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Photochromic Dendrimers Containing Six Azobenzenes

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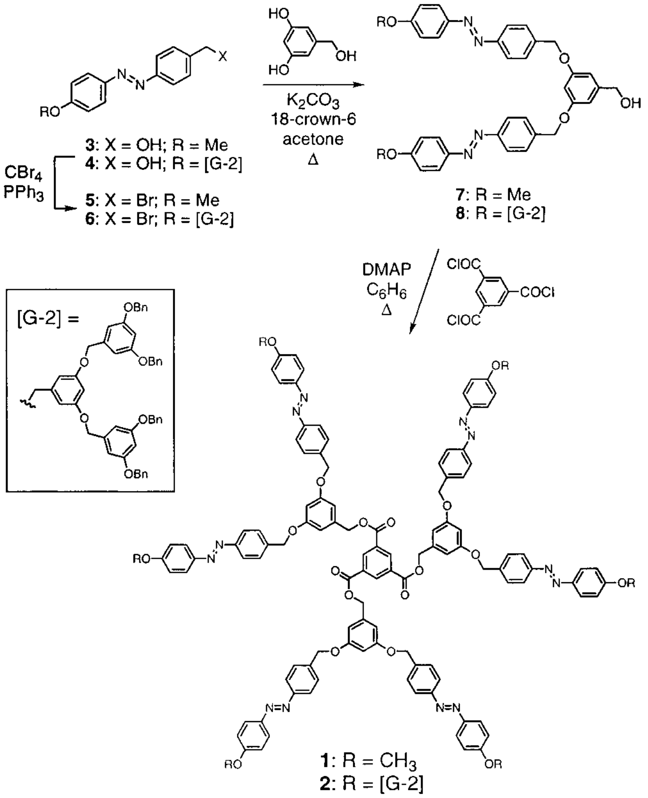
Dendritic macromolecules with precisely placed groups within their structural interior or at their periphery have recently attracted intense interest.[1−8] We are exploring the precise placement of photochromic moieties within dendrimers and the effect of the photochromic behavior on dendrimer properties. Previously, we have reported photoresponsive benzyl aryl ether dendrimers with azobenzene-containing cores.[9−12] When three azobenzenes are incorporated into the center of these dendrimers, four discrete states are observed depending on the *E*/*Z* configuration of the individual azobenzenes (*EEE*, *EEZ*, *EZZ*, and *ZZZ*).[10] In addition, these dendrimers exhibit photomodulated physical properties such as polarity and hydrodynamic volume. The extent of photomodulation is dependent on both the relative placement of the photochromic units within the dendrimer structure and the property in question.[12] Here, we provide the first example of a dendrimer containing a generational shell of azobenzene subunits embedded in the structural interior. Investigation of the photomodulation of physical properties of these dendrimers demonstrates that this shell of six azobenzenes is particularly effective at modulating dendrimer size in solution upon irradiation.

Scheme 1. Synthesis of Hexakis(azobenzene) Dendrimers 1 and 2



First and third generation hexakis(azobenzene) dendrimers **1** and **2** were prepared (Scheme 1). Compound **3** and dendron **4** were converted into their corresponding bromides and coupled to 3,5-dihydroxybenzyl alcohol to yield dendrons **7** and **8**. The reactions of **7** and **8** with 1,3,5-benzenetricarbonyl trichloride in the presence of DMAP in benzene under Dean−Stark conditions provided dendrimers **1** and **2**, respectively. Structural characterization of **1** and **2** was performed by ^{1}H and ^{13}C NMR, MALDI mass spectrometry, and combustion analysis.

