

Fast, Reversible, and General Photomechanical Motion in Single Crystals of Various Azo Compounds Using Visible Light

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Harnessing molecular motion to control macroscopic properties reversibly, such as shape and size, is a subject of much current interest in the scientific and engineering research communities. Various clever systems have been designed to exploit this motion at the nanoscale yielding new classes of smart materials including molecular switches,^[1] motors,^[2] and even 'nanocars',^[3] each driven by some external stimuli such as chemicals, heat or electromagnetic fields. Light-activated materials are especially interesting due to ongoing parallel research into alternative materials for solar energy harvesting,^[4] with molecular chromophores being designed to respond to light sources that mimic solar wavelengths and intensities.^[5] Here, we demonstrate how to convert the concerted, fast, visible-light-induced molecular isomerization to an easily-observable reversible motion of various macroscopic azobenzene and pseudostilbene single crystals (**Figure 1**).

Photomechanical motion in bulk crystalline materials was first observed recently, most notably in a reversible shape and color change of diarylethene crystals,^[6] where the visible structural change was initiated by a pericyclic ring opening/closing reaction, and photoelongation of crystals of anthracene derivatives due to reversible [4 + 4] photodimerization.^[7] Subsequent investigations followed, including studies of diarylethene co-crystals,^[8] twisting of anthracene ester crystals,^[9] and a salicylideneaniline system,^[10] where shape change was governed by intramolecular proton migration under irradiation. It was postulated that the especially dramatic and facile photomechanical motion of diarylethene crystals arises from the relatively small free-volume change of the transition state of the ring opening/closing reaction. Azobenzene *trans-cis* isomerization requires a much greater free-volume change (between 120 and 250 Å³)^[11] and thus harnessing such isomerization in the solid state poses a greater challenge. However, the examples of amorphous soft 'plastic motors'^[12] and multiple photochromic effects in azobenzene functionalized polymer films^[13] and liquid-crystalline actuators^[14] suggested that *trans-cis* isomerization at least in the surface layers in the crystalline state was also feasible. The observation of photomechanical crystal bending of two azobenzene derivatives was indeed reported^[15] with displacement magnitudes comparable to those of the other systems mentioned above.

One of the limitations of previous crystal photomechanical systems, however, was their reliance on high-energy ultraviolet light for driving the underlying molecular transformation, whether it is a pericyclic reaction, *trans-cis* isomerization or proton migration. Using lower energy visible light is preferable since it is far less damaging to organic molecules, and comprises a larger portion of the solar spectrum available. Furthermore, the length of the photomechanical cycle (from the beginning of irradiation until the crystal returns to its original shape) for previously reported azobenzene crystals was on the order of minutes,^[15] consistent with the rates usual for this spectral class of dyes, which limits many practical applications. With azobenzene chromophores, however, the absorbance maximum can be easily red-shifted by substitution. A special case, where a strong 'pull' electron withdrawing group is combined with a strong 'push' donor gives rise to a class of azo molecules known as pseudostilbenes, which are characterized by comparatively short lifetimes of the *cis*-isomer, down to milliseconds, as well as absorption maxima in the visible spectrum deep into the blue or green.^[16] In this paper, we establish that the electronic structure of pseudostilbenes indeed enables rapid and reversible photomechanical motion in response to visible light, and correlate photomechanical bending properties to structural features of the chromophore and their crystals such as crystal packing, crystal thickness, and relative orientation of the absorbing molecules to the irradiated crystal faces. While a UV-lamp was used as a light source in previous studies of crystal photomechanical properties, we instead employed a tunable Ar⁺-ion laser, for better localization, higher power, and better control over wavelength, intensity, and polarization. Crystals were grown by sublimation on glass microscope slides under

