

# Shaping Crystals with Light: Crystal-to-Crystal Isomerization and Photomechanical Effect in Fluorinated Azobenzenes

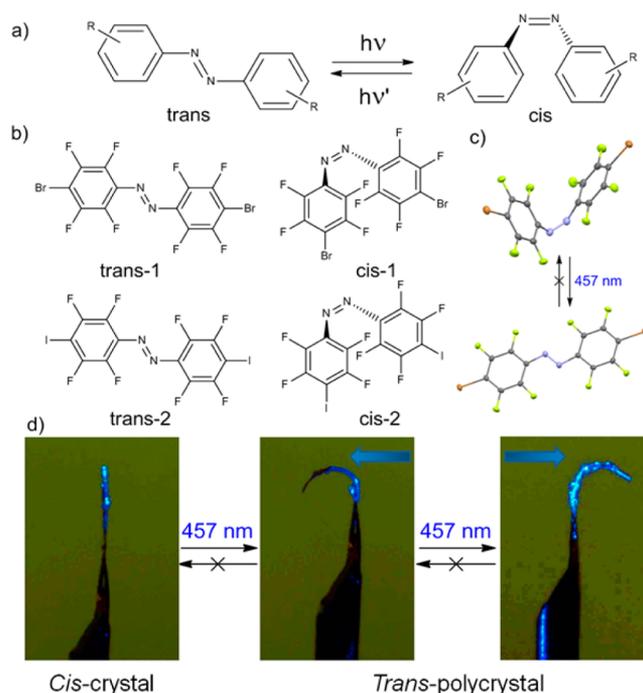
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**S** Supporting Information

**ABSTRACT:** Unusually long thermal half-lives of perhalogenated *cis*-azobenzenes enabled their structural characterization and the first evidence of a crystal-to-crystal *cis* → *trans* azobenzene isomerization. Irradiation with visible light transforms a perhalogenated *cis*-azobenzene single crystal into a polycrystalline aggregate of its *trans*-isomer in a photomechanical transformation that involves a significant, controllable, and thermally irreversible change of crystal shape. This is the first demonstration of permanent photomechanical modification of crystal shape in an azobenzene.

The azobenzene (azo) chromophore is one of the best studied photochromic groups,<sup>1</sup> and its clean, reversible isomerization has been investigated in a variety of applications (Figure 1a).<sup>2</sup> While the isomerization efficiency and chemical stability of the chromophore under multiple isomerization cycles are high, a recent fascinating aspect of azobenzene-containing solids is the photomechanical effect,<sup>3</sup> i.e., the direct conversion of visible light into mechanical motion based on the ability of molecular building blocks to change shape upon irradiation. Such solid-state molecular motion alters bulk material properties, including shape, thickness, surface energy, etc.<sup>4</sup> Photomechanical effect in azobenzene solids was studied in polymers,<sup>5</sup> thin films,<sup>6</sup> or liquid crystals<sup>7</sup> and is manifested in macroscopic bending of the material or surface relief gratings formation<sup>8</sup> on its surface upon *trans* → *cis* conversion. Previous work has focused on reversible systems in which photochemical bending is accompanied by thermal *cis* → *trans* relaxation, which restored the object to its initial shape.<sup>3b,c,5–7</sup> However, azobenzene isomerizations in crystals remain almost unexplored, possibly due to a general opinion that underlying stereochemical change (120–250 Å<sup>3</sup>)<sup>9</sup> would be hindered in a crystal and, consequently, that crystalline azobenzenes are generally not capable of photomechanical effect. It was recently demonstrated, however, that sufficiently thin azobenzenes crystals allow photochemical *trans* → *cis* isomerization and thermal relaxation<sup>10</sup> leading to a rapidly reversible photomechanical effect. A peculiarity of azobenzene crystal chemistry is the paucity of *cis*-isomer structures, associated with their short half-lives hindering the isolation of single crystals.<sup>11</sup> The lack of crystallographic data on *cis*-azobenzenes is notable considering that azobenzene isomerization was reported nearly 200 years ago and addressed in tens of thousands of papers since.



**Figure 1.** (a) Azobenzene isomerization; (b) *cis*- and *trans*-forms of **1** and **2**; (c) *cis* → *trans* isomerization of **1** depicted with molecular structures based on single crystal X-ray diffraction; (d) irreversible bending of a thin crystal of *cis*-**1** by 457 nm light, with the arrow at the top of the figures indicating the direction of irradiation.

