

Photoresponsive Azobenzene-Containing Dendrimers with Multiple Discrete States

Denise M. Junge[†] and Dominic V. McGrath*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Department of Chemistry, University of Connecticut
Storrs, Connecticut 06269

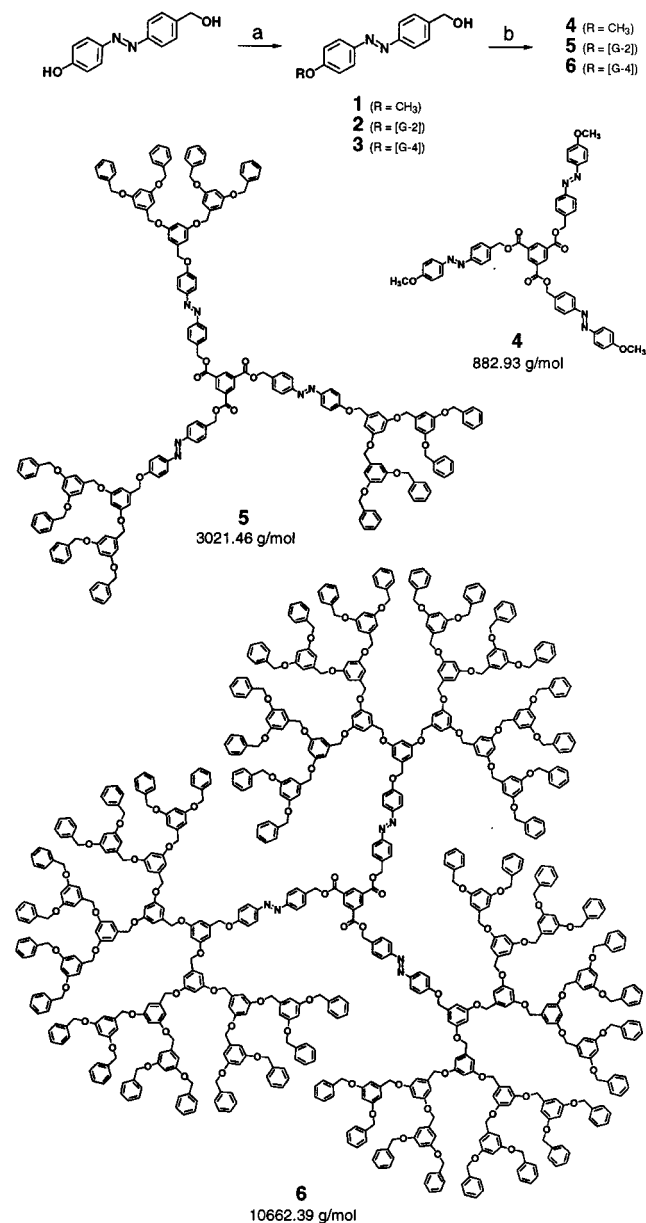
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Dendritic macromolecules with precisely placed groups within their structural interior or at their periphery have recently attracted intense interest.¹ Dendrimers with electroactive,² photoactive,³ and recognition elements⁴ have been reported as potential functional materials. However, few examples of dendrimers that respond to environmental stimuli such as solvent⁵ and pH⁶ are known. Incorporation of the photochromic azobenzene moiety in *non-dendritic* macromolecular systems has enabled reversible switching of a wide spectrum of polymer and polymer solution properties⁷ driven by photochemical *trans*–*cis* (*E/Z*) isomerization of the azo units and subsequent associated changes in macromolecular conformation.⁸ Azobenzene-containing polymers have also been prepared and optimized for applications in liquid crystal displays and devices, reversible optical storage systems, nonlinear optical waveguides, photorefractive switches, and holographic gratings.⁹ Precise placement of photochromic moieties within a dendrimer interior would lead to reversible photoinduced configurational and constitutional changes, potentially allowing reversible alteration of previously demonstrated dendrimer behaviors such as self-assembly,^{4,10} liquid crystallinity^{10,11} and encapsulation.¹²