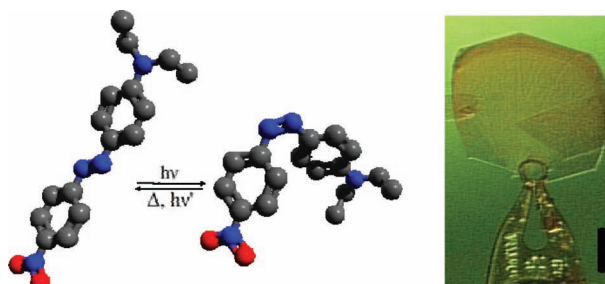


Figure 1. 4-diethylamino-4'-nitroazobenzene microcrystal (700 μm × 600 μm × 2 μm) exhibits fast, reversible, photomechanical motion upon irradiation of the (001) face with visible light. The scale bar is 200 μm. The molecular geometry was optimized by molecular mechanics using the universal force field algorithm in Avogadro 1.03.

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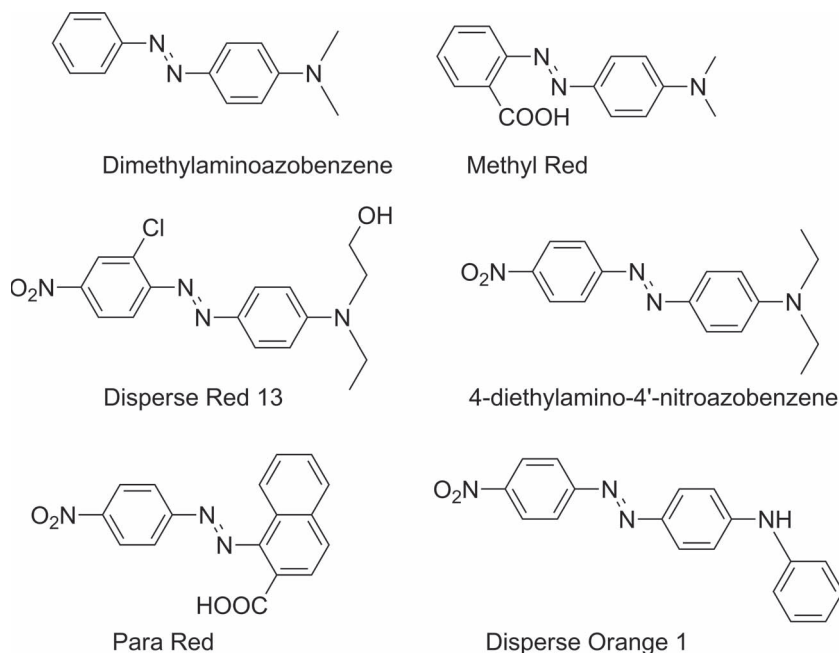


Figure 2. Structures of the studied compounds.

reduced pressure at, or slightly below, the melting point of a particular compound. Crystals of larger sizes were chosen for X-ray single-crystal structure determination (Bruker Smart Apex 2), while the thinner crystals were subjected to bending analysis with the laser light (see Supporting Information for sublimation conditions (Table S1), and the experimental setup).

In contrast to isolated cases reported in previous studies where bending was observed in only some samples, here we demonstrate bending motion for all of the compounds investigated (Figure 2), suggesting the general nature of the photomechanical effect of the solid state in pseudostilbene derivatives, if suitable conditions are found. Another important difference was observed in the relaxation process, which occurs at least one order of magnitude faster than that for the aminoazobenzene crystals. Previously studied aminoazobenzene systems^[15] thermally relax on a time scale of tens of seconds or minutes and the relaxation can be accelerated by irradiation with the light corresponding to the absorption of the *cis*-isomer. For the diarylethene derivatives the irradiation for the reverse

motion is mandatory. At the same time, the crystals based on the pseudostilbene derivatives studied here revert back to their original shape naturally when irradiation is ceased on a time scale of milliseconds without any supplemental irradiation, owing to the extremely short lifetimes of the *cis*-isomer, thus demonstrating suitability to fast switching applications. The observation of forward bending rates on the microsecond timescale (faster than the millisecond video-capture limit) represents the fastest azo photomechanical systems yet reported.