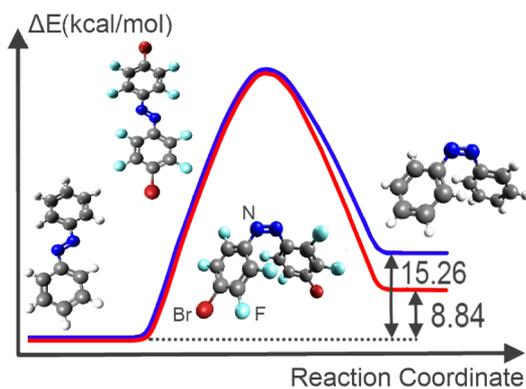
We now report that photochemical *cis* → *trans* azobenzene isomerization can take place in a crystal-to-crystal fashion. The very long half-lives (ca. 2 months) of *cis*-forms of azobenzenes **1** and **2** (Figure 1b,c) allowed their isolation as crystals capable of *cis* → *trans* isomerization<sup>12</sup> upon visible light irradiation. This photomechanical effect is irreversible, which is a new development in the area of photomechanical azobenzene solids, which has so far focused on reversible switching. Thin crystals of *cis*-**1** and **-2** can be shaped by light into thermally stable cyclic or zigzag forms (Figure 1d and Figures S4 and S5 in the Supporting Information (SI)).

Both **1** and **2** were synthesized by conventional oxidative coupling, and obtained predominantly as *cis*-forms (synthetic procedure in SI). The long half-lives of *cis*-azobenzenes **1** and **2**

Received: June 22, 2013

are in agreement with the recent report by Hecht et al.,<sup>13</sup> which showed that *o*-fluorinated azobenzenes can exhibit significantly separated *trans*- and *cis*-form  $n-\pi^*$  absorption maxima leading to long *cis*-isomer half-lives. Indeed, the half-life of *cis*-1 and -2 determined by kinetic UV-vis experiments in solution is 60 days in  $\text{CH}_2\text{Cl}_2$ . The  $n-\pi^*$  transitions for both **1** and **2** are separated by 40 nm (420 nm *cis*, 460 nm *trans*, Figure S1 (SI)), which in solution allows for switching between photostationary states using visible green (*trans*  $\rightarrow$  *cis*) and blue (*cis*  $\rightarrow$  *trans*) light. The *trans*  $\rightarrow$  *cis* isomerization is also achievable with ultraviolet light of 320 nm for **1** and 330 nm for **2** via  $\pi-\pi^*$  excitation. Absorption maxima do not change appreciably with the solvent.

Computational studies of **1** and **2** were done using a density functional theory (DFT) method used for similar systems.<sup>14</sup> Compound **1** and the parent azobenzene were treated with B3LYP level of theory with Pople 6-31G(d) basis set. For **2**, calculations required an increased basis set due to the presence of iodine, and so DGDZVP was used. The calculations (see SI) predict that the energy difference between *cis*- and *trans*-isomers of **1** and **2** are approximately half of the value calculated for azobenzene: 8.84, 8.88, and 15.26 kcal mol<sup>-1</sup>, respectively (Figure 2, also see SI).



**Figure 2.** Energy profiles for *trans*–*cis* isomerization of **1** (red) and the parent azobenzene (blue); the *cis*-form of **1** is relatively more stable with respect to the corresponding *trans*-isomer compared to azobenzene.

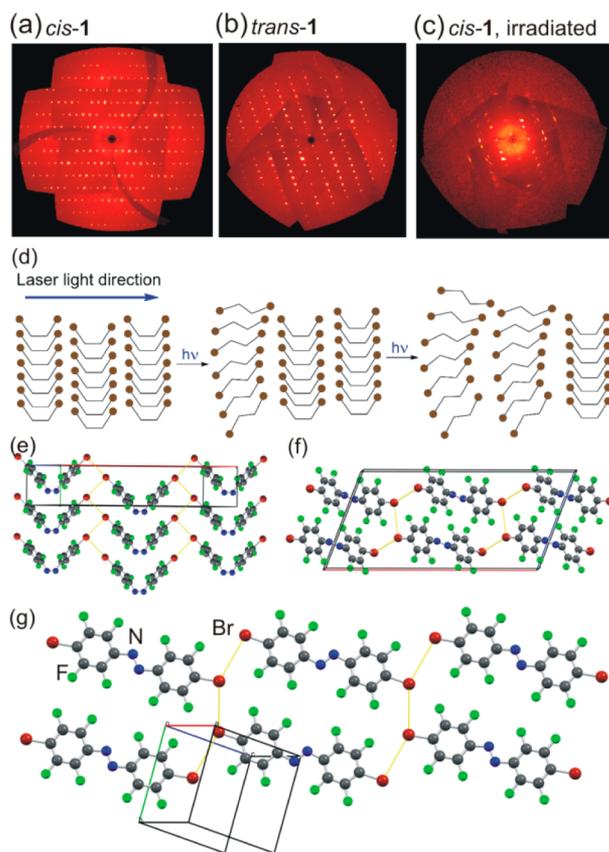
Long half-lives of *cis*-1 and *cis*-2 allowed the isolation of both *trans*- and *cis*-forms of **1** and **2** and their structural characterization by single crystal X-ray diffraction. Two concomitant polymorphs of *cis*-1 (SI Table S1) were found: *cis*-1 and *cis*-1a. Only *cis*-1 could be obtained as thin needles suitable for photomechanical studies and is the relevant form for this work. Crystal structures of *trans*-1 and -2 reveal planar molecules, while *cis*-1 and -2 are V-shaped with intramolecular angles between phenyl moieties between 74° and 82° (see SI for further details, Figures S6, S7).

