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Driving Dendrimers with Light: Dendrimers with Azobenzene Central Linkers

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SUMMARY: Several new classes of azobenzene-containing dendrimers have been prepared and characterized. Three central linker azobenzenes, *p*-(*p*'-hydroxyphenylazo)phenol (**A**), aniline *p*-(*p*'-chlorocarbonylphenylazo)benzoyl chloride (**B**), and *p*-(*p*'-aminophenylazo) (**C**) were reacted with the appropriate dendritic fragment ([G*n*]Br for **A** and **C**; [G*n*]OH for **B**) to yield dendrimers **1-3** of varying generational size. The photoresponsive characterization of these dendrimers illustrates the insensitivity of the photoresponsive behavior of the azobenzene with respect to the nature of the attached dendritic fragment.

Introduction

The preparation of dendritic macromolecules has attracted increasing recent interest, particularly with respect to the synthesis of dendrimers with precisely placed groups within the dendrimer interior or at the periphery.1) Dendrimers with electroactive,2) photoactive,3) and recognition elements4) have been prepared and characterized, but few examples are known of dendrimers which respond conformationally to environmental stimuli such as solvent5) and pH.6) We reasoned that the precise placement of photoresponsive moieties, groups which undergo reversible variations of their structure and conformation upon exposure to light and dark conditions,7) within the interior of dendrimer architectures8) should allow us to drive their properties through light stimuli, allowing potential reversible alteration of function. Hence, we initiated a program to incorporate azobenzene moieties,9) which undergo a well-defined, reversible *trans-cis* isomerization when irradiated with ca. 350 nm light, into dendritic structures. In preliminary work10) we developed methods for the synthesis of dendrimers with azobenzene *central linkers* and

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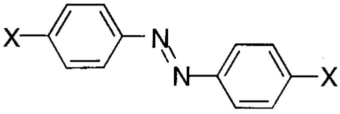


A (X = OH)
B (X = COCl)
C (X = NH_2)

characterized their photoresponsive behavior. In this paper, we report the preparation and characterization of benzyl aryl ether dendrimers up to the fourth generation using amino-, hydroxy-, and carbonyl chloride-substituted azobenzenes **A-C** as central linkers. The photoresponsive behavior of these dendrimers has been observed and the kinetics of the thermal *cis-trans* isomerization has been determined for a series of dendrimers of increasing size.

Experimental

All procedures were carried out in dry glassware using dry, degassed solvents, unless otherwise indicated. Central linkers **A**,(11) **B**,(12) and **C**,(13) and benzyl aryl ether dendrons(14) were prepared according to published procedures. Potassium carbonate (granular, J.T. Baker) was dried at 150 °C at reduced pressure for at least 12 h and stored in a dessicator. All other reagents were purchased from commercial suppliers and used as received. Flash chromatography was performed by the method of Still et al.(15) using silica gel (32-63µ, Scientific Adsorbants, Inc., Atlanta, GA).

Typical Procedure for Central Linker A. A mixture of compound **A** (102 mg, 0.48 mmol), benzyl bromide (125 µL, 1.05 mmol), K_2CO_3 (164 mg, 1.19 mmol) in 10 mL dry acetone was heated to reflux and stirred under nitrogen for 12 h. The solution was allowed to cool and evaporated to dryness. The resulting residue was then partitioned between water (20 mL) and CH_2Cl_2 (20 mL) and the aqueous layer was further extracted with

CH_2Cl_2 (3 x 25 mL). The combined organic layers were then dried (Na_2SO_4) and concentrated to give crude **1a**. Flash chromatography (SiO_2, CH_2Cl_2) gave dendrimer **1a** as yellow crystals (148 mg, 80%): ^{1}H NMR (400 MHz, acetone-d_6) 7.87 (d, *J* = 9 Hz, 4H), 7.51 (d, *J* = 7 Hz, 4H), 7.41 (t, *J* = 7 Hz, 4H), 7.34 (d, *J* = 7 Hz, 2H), 7.18 (d, *J* = 9 Hz, 4H), 5.24 (s, 4H).

Typical Procedure for Central Linker B. A mixture of [G-2]-OH$^{14)}$ (203 mg, 0.272 mmol) and DMAP (44 mg, 0.361 mmol) in 10 mL benzene was refluxed under Dean-Stark conditions for 2 h under nitrogen. The solution was then allowed to cool and **B** (42 mg, 0.136 mmol) was added. The solution was then allowed to reflux for 24 h. The solution was allowed to cool and the solvent was removed via rotary evaporation to give crude **2a**. Recrystallization from toluene/hexane yielded dendrimer **2a** (211 mg, 90%) as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 4H), 7.93 (d, *J* = 8.5 Hz, 4H), 7.39-7.23 (m, 40H), 6.66-6.54 (m, 18H), 5.30 (s, 4H), 5.00 (s, 16H), 4.97 (s, 8H).