To best characterize and compare photomechanical motion between different compounds with an inherent distribution of linear dimensions for crystals, we monitored deflection angle as opposed to deflection distance. Furthermore, as was noted in the preceding investigation,^[15] bending magnitudes along different crystallographic axes in the unit cell can vary significantly; here the values are reported along the axis of maximum bending. Relaxation rates and maximum deflection magnitudes are summarized in Table 1 alongside the dimensions of crystals for which

they were obtained. The magnitude of bending depends on the power of incident radiation, as depicted in Figure 3. It is noteworthy that the threshold power at which the photomechanical effect is observable varies significantly for different compounds. While for dimethylaminoazobenzene the motion initiates at the power as low as 1 mW cm⁻², 4-diethylamino-4'-nitroazobenzene at 50 mW cm⁻², and Disperse Red 13 at 100 mW cm⁻², the Para Red crystal can be moved only at 200 mW cm⁻².

The power dependence can be correlated with the size and/or rigidity of the substituents on the azobenzene parent structure and, as will be discussed further, with the density of crystal packing. As the size of the donor group substituents grows larger and with the inclusion of a nitro group, the free-volume change required for the *trans-cis* isomerization increases, thus inhibiting the bending. Consequently, a larger number of simultaneously isomerizing molecules is needed to move the crystal which is achieved by a higher power density. Macroscopic crystal bending depends strongly on the thickness of the crystal specimen, and is driven only by a relatively thin 50–100 nm

Table 1. Summary of photomechanical behavior of the studied compounds, orientation of the molecules and density of crystal packing.

Compound	Crystal dimensions [μm]	Deflection [°]	Half life [s]	Orientation of the molecular plane with respect to irradiated face [°]	Volume per non-hydrogen atom in the unit cell [Å ³]
Dimethylamino azobenzene	600 × 400 × 1	20 ^{a)}	1	83.3, 85.9 ^{b)}	18.1
Disperse Red 13	600 × 500 × 1	15	<0.1	87.2, 89.2 ^{b)}	17.1
4-diethylamino-4'-nitroazobenzene	500 × 300 × 3	8	<0.1	85.6, 88.2 ^{b)}	16.7
Para Red	800 × 300 × 2	5	<0.1	25.6	14.9
Disperse Orange 1	600 × 100 × 5	1	<0.1	65.3	15.9
Methyl Red	400 × 100 × 5	3	<0.1	54.5	14.6

^{a)}Using power density of 0.3 W cm⁻². All of the other values were at 1 W cm⁻²; ^{b)}The 2 values represent the 2 orientations in the herring-bone structures.

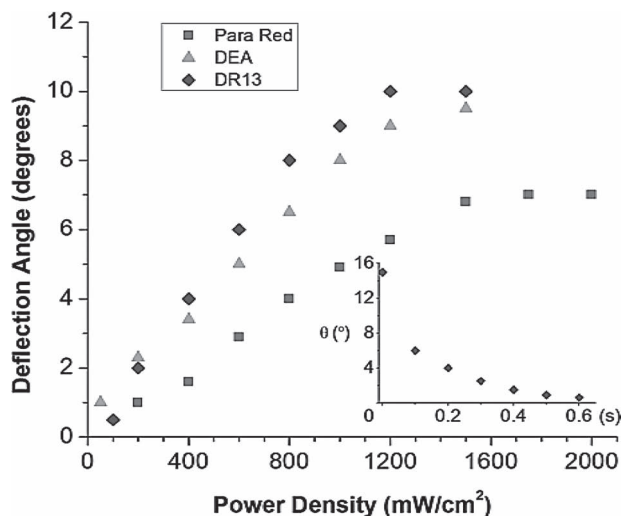


Figure 3. Deflection angle (θ) dependence on power of incident irradiation for crystals of similar dimensions and ca. $2 \mu\text{m}$ thickness of Disperse Red 13 (DRI3), 4-diethylamino-4'-nitroazobenzene (DEA) and Para Red. Inset: relaxation profile of DRI3 in the dark.

surface layer due to the high molar absorptivity of azobenzene-type chromophores.^[17] This simple estimate can be made considering the appreciable extinction coefficients of the azo molecules of the order of $10\text{--}20 \mu\text{m}^{-1}$, and a threshold depth for inactivation where light levels are reduced to 10% of the incident light on the surface. Consequently it is not surprising that only a modest net photomechanical effect was observed for crystals above $10 \mu\text{m}$ in thickness, where the active driving layer comprises only 1% or less of the total thickness, and that plate-like crystals bend more than the needle-like ones.