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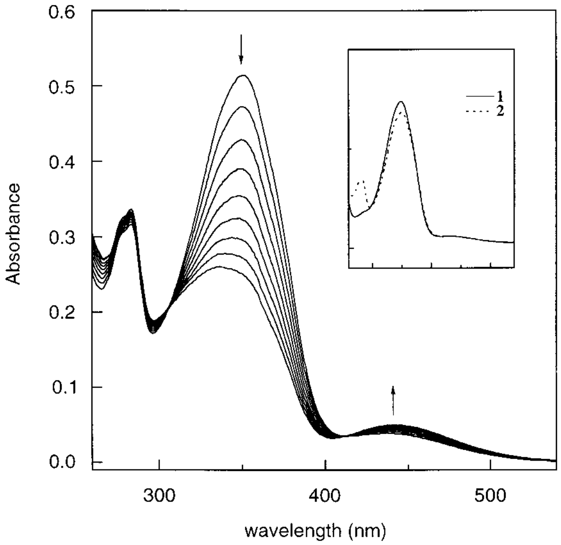


Figure 1. UV absorption spectra of dendrimer **2** (3 μM in $CHCl_3$) under irradiation conditions (350 nm; 1 min intervals). Inset: UV absorption spectrum of dendrimers **1** and **2** (4 μM in $CHCl_3$) after dark incubation.

Table 1. Rate Constants and Activation Energies for Thermal Isomerization of Dendrimers 1 and 2

	k_{30} (10^{-6} s^{-1})	k_{40} (10^{-5} s^{-1})	k_{60} (10^{-4} s^{-1})	E_a (kcal/mol)
1	10.5	3.08	2.46	21.1
2	13.4	3.89	2.50	19.5

As with tris(azobenzene) dendrimers,[10] the generational growth of hexakis(azobenzene) dendrimers **1** and **2** can be observed by UV–vis spectroscopy (Figure 1, inset). Third generation dendrimer **2** gives rise to an absorption band at 281 nm corresponding to the benzyl aryl ether chromophores. When this dendritic fragment is absent, as in **1**, there is a corresponding lack of absorbance in this region. Hexakis(azobenzene) dendrimers **1** and **2** both exhibited expected photoresponsive behavior. Dark incubation of chloroform solutions of **1** and **2** served to maximize the absorption at 349 nm corresponding to the *E*-azobenzene chromophore. Irradiation of a sample of either dendrimer ($CHCl_3$, 3 μM) with 350 nm light resulted in the photoisomerization of the azobenzene moieties to the cis configuration as evidenced by a decrease in absorbance at 349 nm and an increase in absorbance at 442 nm (Figure 1). When left in the dark, thermal isomerization of hexakis(azobenzene) dendrimers **1** and **2** to the more stable trans configuration was observed over the course of several hours at 30, 40, and 60 °C. From these data, first-order rate constants (k) and activation energies (E_a) were calculated (Table 1), the magnitudes of which reveal typical azobenzene behavior similar to that seen for similar photochromic dendrimers in dilute solution.[9–12]

The effect of the placement of azobenzene subunits within the architecture of dendrimers **1** and **2** on their physical properties was initially studied by absorption chromatography. Since *Z*-azobenzene is more polar than *E*,[13] the increasing *Z* content of the diastereomers results in a dendrimer with a longer retention time on silica supports. We had previously reported that the chromatographic retention times of the individual diastereomeric states of tris(azo) dendrimers—*EEE*, *EEZ*, *EZZ*, and *ZZZ*—increase with increasing *Z* content of the trisazo core.[10] Similarly, monitoring the distribution of the isomers of **1** and **2** as a function of irradiation time was also possible. Separation of multiple photoisomers of dendrimer **1** was observed by thin-layer chromatography (TLC). When a sample of dendrimer **1** is initially dissolved ($CHCl_3$), two isomers, *EEEEEEE* and *EEEEEEZ*, are detected (Figure 2). Irradiation of the sample (350 nm, 5 min) results in the isomerization of the azobenzene moieties, and seven spots were observed. After 10 min of irradiation, a photostationary state was reached, the *ZZZZZZ* form presumably having the lowest R_f value. Exposure to room light (5 min) accelerates the isomerization of the azobenzene moieties from the *Z* to the *E* configuration, and seven spots are again observed. On the basis of these observations, we conclude that hexakis(azobenzene) dendrimers **1** and **2** exhibit seven discrete polarities related to the seven possible ratios of the configurations of the azobenzene subunits (*EEEEEE*, *EEEEEZ*, *EEEEZZ*, *EEEZZZ*, *EEZZZZ*, *EZZZZZ*, and *ZZZZZZ*).

