, Rakesh Puttreddy, Kari Rissanen, Georg Gescheidt, and Rainer Herges*

Abstract: Photochromic systems have been used to achieve a number of engineering functions such as light energy conversion, molecular motors, pumps, actuators, and sensors. Key to practical applications is a high efficiency in the conversion of light to chemical energy, a rigid structure for the transmission of force to the environment, and directed motion during isomerization. We present a novel type of photochromic system (diindane diazocines) that converts visible light with an efficiency of 18% to chemical energy. Quantum yields are exceptionally high with more than 70% for the cis–trans isomerization and 90% for the back-reaction and thus higher than the biochemical system rhodopsin (64%). Two diastereomers (meso and racemate) were obtained in only two steps at high yields. Both isomers are directional switches with high conversion rates (76–99%). No fatigue was observed after several thousands of switching cycles in both systems.

Photochemically induced cis–trans isomerizations (e.g. of retinal) are the key processes in the perception of light and for retinal-based photosynthesis (pumping protons through ion channels in halophilic bacteria).[1] Notwithstanding the very different functions (sensing and directed motion), both systems are based on the same reversible chemical reaction: the photoisomerization of retinal.[2–4] Nature has optimized these systems for more than 2 billion years to achieve high quantum yields (64–67%), conversion rates (between the (meta)stable states), and fatigue resistance.[5] Within the last four decades a number of artificial photoswitches have been developed and optimized, aiming at a plethora of applications, such as motors, pumps, actuators, switchable drugs, sensors, and switchable liquid crystals. However, to the best of our knowledge, the quantum yields of biological systems are still unmatched (Figure 1)[6] with the exception of diazocine, which was developed by our group.[7]

Whereas previous artificial systems exhibit high conversion rates and fatigue resistance, their energy conversion process is not adequately efficient. The efficiency of converting light into chemical energy or to perform work is a function of the wavelength $\lambda$ of the absorbed light, the quantum yield $\Phi$, and the amount of energy $E$ or work $W$ produced. Particularly for the conversion of light into useful work, further properties such as directional motion (e.g. chiral switch) and sufficient rigidity for the transmission of the molecular force to the environment are prerequisites. Additional important parameters are conversion rates (photostationary states, PSS) and fatigue resistance (long-term stability). We therefore set out to systematically improve the performance of the most frequently used artificial photoswitch azobenzene 1 and have been successful in enhancing all above parameters. The conversion wavelengths are shifted into the visible range, the quantum yields improved to 70–90% (surpassing even the most efficient biological system rhodopsin), the strain energy produced increased to 18 kcal mol$^{-1}$, the molecular switching movement is directional, the molecular framework is rigid (no conformational degrees of freedom), and the fatigue resistance amounts to at least a few thousand cycles.

Moreover, our new switches (3 and 4) presented here are accessible from commercially available starting materials in only two steps at high yields. Figure 1b compares the efficiency of converting light into chemical energy (strain) of azobenzene 1 (14%), diazocine 2 (7.6%), and meso-diindenediazocine 3 (18.1%) upon irradiation at their peak absorption wavelengths 317, 385, and 400 nm. meso-Diindenediazocine 3 is not suitable for immediate long-term chemical energy storage;[15] however, the short lifetime of the metastable state and the superior photophysical properties make it an ideal motor for ATP-synthase type light-driven synthesis[16] and other light-to-chemical-energy conversion systems.[17]
Arguably, the most frequently used artificial photoswitch is azobenzene 1. Azobenzene derivatives are easily accessible, robust, reliable, chemically inert, and fatigue resistant. However, UV light is needed for the isomerization of the trans to the cis isomer, conversion rates are usually not high, and quantum yields are relatively low.\textsuperscript{[15,18]} By the introduction of ethylene bridges between the \( o_o \)′ positions of azobenzenes, we have been able to improve the photophysical properties considerably.\textsuperscript{[7]} Compared with 1, these diazocines 2 exhibit enhanced quantum yields, switching wavelengths in the visible range, and very high conversion rates. Moreover, diazocines 2 are thermodynamically more stable in their cis configuration, which is of advantage in applications such as photopharmacology and mechanosensing.\textsuperscript{[19–22]}

However, neither the parent azobenzene 1 nor diazocine 2 are directional switches and are therefore unable to induce directional motion (Figure 2a,b). Curved arrows in 3 and 4 indicate the directionality of the molecular movement during isomerization. Introduction of additional bridges into the tricyclic diazocine system should further reduce conformational movements and introduce directionality into the switching motion. Moreover, the elimination of conformational degrees of freedom should concomitantly increase the quantum yields of the switching processes by preventing unproductive relaxation pathways.\textsuperscript{[23,24]}