The magnitude of bending of azobenzene crystals thus depends on the power of irradiation, the bulkiness of the ring substituents, and crystal shape and thickness. Another dependence, however, can be traced: that of the crystalline structure. The orientation of the constituent molecules relative to the most prominent faces of the crystal may also influence the photomechanical behavior of the macroscopic crystal, so crystal structures of all compounds were obtained for comparison.

Multiple bending experiments on various crystals of all of the tested compounds suggest strong dependence of the magnitude of bending on its orientation with respect to the irradiating beam. Some of the systems, namely dimethylaminoazobenzene, 4-diethylamino-4'-nitroazobenzene and Disperse Red 13, which coincidentally form crystals of similar size and planar shape, exhibited the highest bending magnitudes. Other systems of Disperse Orange 1, Para Red, and Methyl Red which form needle-like crystals exhibited a strong preference to bending at specific incident irradiation directions while showing no response upon irradiation of other faces. This suite of observations taken together leads us to believe that molecular orientation and packing in the crystals are largely responsible for the direction and magnitude of the photomechanical effect. As was noted in a prior investigation^[15] the molecules in dimethylaminoazobenzene are arranged almost perpendicular to the (001) face of the irradiated crystal which is the most prominent face.

We determined the orientation of the constituent molecules relative to the irradiated crystalline face in the studied crystals by single-crystal X-ray diffraction and face indexing. In all three of the compounds showing the highest photomechanical effect, molecules run nearly parallel to the c -axis resulting in a roughly perpendicular arrangement relative to the irradiated (001) face (Figure 4a), which is in all cases the largest face of these plate-like crystals. The long c -axis characteristic of all three of the structures may be responsible for directing the preferential planar growth of the crystals under sublimation conditions, allowing for the most suitable plate-like photoresponsive crystals. For the other studied compounds (Disperse Orange 1 (Figure 4b), Para Red, and Methyl Red) the internal orientation of the molecules is not perpendicular to the largest irradiated (010) faces and the observed deflection magnitudes are lower than for crystals with perpendicular arrangement.

The density of the crystal packing likely plays a crucial role in determining the magnitude of the photomechanical effect by governing the free-volume requirements for molecular isomerization. Calculated densities are not representative due to different elemental composition of the studied dyes, but a crystallographically determined density that remains accurate regardless of the elemental composition is the volume per non-hydrogen atom in the unit cell. For all of the crystals which exhibited maximum bending this volume was the highest (ca. $17\text{--}18 \text{ \AA}^3$ per non-hydrogen atom) showing low packing density of these crystals compared with the other studied analogues

