Physical and Photochemical Properties of Macrocyclic Azobenzenes

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Photoisomerization of azobenzene is a reversible photochemical reaction and has potential applications to reusable photo-functional materials. Azobenzenophane (macrocyclic azobenzene), possessing multiple azobenzene moieties in a macrocyclic molecular skeleton, have been of interest due to their unique strained structure, isomerization properties such as multi step isomerization, molecular motion, and potential application to photoresponsive materials. In this paper, from the viewpoint of material applications, physical and photochemical properties of azobenzenophane are reviewed and the uniqueness arising from the cyclic molecular structure is discussed.

Keyword: azobenzene, azobenzenophane, macrocyclic azobenzene, photoisomerization, molecular machine, phase transition

1. Introduction

Azobenzene exhibits isomerization from trans isomer to corresponding cis isomer upon irradiation of ultraviolet light, while the cis isomer reverts to original trans isomer either by irradiation of visible (blue to green) light or by heat (without light). Photoisomerization of azobenzene are widely recognized and has been utilized to switch various kinds of physical and chemical properties of materials [1-5]. One of the advantages in applying azobenzene to photoresponsive materials is a reversible nature of the chromophore, so the azobenzene-based materials can be used repeatedly and easily recyclable. In contrast, conventional photo-responsive materials generally utilize irreversible photoreactions (such as photo-polymerization, photo-cross linking, and photo-degradation) and they cannot be used repeatedly. Thus, the azobenzene-based materials are expected to save resources and to contribute to build a sustainable society.

Figure 1. Isomerization of azobenzene

Figure 2. General formula of azobenzenophane (macrocyclic azobenzene)

Azobenzenophanes (or macrocyclic azobenzenes), possessing multiple azobenzene units in a single macrocyclic molecular skeleton, have been of interest due to their unique cyclic strained structure and isomerization properties such as multi-state photoisomerization and dynamic molecular motion. In addition, it can be expected that self-assembling nature of azobenzenophanes

can be altered by irradiation of light because the molecular shape change drastically upon isomerization. Azobenzenophanes have pore and space inside the ring of molecule. This may provide the material the cavity for mass transport or free space required for the isomerization. These molecular properties may lead to novel functional materials. This review focuses on the unique properties and functions of azobenzenophanes (macrocyclic azobenzenes) having at least two azobenzene moieties in a molecule. Synthesis of azobenzenophanes is challenging in some cases and reaction condition should be optimized according to the molecular design. The synthesis of azobenzenophane is collected elsewhere [6].

2. Properties in Solution

2.1. Rotation or Inversion?

Azobenzenophane became widely known by the contribution of Rau et al. who synthesized a macrocycle **1**, where two azobenzenes are connected at *para* position by $-\text{CH}_2-\text{S}-\text{CH}_2-$ bridges [7-9]. They determined the single crystal structure of trans,trans (*t,t*) isomer [7]. In addition, they analyzed the photochemistry of **1** for two major purposes. Firstly, they regarded **1** as a model compound to study the isomerization mechanism of azobenzene [9,10]. There have been proposed two mechanisms: twisting around the central $\text{N}=\text{N}$ bond (rotation mechanism) and in-plane bending motion of $\text{C}-\text{N}-\text{N}$ angle (inversion mechanism). They regarded that in the macrocycle **1**, only the inversion mechanism is possible, while the rotation mechanism is blocked by the ring structure. However, recent theoretical study of **1** revealed that the rotation path is not

blocked and the isomerization of **1** proceeds mainly via rotation mechanism [11].

2.2. Tetrazetidine

Secondly, they explored the possibility to synthesize tetrazetidine, a four-membered ring system consists only nitrogen atoms, starting from azobenzenophane **1** and

analogues [12,13]. Although experimental and theoretical studies have been carried out, it is still far from a decisive conclusion of the formation of tetrazetidine because of lack of direct evidence.

2.3. Light Energy Dependence

A cyclic strain is present in azobenzenophane especially having two azobenzene moieties. This strain often affects the photoisomerization properties of azobenzenophanes [9]. Tamaoki et al. synthesized **2**, where two azobenzenes are connected at *para* position by $-\text{CH}_2-\text{CH}_2-$ bridges, and demonstrated that the photoisomerization of **2** is dependent on light intensity in solutions as well as in polymer film and proposed that it can be used as photochromic memory with nondestructive read-out property [14-17]. It is because the photoisomerization from the *t,t* isomer to the *c,c* isomer proceeds via the highly strained *t,c*

isomer, which is thermally unstable and short lived.

2.4. Structure-Property Relationship

Although it was regarded that the ring strain of azobenzenophane having two azobenzene moieties affects the isomerization properties such as isomer ratio at the photostationary state, quantum yield, and stability of isomers, relationship between molecular structure and properties was unknown. The experimental data of molecular structure of *t,c* and *c,c* isomers was lacking.

Tamaoki et al firstly clarified the crystal structure of all three isomers of azobenzenophane **3**, where two azobenzene moieties are connected at meta position by $-\text{CH}_2-$ bridges [18,19]. As expected, *t,c* isomer has highly strained structure. The *t,t*-

isomer is slightly strained, while the c,c isomer has very small ring strain. In addition, they determined the crystal structure of all-trans isomer of azobenzenophanes having three (4) and four (5) azobenzene moieties [19]. Interestingly, 4 in the crystal phase forms one-dimensional tube-like column structure and solvent (chloroform) molecules are linearly aligned inside the tube, implying that the self-assembling nature of the macrocycle can be applied to functional materials in the condensed phases.