Aiming at the improvement of our parent diazocine switches along the above lines, we pursued a design strategy based on ring strain. Figure 2c illustrates our approach by means of a simplified model. Starting from the parent cis and trans diazocine 2 and introducing two ethylene bridges between positions 1–11 and 10–12, 8 different isomers of bridged diazocines (diindanodiazocines) are conceivable (Figure 2c). Concomitant introduction of two stereocenters leads to a meso compound (m) 3 and a racemate (r) 4. Cis and trans isomers are denoted with c and t. Syn annulations are favorable (f) and anti annulations are strained and unfavorable (u). Hence, four meso isomers result: m-c-uu, m-c-ff, m-t-uf, and m-t-fu. Analogously, the racemate comes as r-c-u, r-c-ff, r-t-uf, and r-t-fu. Meso 3 and racemate 4 do not interconvert because that would imply an inversion at a sp\(^3\) carbon. Hence, the conformational degrees of freedom of meso 3 and racemate 4 can be analyzed separately. Besides cis–trans isomerization, there are two conceivable conformational transitions: ring inversion of the cis-boat, and twist- and twist-chair inversion of the trans isomer. Simple molecular model considerations reveal that the inversion at azo nitrogen atom 5 induces a rotation of the 12 methylene group and thus a change from a favorable (f) to an unfavorable bridge (u) or vice versa. Likewise the inversion at N6 (atom numbering see Figure 2b) interconverts the pseudo axial and pseudo equatorial hydrogen atoms at position 11 and thus changes the strain of the corresponding bridge. Both boat inversion and twist inversion change both bridges from favorable to unfavorable or vice versa. From these simple model considerations, the reaction network shown in Figure 2c,d can be derived. The relative energies of the 8 isomers can be estimated as well without explicit calculations. The cis isomer of diazocine is approximately 8 kcalmol\(^{-1}\) more stable than trans, and if we assume that an unfavorable bridge induces about 10 kcalmol\(^{-1}\) strain, the most stable meso cis structure m-c-ff is about 18 kcalmol\(^{-1}\) more stable than its trans isomer, whereas the cis (r-c-uf) and trans (r-t-ff) racemate should be almost isoequivalent. Structures m-c-uu and r-t-uf with two strained bridges are extremely unfavorable and probably not accessible. We should not observe the r-c-uf \( \leftrightarrow \) r-c-ff ring inversion and the m-t-uf \( \leftrightarrow \) m-t-fu twist inversion because a high activation barrier can be expected, since both conformational movements include the simultaneous change of the strain of two bridges. Explicit DFT calculations at the PBE(D3(BJ))/def2TZVP level of density functional theory (Supporting Information Figures S26 and S27, Table S7) support our qualitative picture (blue numbers in Figure 2a–c). Upon irradiation, the meso cis compound (m-c-ff) should convert into a high-energy trans isomer (m-t-uf) with a strain energy of 18.5 kcalmol\(^{-1}\). The cis and trans isomers of the racemate are close in energy (3.5 kcalmol\(^{-1}\) in favor of the cis isomer). Transition state calculations confirm the expected high

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a) Quantum yields of diindane diazocines (DID meso 3 and DID rac 4) presented in this work compared to frequently used artificial photoswitches and natural systems.\textsuperscript{[4,6,8–14]}. For an extended list of photoswitches and quantum yields see Supporting Information Table S1.

b) Efficiency of the conversion of light to chemical energy (strain energy, see Supporting Information Figure S28).

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Figure 1. Switching properties of selected photochromic compounds. a) Quantum yields of diindane diazocines (DID meso 3 and DID rac 4) presented in this work compared to frequently used artificial photoswitches and natural systems.\textsuperscript{[4,6,8–14]}. For an extended list of photoswitches and quantum yields see Supporting Information Table S1. b) Efficiency of the conversion of light to chemical energy (strain energy, see Supporting Information Figure S28).
barriers for boat and twist inversions (Figure 2c,d, Supporting Information Figures S26 and S27). The bridging strategy in diindane diazocines 3 and 4 restricts the conformational degrees of freedom to only one conformation in each configuration. The synthesis of the meso compound 3 and racemate 4 of diindane diazocine (DID) is quite straightforward. It includes only two steps starting from commercially available 4-nitroindane 5. Treatment of 4-nitroindane 5 with tert-butoxide and bromine afforded a mixture of the dinitro compounds 6 and 7, which were separated by crystallization. The dinitro compounds 6 and 7 were converted into the diazocines 3 and 4 (Figure 3). The yields are 53% for the meso compound 3 and 70% for the racemic mixture 4. An X-ray crystal structure of