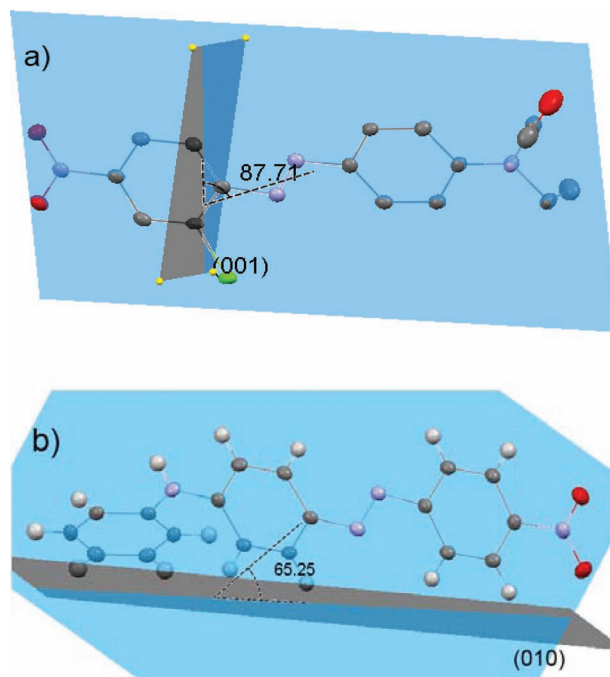


Figure 4. a) Molecular orientation in crystals of Disperse Red 13. The grey planes represent the irradiated face, the blue planes – the least squares plane drawn through the azobenzene fragment. Molecules align nearly perpendicular to the (001) face and crystals exhibit significant bending. b) Molecular orientation in crystals of Disperse Orange 1. Molecules are strongly tilted with respect to the irradiated (010) face and the crystals exhibit relatively little bending.

(ca. 15 \AA^3). For a structure of 20 non-hydrogen atoms, such a difference amounts to a 40–60 \AA^3 difference in free space, a value of the same order of magnitude as required for the isomerization of the parent azobenzene chromophore (120–250 \AA^3),^[11] which allows more facile crystal motion and higher net photomechanical effect.

Crystal structure also plays a crucial role in the resilience of crystals under different irradiation powers. While dimethylaminoazobenzene crystals crack at power densities greater than 1 W cm^{-2} and with 4-diethylamino-4'-nitroazobenzene over 2 W cm^{-2} , Para Red crystals survive irradiation with powers of up to 4 W cm^{-2} . Such a four-fold increase in crystal resiliency can be attributed to an increase in strength of molecular interactions. The nitro group in 4-diethylamino-4'-nitroazobenzene and Para Red increases the strength of dipole interactions, while extra reinforcement is possible in Para Red due to intramolecular hydrogen bonds and more efficient π - π interaction between naphthalene fragments.

To confirm that the fast relaxation process was not caused by thermal effects of irradiation by the laser, we tested crystals of previously reported dimethylaminoazobenzene (Supporting Information, Video 1). Blue light of 457 nm wavelength was employed at power densities of 100–300 mW cm^{-2} to initiate bending of a $600 \mu\text{m} \times 400 \mu\text{m} \times 1 \mu\text{m}$ crystal, with both forward bending (seconds) and the relaxation times (tens of seconds, Table 1) were comparable to values reported previously using UV-light.^[15] Green light (532 nm) of the same power was unable to initiate bending due to the negligible absorption of the compound at longer wavelengths. In a separate set of experiments photomechanical bending was studied under the liquid nitrogen stream on a Bruker Smart Apex II diffractometer which allows controlled cooling to 90 K. In the course of the experiment, we observed bending at as low as 180 K, at which point the studied crystals become too brittle and fracture under the stress generated by bending. Repeated attempts to cool crystals below 180 K all led to fracturing of the crystals. We observed a decrease of speed of the relaxation at low temperatures which is consistent with the slower thermal relaxation of the *cis*-azobenzenes at low temperatures. Additionally, as a test for photothermal contribution to photomechanical bending, needle-like single crystals of alizarin dye were grown by ethanol vapor diffusion into DMF and tested in identical conditions. At similar thickness (3–10 μm) and aspect ratios alizarin failed to produce any bending at any of the used irradiation wavelengths and power of up to 10 W cm^{-2} . Furthermore, utilizing the previously developed model^[17] for temperature increase in irradiated azo-containing polymer films we do not anticipate any significant thermal contribution to crystal bending, even at the relatively high irradiation powers employed. No significant dependence of the polarization direction of the light source on rate or magnitude of deflection was observed.