To study photoresponsive behavior, we irradiated thin needle crystals of *cis*-1 with blue 457 nm laser light. Remarkably, even relatively thick needles of ca. 10–20  $\mu\text{m}$  bent readily and irreversibly away from the light source, reaching deflection angles of up to 180° for the tip of the needle (Figure 1d, Video S1 (SI)). Controlled photomechanical bending of such magnitude is unprecedented in crystalline azobenzene systems and has only very recently<sup>15</sup> been reported in alternative<sup>16,17</sup> crystalline photomechanical systems. Earlier *trans*-azobenzene or pseudostilbene photomechanical systems exhibited motion

of considerably lower extent and only if crystal was less than 5  $\mu\text{m}$  thick, with optimum effect at 1  $\mu\text{m}$ .<sup>10</sup> Bending of *cis*-1 was accompanied with change of color of the irradiated part of the crystal from yellow to orange-red, consistent with *cis*  $\rightarrow$  *trans* isomerization. Irradiation of the opposite face of the crystal allows bending in the opposite direction. This results first in straightening of the crystal, and then bending in the opposite direction (Figure 1d, Video S2 (SI)). After irradiating both prominent faces, the crystal became inactive to laser light, which was explained by isomerization of all *cis*-1 molecules on the surface to *trans*-1. With the provision of sufficient spatial control, such irreversible bending allows shaping of the crystalline material. Video S3 (SI) shows a crystal being molded into an S-shape by irradiation from two different directions at two different regions. Similar behavior was also observed for *cis*-2, although this material was not obtained as individual needles or plates, and polycrystalline aggregates were used instead (Figure S4 (SI)).

That photomechanical behavior of *cis*-1 is related to isomerization is evidenced by powder X-ray diffraction, which demonstrated the concomitant disappearance of X-ray reflections of *cis*-1 and the appearance of those corresponding to *trans*-1 (see SI) upon irradiating a powder sample of *cis*-1. We next attempted to follow the transformation of *cis*-1 into *trans*-1 via single crystal X-ray diffraction. Importantly, photomechanical isomerization of crystalline azobenzenes has never been ascertained in this manner. It was, therefore, surprising and gratifying to discover that a single crystal of *cis*-1 upon irradiation with 457 nm laser light transformed into a polycrystalline sample of *trans*-1. The transformation is clearly visible from composite diffraction images (Figure 3a–c shows composite images for diffraction of  $h0l$  planes; further ones are provided in the SI Figure S8). The X-ray reflections of irradiated *cis*-1 single crystal could be completely indexed to several differently oriented domains with unit cell parameters identical to those of *trans*-1. In particular, 903 out of a total of 1125 X-ray reflections could be indexed by considering five such domains (see SI). Indexing of all reflections was accomplished by considering a total of 16 domains with crystallographic parameters corresponding to those of *trans*-1. Although X-ray diffraction data collected from these domains was poor and highly overlapped, using reflections from one such domain allowed the structure of *trans*-1 to be solved and even refined, using a constrained isotropic model, to a reasonable degree with respect to data quality. Within the limitations of the available data, the resulting structure was identical to that of *trans*-1 obtained from a separately grown single crystal, unambiguously confirming the crystal  $\rightarrow$  crystal nature<sup>18</sup> of the *cis*  $\rightarrow$  *trans* transformation in **1**.