**Figure 2.** Stepwise reduction of conformational degrees of freedom by the introduction of bridges into azobenzene. a) azobenzene 1, b) diazocine 2, and c,d) doubly bridged diazocines (diindane diazocines) 3 and 4. a) trans azobenzene 1 (C2h), upon irradiation, gives two enantiomeric cis azobenzenes 1 (C2) that rapidly interconvert at room temperature by almost free rotation of the phenyl groups. b) In diazocine 2 the phenyl rings are fixed by an ethylene bridge connecting the two rings. Conformational movements are restricted to twist inversions and twist-chair inversions of the trans configuration. The cis configuration undergoes boat inversion at room temperature. c,d) There are two diastereomers of diindane diazocine: meso 3 and racemate 4. Both compounds are conformationally rigid. There is no boat inversion and no twist inversion, which restricts each of the cis and the trans isomers to only one conformation. The CH2—CH2—bridge is either favorable (syn annelation, green) or strained (anti annelation, orange). Relative energies (kcal mol⁻¹) at the PBE(D3(BJ))/def2TZVP level of density functional theory are given in blue numbers. Structures m-c-u and r-t-u could not be located as minima on the potential energy surface, probably because of very high strain. The curved arrows in 3 and 4 indicate the directionality of the isomerization. Other molecular movements, for example, flapping in the reverse direction, are prohibited by the molecular framework.
the dinitro compound 7 reveals that the two nitro groups are suitably oriented for ring closure (Figure 3, top right), which explains the high yield (70%) of the azo cyclization. The single-crystal X-ray diffraction study of diazocines 3 and 4 (Figure 3, bottom left and right, respectively, Supporting Information Table S6) proves the markedly different molecular geometries between the m-c-ff form of 3 and the r-t-ff form of 4. The cis configuration of the -HC\textsubscript{CH} bridge with the H\textsubscript{CH} torsion angle of 39.3° in the diazocine 3 causes increased steric hindrance of the CH hydrogens and results in a slightly more twisted azo group (C=N=N=C torsion of 9.0°). The r-t-ff form of 4 is more relaxed with H\textsubscript{CH} torsion angle of 167.2° and C=N=N=C torsion of 4.6°.

The highly strained diindane diazocines 3 and 4 exhibit unusual properties regarding the half-lives of their thermal relaxation. While the half-life of the racemic mixture 4 is about four times longer than the half-life of the parent system 2 (117 h vs. 27.6 h), the thermal relaxation for the meso compound 3 is about four orders of magnitudes faster than the parent system 2 (3 s). This is due to the high strain of the pincer-shaped molecule 3.

Half-lives and photostationary states (PSS) were determined via NMR experiments in acetone (Table 1, Supporting Information Figures S13–S16). The half-life of the meso compound 3 was extrapolated from low-temperature measurements via Arrhenius plots (Supporting Information Figure S14). Additionally, the thermal relaxation of the trans → cis isomerization was monitored via low-temperature UV spectroscopy at 233 K (Figure 4a). The UV spectrum of the meso diazocine 3 shows almost completely separated maxima for the n–\pi* transitions, (cis 411 nm, trans 468 nm), resulting

Table 1: Photophysical properties of DID 3 and 4 in comparison to the parent diazocine 2.

| Diazocine | t\textsubscript{1/2} [h] | PSS (385 nm) | PSS (530 nm) | Φ\textsubscript{Z–c} | PSS (385 nm) | Φ\textsubscript{Z–c} | PSS (530 nm) |
|-----------|-----------------|--------------|--------------|-----------------|--------------|-----------------|--------------|
| 2         | 27.6[^a]        | 87%[^b]      | >99%[^c]     | 0.72[^d]        | 0.9[^e]      | 0.9[^e]         |              |
| 3         | 8.77 \times 10^{-9}[^f] | 84%[^g] | >99%[^h] | 0.7[^i] | 0.9[^i] | 0.9[^i] |              |
| 4         | 11[^j]          | 76%[^k]      | >94%[^l]     | 0.8[^m]        | 0.9[^n]      | 0.9[^n]        |              |

[^a] In acetone at 300 K. [^b] In acetone at 293.15 K. [^c] In acetone 233 K. [^d] In acetone at 269.15 K. [^e] In acetone at 298.15 K. *m measured at five temperatures (233 K, 238 K, 240 K, 243 K) and extrapolated to room temperature.