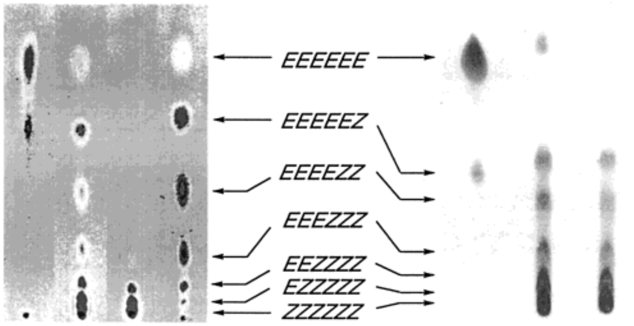


Figure 2. Thin-layer chromatography (TLC) of **1** and **2** on SiO_2-coated plates. Left: TLC of **1** (19:1 CH_2Cl_2–Et_2O). Right: TLC of **2** (39:1:1 CH_2Cl_2–Et_2O–hexane). Lanes 1–4 in each set are after dark incubation (lane 1), 5 min irradiation at 350 nm (lane 2), 10 min irradiation at 250 nm (lane 3), and exposure to bright sunlight (lane 4, **1** only).

The TLC experiments suggest that there are seven possible configurational isomers of **1** and **2** and, hence, seven discrete polarity levels. However, closer inspection reveals that the constitution of these molecules dictates that there are actually 10 different configurational isomers as represented in Chart 1. The additional isomers arise from the two possible constitutional arrangements of azobenzenes in the *EEEEZZ*, *EEEZZZ*, and *EEZZZZ* stereoisomers. While there is only one possible constitutional arrangement for isomers with *EEEEEE*, *EEEEEZ*, *EZZZZZ*, and *ZZZZZZ* azobenzene distributions, isomers with *EEEEZZ*, *EEEZZZ*, and *EEZZZZ* azobenzene distributions have two possible constitutions. For example, the *EEEEZZ* isomer can have both *Z* azobenzenes on the same dendron or two different dendrons (Chart 1). Therefore, dendrimers **1** and **2** can exist in 10 different diastereomeric states rather than merely seven.

To attempt to identify the existence of these 10 isomers of **1** in solution, we utilized NMR spectroscopy. Multiple photoisomeric states of hexakis(azobenzene) dendrimer **1** in solution were detected using ^{1}H NMR spectroscopy (Figure 3). The aromatic protons of the azobenzene subunits reflect a decrease in *E* azobenzenes and a concomitant increase in *Z* azobenzenes (Figure 3, middle). However, little information is available in this region as to the distribution of the 10 diastereomeric states. The aromatic protons of the trimesate core also did not display dispersion significant enough for identification of individual diastereomers (Figure 3, left). However, the methoxy protons proved to be quite