The amenability of *cis*-1 and -2 crystals to photomechanical shaping is unique in azobenzene chemistry, compared to studied *trans*-azobenzenes and pseudostilbenes. Permanent bending in previously studied *trans*-azobenzene systems was not achievable due to the rapid equilibrium formed upon irradiation, in which molecules photochemically isomerize to the *cis*-form but also thermally relax back to the *trans*-form. As a result, a sufficiently high concentration of the *cis*-form required for permanent photomechanical bending of the *trans*-crystal is difficult to achieve. In the case of *cis*-1, however, we have not observed any tendency for reversal of the *cis*  $\rightarrow$  *trans* isomerization in the crystal using either blue (457 nm), green (514 nm), or red (633 nm) light. While the irreversible nature of the isomerization in *cis*-1 is probably aided by the metastable



**Figure 3.** Composite diffraction images for the  $h0l$  planes of single crystals of (a) *cis*-1, (b) *trans*-1, and (c) *cis*-1 after 4 h irradiation at 457 nm, demonstrating the conversion of a single crystal of *cis*-1 into polycrystalline *trans*-1. (d) Tentative model of the photomechanical bending of *cis*-1 crystal as *cis*-molecules progressively isomerize into *trans*-1 upon light penetration. Molecular stacks are parallel to the long axis of the crystal needle. Crystal structure of *cis*-1: (e) molecular stacks viewed in the crystallographic  $ab$ -plane perpendicular to irradiation and (f) down the crystallographic  $b$ -direction parallel to the crystal needle axis, displaying the retained zigzag motif of Br $\cdots$ Br contacts. (g) The (30–2) plane in *trans*-1 with molecular arrangement resembling that of *cis*-1 in (f).

nature of the *cis*-isomer, it is likely that thickness of the crystal or more efficient molecular packing of *trans*-azobenzene in the crystal is the key for permanent bending. The latter possibility is supported by the lower density of *cis*-1 compared to *trans*-1. For *cis*-1 the volume of the unit cell per molecule is 339.5 Å<sup>3</sup>, while the corresponding value for *trans*-1 is 325.5 Å<sup>3</sup>. We note a similarity between the herein reported photomechanical shaping of perhalogenated azobenzene crystals and previously studied bending of haloarene crystals by mechanical force.<sup>19</sup> In crystals of *cis*-1 and *cis*-2, molecules are arranged into stacks, which, we propose, could expand upon photochemical *cis*  $\rightarrow$  *trans* isomerization without generating extensive stress on the nearby stacks. In *cis*-1 the stacks are parallel to the crystallographic  $b$ -direction, which coincides with the needle crystal long axis. Molecules in neighboring stacks interact by networks of Br $\cdots$ Br interactions parallel to and perpendicular to the needle axis (Figure 3d,e). Progressive photomechanical expansion of molecular stacks that are closer to the source of irradiation might allow the crystal to bend away from the light source with minimum fracturing by sacrificing only the Br $\cdots$ Br interactions along the needle axis (Figure 3e). Although no

clear topochemical relationship was established between the photochemically generated domains of *trans*-1 and the parent *cis*-1 crystal,<sup>18</sup> we note a correspondence between arrangements of molecules populating the crystallographic (010) planes of *cis*-1 and the (30–2) planes of *trans*-1. Both planes exhibit a zigzag net of Br $\cdots$ Br contacts (3.95 Å in *cis*-1 and 4.02 Å in *trans*-1), suggesting that this supramolecular motif, normal to the needle axis of the starting crystal, might be conserved upon photomechanical bending (Figures 3f,g).

In summary, the exploration of two new perhalogenated azobenzenes with long-lived *cis*-forms provided the first demonstration of an irreversible photomechanical effect in a crystalline azobenzene solid. Single crystal and powder X-ray diffraction revealed that the photomechanical effect involved a single crystal  $\rightarrow$  polycrystal transformation, so far unprecedented in solid-state chemistry of azobenzenes. The metastable nature of the starting *cis*-azobenzene and its large photomechanical response highlight photomechanical shaping as a new exciting opportunity in the solid-state photochemistry of crystalline azobenzenes. We therefore believe that the irreversible photomechanical effect of 1 and 2 opens new possibilities in the design of photoresponsive azobenzene solids.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Details of synthesis, videos, images of crystal bending, selected UV–vis spectra, powder X-ray diffraction data, DFT calculations and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### 📄 Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We acknowledge Prof. D. S. Bohle for aid in obtaining single crystal X-ray diffraction data. The financial support of the Vanier Canada Graduate Scholarship is acknowledged (O.S.B.), as well as the support of the NSERC Discovery Grant, Canada Foundation for Innovation Leader's Opportunity Fund, and FRQNT Nouveaux Chercheurs program.

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