Typical Procedure for Central Linker C. A mixture of compound **C** (112 mg, 0.53 mmol), benzyl bromide (115 μL, 1.06 mmol), NaH (60% oil dispersion, 52 mg, 1.30 mmol), in 10 mL dry THF was heated to reflux and stirred under nitrogen for 48 h. The solution was then allowed to cool and water (10 mL) was added. The aqueous layer was then extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to give crude **3a**. Flash chromatography (SiO_2, 1:3 ethyl acetate-petroleum ether) gave dendrimer **3a** as orange crystals (91 mg, 44%): ^{1}H NMR (400 MHz, acetone-d_6) 7.64 (d, *J* = 9 Hz, 4H), 7.40 (d, *J* = 7 Hz, 4H), 7.32 (t, *J* = 7 Hz, 4H), 7.24 (d, *J* = 7 Hz, 2H), 6.74 (d, *J* = 9 Hz, 4H), 6.08 (br, 2H), 4.44 (d, *J* = 6 Hz, 2H).

Results and Discussion

Photoresponsive dendrimers with azobenzene central linkers have been prepared using azobenzene derivatives **A-C** and benzylaryl ether dendrons of various sizes (Figure 1). The

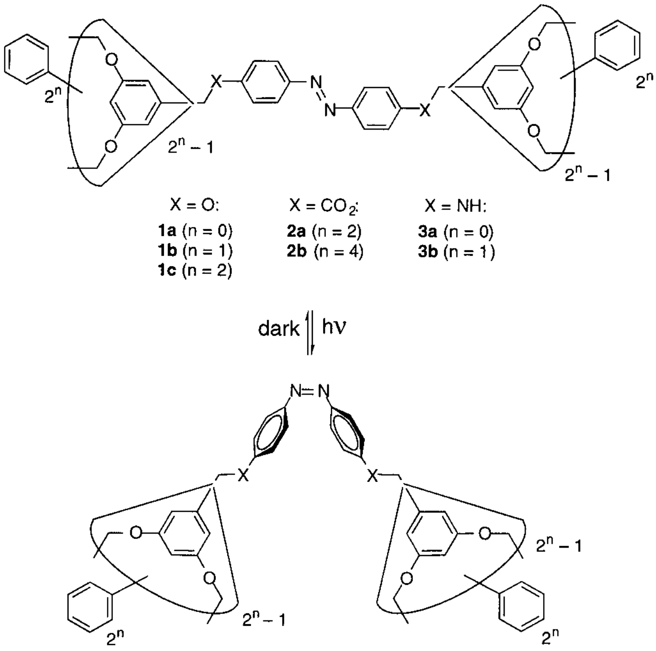


Figure 1. Dendrimers with photoresponsive azobenzene central linkers.

different linking functionality (e.g., ether, amine, ester) between the azobenzene and dendritic sector of the materials serves to alter the position of the π–π* band of the chromophore (see Figure 2). We have established the photoresponsive behavior of the azobenzene-containing dendrimers to be essentially identical to that of small-molecule azobenzenes. For example, dark incubation of a methylene chloride solution (40 μM) of second generation dendrimer **1c** served to maximize the absorbtion at 360 nm (ε_{max} = 32,500) corresponding to the *trans* azobenzene chromophore. Irradiation of a dark-incubated solution **1c** with 350 nm light resulted in clean photoisomerization to predominantly *cis*-dendrimer as evidenced by a decrease in the absorbance at 360 nm and an

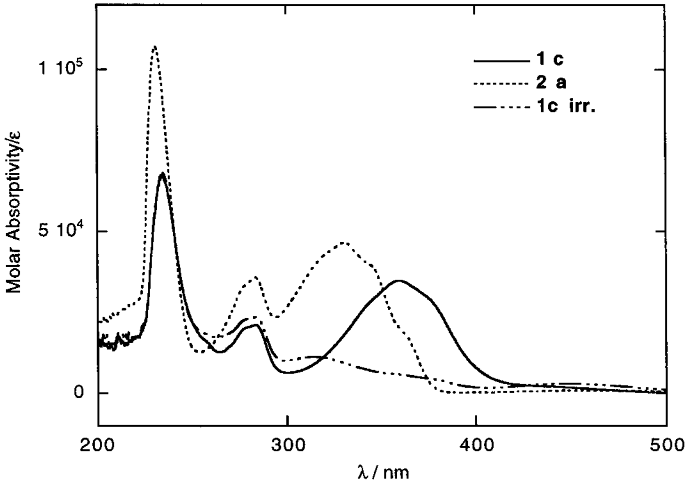


Figure 2. Absorbance spectra of chloroform solutions of second generation dendrimers **1c** and **2a** and an irradiated (350 nm) solution of **1c**.