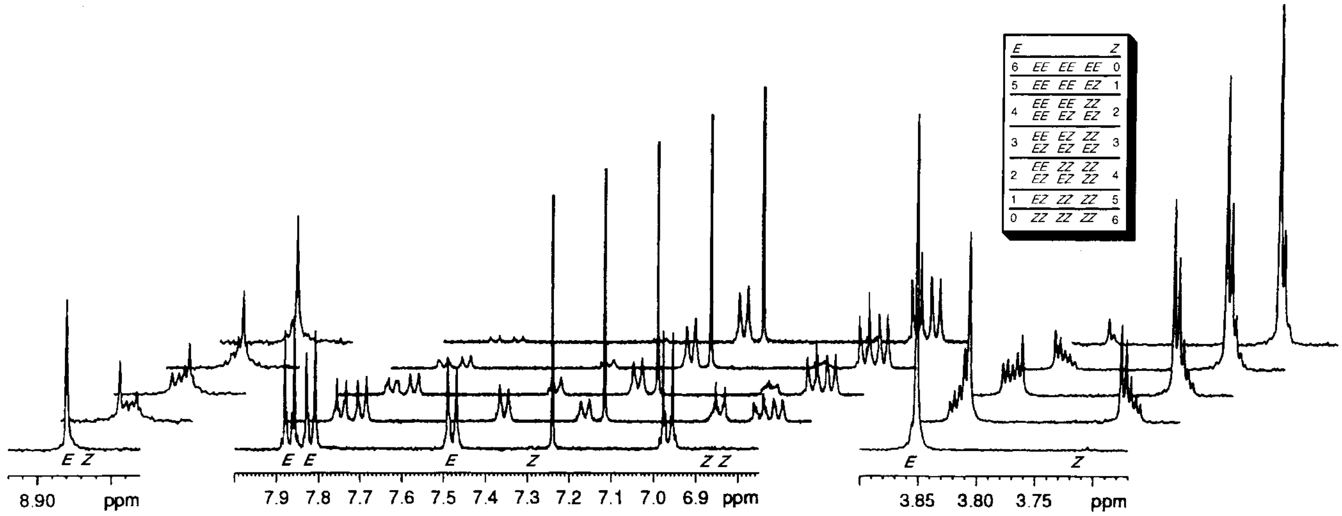
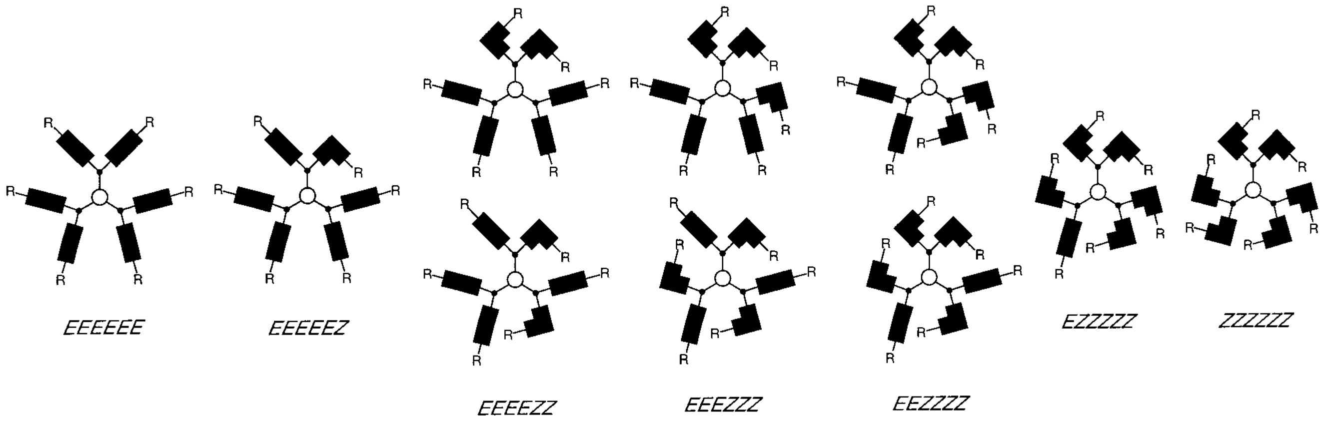


Figure 3. ^1H NMR spectra ($CDCl_3$) of dendrimer **1** in the region corresponding to the protons of (a) the 1,3,5-triacylbenzene central linker, (b) the azobenzene protons, and (c) the methoxy groups. Stack plots correspond to irradiation of the sample with 350 nm light (0, 5, 10, 15, and 25 min).