Figure 3. The diindane diazocines 3 and 4 were obtained by oxidative C–C coupling of 4-nitroindane 5, followed by reductive azo cyclization of the corresponding dinitro compounds 6 and 7. The thermal ellipsoids of the X-ray crystal structures are shown at the 50% probability level.

Figure 4. a) Selected UV spectra of the thermal relaxation of the meso diazocine 3 in THF at 233 K after irradiation at 385 nm. b) UV spectra of the n–\pi* transition of the diazocines 3 (top) and 4 (bottom) before and after irradiation at 385 nm in THF at 298 K. The UV spectra of the pure trans isomers 3 and 4 were obtained through extrapolation.
in a PSS of 84%, which is consistent with the PSS of the parent system 2 (Figure 4b). The racemic diazocine 4 exhibits a cis→trans conversion of 76% (385 nm). The n→π* transition for the cis→trans isomerization has a bathochromic shift resulting in a maximum at 431 nm and because the trans→cis n→π* transition is not shifted equally (478 nm), resulting in an overlap of absorption bands (Figure 4b). Trans→cis conversions of 3 and 4 are achieved upon irradiation with green light (530 nm) and are quantitative within the limits of detection (UV and 1H NMR).

The photostabilities of compounds 3 and 4 were determined via long-term irradiation experiments. The photo-switching of the racemic diazocine 4 in acetonitrile was monitored via UV spectroscopy. The solution was irradiated at 385 nm and 530 nm for 30 seconds each in an alternating sequence. After 5000 cycles, UV spectra of several additional irradiation cycles were recorded showing no loss of absorption (Figure 5a). The meso diazocine 3 was irradiated at 400 nm for 3.5 days (stirred solution 800 rpm, concentration: 1 mM, path length 1 cm, light intensity: 0.3 mW cm⁻²). This corresponds to ca. 2900 cis→trans isomerizations of one single molecule based on the molar absorption and the photon flux. The comparison of the UV spectra before and after illumination shows no sign of fatigue (Figure 5b). The photochemical quantum yields of the isomerization of diindane diazocine 3 and 4 were measured in an online UV/Vis spectroscopy experiment (Supporting Information Figures S17–S19) confirming the rigidity of the diindane diazocines 3 and 4 in comparison to the parent diazocine 2. When diazocine 2 is heated from 298 K to 343 K the signal of the ethylene bridge protons is broadened, confirming a boat inversion at higher temperatures. The relevant signals of the diindane diazocines 3 and 4, on the other hand, exhibit no broadening from 298 K to 343 K.

Stepwise and systematic elimination of the conformational flexibility from azobenzene 1 to diazocine 2 drastically improved the photophysical properties. We introduced further bridges into the diazocine framework, preventing all conformational degrees of freedom leading to unproductive relaxation (boat, twist, and twist-chair inversions) leaving only a well-defined pincer-type molecular movement for the cis→trans isomerization. The quantum yields of these diindanodiazocines 3 and 4 surpass even the natural systems rhodopsin, bacteriorhodopsin, and halorhodopsin. Concomitantly, we have been able to introduce considerable strain into the meso isomer of diindano diazocine 3. The trans configuration is 18.5 kcal mol⁻¹ higher in energy than the cis isomer. The high quantum yield (70%) combined with the large ring strain that builds up upon cis→trans isomerization of meso diindanodiazocine 3, leads to an exceptionally high light-to-chemical-energy conversion efficiency of 18%. The syntheses of meso 3 and rac 4 diindane diazocine include only two steps from commercially available chemicals. Multigram amounts can be prepared within a few days with standard laboratory equipment. Moreover, no fatigue has been observed over thousands of switching cycles. In contrast to azobenzene and most other photochromes, the molecular motion during isomerization is directional. Thus, meso diindanodiazocines (such as 3) are ideal actuators to power molecular machines. Rac diindano diazocine 4 is the smallest chiral photoswitch known to date. It is also ideally suited as a component to switch chiroptical properties and to control the chirality of liquid crystals.[27–30]

Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG) within the Sonderforschungsbereich 677, “Function by Switching”. E.S. and G.G. thank NAWI Graz for support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: diazocine · energy conversion · photochemistry · photochromism · quantum yields

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