By making the bridge length shorter, drastic change in the stability of azobenzene was observed. Norikane et al found that the c,c isomer is thermodynamically most stable in azobenzenophane (6) that consists of two azobenzenes connected without bridging atoms [20]. Compound 6 also exhibits thermal trans-to-cis isomerization, which is in the opposite direction from general azobenzene. It is the first report on the thermodynamically stable cis isomer of an azobenzene derivative.

2.5. Light-Driven Molecular Hinge

The molecular motion of the isomerization of azobenzenophane was applied to a kind of molecular machine. Tamaoki et al. developed a light-driven molecular hinge (7) which is initially flat (t,t) shape changes its shape to the bent (c,c) conformation [21,22]. Clear evidence of the crystal structure of both flat and bent structures proves the hinge-like molecular motion is operating in solution. The photochemical bending reaction (from t,t to c,c isomer) is dependent on the light intensity because of the short lifetime (ca. 30 seconds) of the intermediate t,c isomer.

2.6. Isomer Distribution Analyses

Since azobenzenophanes have multiple azobenzene moieties in a molecule, isomer distribution is sometimes complicated. As described above, there are three isomers in azobenzenophane having two azobenzene moieties (1, 2, 3, 6 and 7). When a molecule has three azobenzenes (such as 4), four isomers ((t,t,t), (t,t,c), (t,c,c), and (c,c,c)) are possible. Isomer distribution were analyzed by using HPLC and NMR, indicating that the major component (isomer) can be controlled by solvent, irradiation wavelength, and irradiation time [15,19,23,24].

3. Properties in Condensed Phases

3.1. Photochromic Memory with Non-Destructive Read-out

Generally speaking, to apply the unique properties of compounds to the functional materials and devices, solid or solid-like materials are required because it is difficult to handle solution-based materials. Therefore, exploring the properties in condensed phase such as in polymer, liquid crystal, gel, on the surface, and crystal is important.

Tamaoki et al demonstrated that a polycarbonate film containing **2** can be used as a photochromic memory with a non-destructive read-out property [17]. While relatively strong UV light (5 mW cm^{-2}) is used for the writing process, the intensity of the UV light used for the read-out process required only $20 \text{ }\mu\text{W cm}^{-2}$.

3.2. Liquid Crystal System

Azobenzene has been incorporated in a liquid crystal (LC) system to switch the macroscopic property of LC. Spada et al. demonstrated that the cholesteric pitch of a cholesteric LC phase can be switched by an azobenzene derivative having a chiral group (8) [25]. Although the helical twisting power (β value) is relatively small, photoinduced switching of β value was observed upon irradiation with UV and visible light.

Azobenzophane having polymerizable side chains was synthesized and exhibited photoisomerization in lyotropic columnar LC phases [26]. Photo-conversion to the *cis* azobenzene containing isomers was ca. 40 % in the unpolymerized lyotropic LC state. Although the photoisomerization disrupted

the LC state before polymerization, cross-linking the LC state prevented the disruption of the LC order. This concept of material can be applied to photo-regulated mass transport because the pore size of the macrocyclic segment is controlled by light.

3.3. Gels and Host-Guest Crystals

Gelation of benzene by using an azobenzenophane having three azobenzene moieties connected with Schiff base bridges was reported [27]. Compound 10, obtained by reduction of the Schiff base moieties, showed host-guest crystals containing solvent molecule, which is similar to the crystal structure of 4.

3.4. Self-Assembly on Surface

Macrocyclic azobenzene changes its molecular shape upon photoirradiation on a self-assembled surface. The change in molecular shape was observed directly by STM [28]. Compound 11, previously synthesized by Tamaoki et al [15], and 1,3,5-tris(10-carboxydecyloxy)-benzene (TCDB) were deposited on a HOPG and surface was analyzed by STM. The STM image showed that the compound 11 was immobilized in the TCDB network and the stoichiometry of TCDB/macrocyclic affects

the network structure. Photoisomerization of the macrocycle (from t,t,t,t to t,t,t,c and t,c,t,c) was observed upon UV irradiation on the HOPG sample.

3.5. Photochemical Phase Transitions

Norikane et al. synthesized macrocyclic azobenzenes having alkoxy chains (12 and 13) [29]. These molecules are designed by simply attaching flexible and long chains to the macrocyclic cores. While these compounds are crystalline at room temperature, 12 formed SmC phase (102-135 °C) and 13 exhibited columnar phase upon rapid cooling from isotropic phase to room temperature. Upon photoirradiation, these compounds showed phase transitions from LC phases to isotropic phase. In addition, crystals of these compounds exhibited phase transition to the isotropic phase by irradiation of UV light (365 nm). These materials have potential applications to reusable photoresists, photoresponsive adhesives, and other photoresponsive materials.

4. Conclusion

Although there have been various kinds of azobenzenophanes synthesized, studies from the viewpoint of material science seem to be limited. One of the bottlenecks in the study of azobenzenophanes for materials science is their synthetic difficulties. However, new synthetic strategies with improved yields have been reported [6], and interesting properties of azobenzenophanes have been revealed as described in this manuscript.

Macrocyclic molecular structure is fascinating in designing novel materials such as functional LCs, gels, crystals, and others. Novel functions have been reported and these functions are originated from unique cyclic structure of azobenzenophanes. Impressive

finding has been reported that crystals of the material based on macrocyclic azobenzenes melt by light irradiation. This phenomenon definitely opens a door to directly control the state of matter by light.

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