We¹³ and others¹⁴ have prepared dendritic macromolecules with photochromic azobenzene units in the exterior,^{14a} interior,^{13,14b} or throughout^{14c,d} the dendritic architecture with various intentions. In prior work¹³ we prepared examples of dendrimers with an

Scheme 1^a



^a Reaction conditions: (a) K₂CO₃, acetone, and either (i) CH₃I, 67% (ii) [G-2]-Br, 87%, or (iii) [G-4]-Br, 87%; (b) benzene-1,3,5-tricarbonyl chloride, 18-crown-6, DMAP, benzene, Δ, 90, 80, and 81%, respectively.

azobenzene moiety as the central linker and demonstrated that the photoresponsive behavior of the azobenzene is not perturbed by incorporation into the dendrimer structure. In the present paper,

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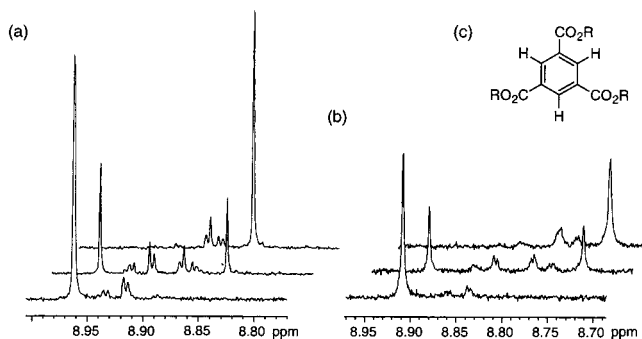


Figure 1. ^1H NMR spectra of dendrimers (a) **5** and (b) **6** in the region corresponding to the protons of (c) the trimesate central linker. Stack plots are of a dark-incubated sample (lower), after irradiation (350 nm) for 5 min (middle), and after irradiation (350 nm) for 10 min (upper).

we describe dendrimers that contain three interior azobenzene moieties radially configured about the core unit. With each azobenzene capable of *E/Z* isomerization, the dendrimer can exist in four discrete states, *EEE*, *EEZ*, *EZZ*, and *ZZZ*. As detailed below, all four states are detectable in solution and exhibit different physical properties. The present system represents an example of a dendrimer that undergoes multiple discrete property changes on external stimulus of interior groups.¹⁵

Second and fourth generation tris(azobenzene)-dendrimers **5** and **6**, as well as model compound **4**, were prepared as shown in Scheme 1. The individual diastereomeric states of **4–6**, *EEE*, *EEZ*, *EZZ*, and *ZZZ*, are easily detected by ^1H NMR in solution (Figure 1). The resonances assignable to the central linker aromatic protons (Figure 1c) for C_3 -symmetric *EEE* and *ZZZ* isomers are singlets, whereas the formally C_{2v} -symmetric *EEZ* and *EZZ* isomers give rise to two mutually coupled multiplets. Irradiation of individual dark-incubated NMR samples (CDCl_3) of **4–6** resulted in a dramatic change in the ratio of these resonances reflective of the increasing *Z* content in the mixture of isomers (Figure 1a and b). The inherently globular nature of dendrimers is evident in the increased dispersion of the resonances arising from the central linker with increasing molecular size. For example, the chemical shift difference between the singlets for the *EEE* and *ZZZ* isomers of increases from 0.07 (**4**) to 0.11 (**5**) to 0.17 (**6**) ppm. More importantly, the relative appearance and disappearance of all four isomers during the course of thermal *E/Z* isomerization, also followed by ^1H NMR, indicates independent,^{15b} rather than simultaneous¹⁶ isomerization of the azobenzene units—the behavior of each dendrimer arm is unaffected by the presence of the other two. Therefore, no cooperativity is imparted to the azobenzene photoresponsive behavior by incorporation into this dendritic architecture.