In conclusion, we examined the influences of electronic structure, molecular geometry, long-range crystal packing, and macroscopic crystal orientation on the photomechanical performance of azobenzene dyes. The push-pull electronic structure of donor/acceptor substituents on pseudostilbenes extends and enhances the photomechanical property of single crystals known from other azobenzene derivatives by simultaneously

imparting sensitivity to visible light and spontaneous, rapid reverse motion of photomechanically bent single crystals. The latter property results from the extremely short thermal lifetimes of *trans-cis* isomerization in pseudostilbenes relative to other azobenzenes. Such short lifetimes allow quick recovery without supplemental irradiation with other light sources as in the previously studied systems. It appears that a combination of lower packing density, lower crystal thickness and perpendicular arrangement of the molecules with respect to the irradiated surface all contribute significantly to the ability of a crystal to exhibit high-magnitude photoinduced bending. After optimizing each of these structural-property relationships, no compounds were identified which failed to undergo photoinduced bending under some conditions, although less compliant systems require higher power density. Crystal structures for Disperse Red 13, 4-diethylamino-4'-nitroazobenzene, Disperse Orange 1 and a new Para Red polymorph were obtained for the first time.

Supporting Information

Supporting Information is available on the Wiley Online Library or from the author. Complete experimental details, summary of crystallographic refinements and statistics, cif files, Tables S1,S2, Figures S1,S2 as well as 3 videos of crystal motion upon irradiation are included.

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- [1] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685; b) A. Coskun, M. Banaszak, R. D. Astumian, J. F. Stoddart, B. A. Grzybowski, *Chem. Soc. Rev.* **2012**, *41*, 19; c) M. M. Russev, S. Hecht, *Adv. Mater.* **2010**, *22*, 3348.
- [2] a) B. L. Feringa, *Acc. Chem. Res.* **2001**, *34*, 504; b) M. von Delius, E. M. Geertsema, D. A. Leigh, *Nat. Chem.* **2010**, *2*, 96.
- [3] a) Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, J. M. Tour, *Nano Lett.* **2005**, *5*, 2330; b) T. Kudernac, N. Ruangsapichat, M. Parschau, B. Macia, N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, B. L. Feringa, *Nature* **2011**, *479*, 208.
- [4] M. Gratzel, *Acc. Chem. Res.* **2009**, *42*, 1788.
- [5] N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa, P. Rudolf, *Prog. Surf. Sci.* **2007**, *82*, 407.
- [6] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778.
- [7] R. O. Al-Kaysi, A. M. Müller, C. J. Bardeen *J. Am. Chem. Soc.* **2006**, *128*, 15938.
- [8] a) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172; b) F. Terao, M. Morimoto, M. Irie, *Angew. Chem. Int. Ed.* **2012**, *51*, 901.
- [9] L. Zhu, R. O. Al-Kaysi, C. J. Bardeen *J. Am. Chem. Soc.* **2011**, *133*, 12569.

- [10] H. Koshima, K. Takechi, H. Uchimoto, M. Shiro, D. Hashizume, *Chem. Commun.* **2011**, 47, 11423.
- [11] T. Naito, K. Horie, I. Mita, *Macromolecules* **1991**, 24, 2907.
- [12] M. Yamada, M. Kondo, J.-I. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem. Int. Ed.* **2008**, 47, 4986.
- [13] a) Y. Yu, M. Nakano, A. Shishido, T. Shiono, T. Ikeda, *Chem. Mater.* **2004**, 16, 1637; b) D. H. Wang, K. M. Lee, Z. Yu, H. Koerner, R. A. Vaia, T. J. White, L.-S. Tan, *Macromolecules* **2011**, 44, 3840; c) K. M. Lee, H. Koerner, R. A. Vaia, T. J. Bunning, T. J. White, *Macromolecules* **2010**, 43, 8185.
- [14] H. F. Yu, T. Ikeda, *Adv. Mater.* **2011**, 23, 2149.
- [15] a) H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.* **2009**, 131, 6890; b) H. Koshima, N. Ojima, *Dyes Pigment.* **2012**, 92, 798.
- [16] K. G. Yager, C. J. Barrett, in *Intelligent Materials*; The Royal Society of Chemistry, Cambridge, UK **2008**, p 424.
- [17] K. G. Yager, C. J. Barrett, *J. Chem. Phys.* **2004**, 120, 1089.
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