Chart 1. Schematic Representation of the 10 Configurational Isomers of Dendrimers 1 and 2



sensitive to the isomeric state of the azobenzene to which they were attached as well as those surrounding them. This allowed greater distinction among distereoisomers (Figure 3, right). Considering first generation dendrimer **1**, the 10 possible diastereomeric states strictly give rise to 24 possible chemical environments for the methoxy groups, 12 corresponding to *E*-methoxy groups, and 12 corresponding to the *Z*-methoxy groups (Figure 3, inset). For example, when dendrimer **1** is in the *EEEEEE* form, all methoxy groups are chemical shift equivalent (in a single environment), while the *EEEEEZ* form contains three different methoxy environments (two *E* environments and one *Z* environment). Hence, one might expect to see up to 24 resonances for the methoxy groups in the ^1H NMR spectra. However, examination of the methoxy region of the spectra reveals only 10 resonances were observed for dendrimer **1**, 5 in the *E* region, and 5 in the *Z* region (Figure 3, right). Since we conclude that it is highly unlikely for any of the 10 isomers to be absent from an equilibrium mixture of these dendrimers, it appears that there is significant overlap in this region of the NMR, and we cannot conclusively account for all 10 isomers in solution.

The effect of azobenzene isomerism on the three-dimensional molecular size of dendrimers **1** and **2** was studied by gel permeation chromatography (GPC). The hydrodynamic volume of azobenzene-containing dendrimers can be significantly modulated when azobenzene units are subjected to irradiation, depending on dendrimer construction.[12] Both dendrimers **1** and **2** exhibited an increase in GPC retention volume—indicating a decrease in hydrodynamic volume—following irradiation of the sample (Figure 4). Although multiple

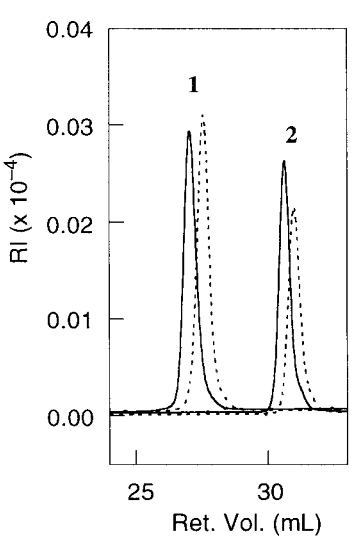


Figure 4. GPC traces for dendrimers (a) **1** (b) **2** before (—) and after (- - -) irradiation with 350 nm light. Conditions: CH_2Cl_2; 1 mL/min; 500, 1000, and 10 000 Å DVB (Jordi) columns (250 × 10 mm); ambient temperature.

isomers of dendrimers **1** and **2** are present together in solution as confirmed by ^{1}H NMR, we did not observe individually resolved peaks in the GPC of equilibrium mixtures after different irradiation times. However, as previously observed with tris(azobenzene) dendrimers,[10] a reproducible limiting elution volume was obtained for both dark incubated and extensively irradiated samples. Dendrimers **1** and **2** exhibited a marked decrease in hydrodynamic volume[14] (19 and 29%, respectively) upon irradiation with 350 nm light to a photostationary state. The contraction for dendrimer **2** represents the largest photomodulation of size observed to date for a photochromic dendrimer.[12,15]

In conclusion, benzyl aryl ether dendrimers containing six photochromic azobenzenes in a single generational shell have been constructed. Photochemical *E*/*Z* isomerization of the azobenzene groups allows for the existence of 10 discrete states, while chromatographic techniques serve to resolve these materials into seven polarity levels. The effect of the isomerization of the photochromic groups on dendrimer size in solution is documented by size-exclusion chromatography.

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Supporting Information Available: Details of the synthesis and characterization of **1**, **2**, **7**, and **8**. This information is available free of charge via the Internet at http://pubs.acs.org.

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(14) GPC elution volumes were converted to corresponding hydrodynamic volume values using the relationship $V_h = 0.4(KM^{a+1})$, where K and a are the Mark−Houwink constants for polystyrene in 1,2-dichloroethane and M is the coeluting polystyrene molecular weight. Hydrodynamic radius was calculated from the volume assuming a spherical shape and using the formula for the volume of a sphere ($V = (4/3)\pi r^3$).
(15) Li, S.; Liao, L.-X.; Szalai, M.; Junge, D. M.; McGrath, D. V., unpublished results.

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