Since it is possible to treat these compounds as ensembles of individual decoupled azobenzene groups, we can use their kinetic behavior to determine the effect of the molecular environment on their photoresponsiveness. Compounds **4–6** all exhibited photoresponsive behavior characteristic of azobenzene-containing materials.^{7,8} Dark incubation of methylene chloride solutions of **4–6** served to maximize the $\pi \rightarrow \pi^*$ transition at 352 nm, and irradiation with 350-nm light resulted in photoisomerization as evidenced by a decrease in the absorbance at 352 nm and an increase in the $n \rightarrow \pi^*$ transition at 442 nm. The presence of observed sharp isosbestic points in the absorption spectra during isomerization was expected on the basis of the independence of the chromophores. Thermal back-isomerization occurred, the rates

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Table 1. Rates and Activation Energies for Thermal Isomerization

compd	FW	k_{294} ($\times 10^6 \text{ s}^{-1}$)	k_{313} ($\times 10^5 \text{ s}^{-1}$)	k_{333} ($\times 10^4 \text{ s}^{-1}$)	E_{act} (kcal/mol)
4	882.93	4.09	3.29	2.65	20.8
5	3021.46	4.35	4.89	2.90	20.9
6	10662.39	4.48	5.16	3.03	20.9

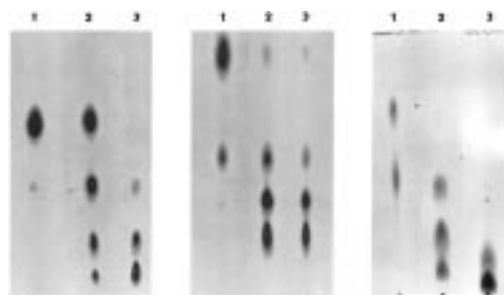


Figure 2. Thin-layer chromatography (TLC) of **4–6** on SiO_2 -coated plates. Left: TLC of **4** (24:1 CH_2Cl_2 – Et_2O). Middle: TLC of **5** (48:1 CH_2Cl_2 – Et_2O). Right: TLC of **6** (99:1 CH_2Cl_2 – MeOH). Lanes 1–3 in each set are after dark-incubation (lane 1), 1-min irradiation (lane 2), and 2-min irradiation (lane 3) at 350 nm.

of which were measured at several temperatures. The results of these measurements (Table 1) lead to the following conclusions. First, the relative invariance of the first-order rate constants and activation energies (E_{act}) of **4–6** indicates no strong steric influence on the *cis*–*trans* thermal isomerization, that is, it is independent of dendrimer size.^{13,17} Second, the values of the same data indicate no alteration of the photoresponsive behavior of azobenzene by incorporation into dendritic architecture.¹⁸ And third, the strict adherence to first-order kinetics further supports the independent behavior of the azobenzenes.

Isomerization of the interior azobenzene moieties in **4–6** markedly affects their macroscopic properties in a predictable fashion (Figure 2). Monitoring the distribution of the isomers of **4** as a function of irradiation time was possible by thin-layer chromatography (TLC) (Figure 2a) or HPLC (SiO_2 , 9:1 CH_2Cl_2 – EtOAc) since each discrete state was easily separable. Since *Z*-azobenzene is more polar than *E*,⁸ it is not unexpected that chromatographic retention times should increase with increasing *Z* content of the isomers of **4**. This difference in chromatographic retention times among the four isomers was also observed for second generation dendrimer **5** (Figure 2b). Remarkably, even in compound **6**, with a molecular weight of over 10.6 kD and the azobenzenes buried in the core, differences in retention time between the isomers are still readily observable, albeit with a much different solvent system (Figure 2c). It is undoubtedly the case that these observed property differences among the isomers of **5** and **6** are still given rise to by the changes in polarity of the individual azobenzene moieties and not, for example, by a molecular size effect.¹⁹ However, modeling suggests that the azobenzenes in **6** are well insulated within the interior of the dendrimer. This behavior, then, may be a manifestation of the high degree of flexibility of dendrimers of this type.²⁰

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Supporting Information Available: Synthetic details and characterization data for compounds **1–6**, representative kinetic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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