Table 1. Rates and Activation Energies for Thermal Isomerization

Cmpd	$k_{21}(\bullet 10^6\ s^{-1})$	$k_{40}(\bullet 10^5\ s^{-1})$	$k_{60}(\bullet 10^4\ s^{-1})$	E_{act} (kcal/mol)
1a	9.79	9.82	6.30	20.7
1b	11.3	9.51	6.75	20.3
1c	10.0	9.45	7.23	21.3
4	9.48	8.47	7.59	21.8
5	9.74	8.04	6.93	21.2

increase in absorbances 314 and 450 nm. A photostationary state was reached within approximately 60 seconds.

When left in the dark, the *cis*-dendrimer reverted to the original *trans*-form over the course of several hours at 293 K. This process was monitored at three different temperatures for

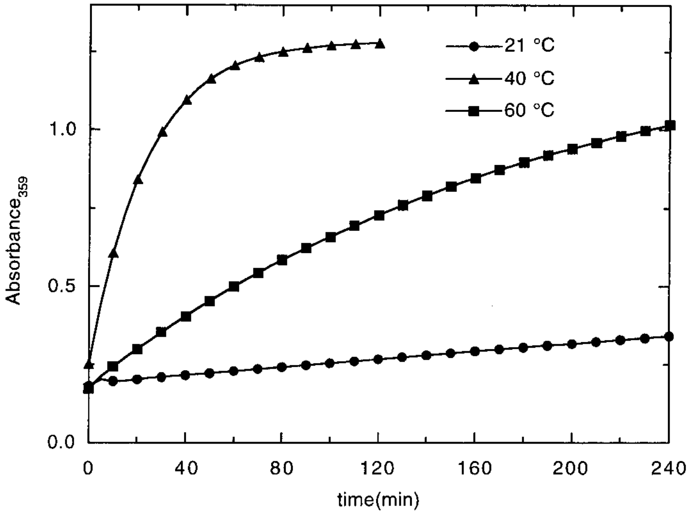


Figure 3. Plot of absorbance at 359 nm of a sample of **1c** kept in the dark at 292, 313, and 333 K after irradiation (10 min at 350 nm).

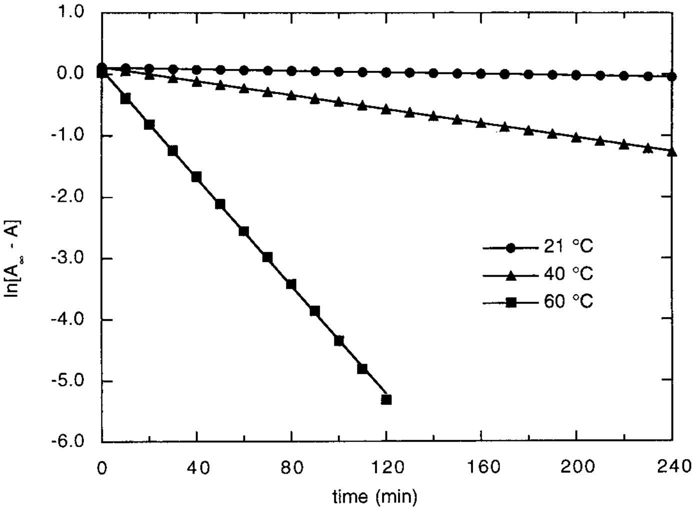
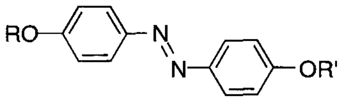
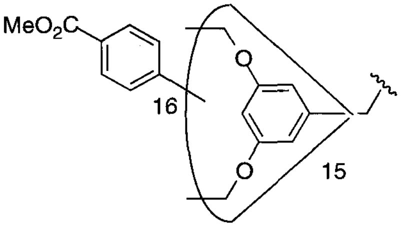


Figure 4. First order rate constant plot of ln[A∞ – A] vs. time (s) for data in Figure 3.



4 (R = R' = **6**)
5 (R = **6**; R' = Me)



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dendrimers **1a-c**, and the results are shown in Table 1 (representative data is shown in Figures 3 and 4). The first-order rate constant for the thermal process *in all dendrimers studied* is ~10^{-7} at ambient temperature—and increases approximately an order of magnitude for each jump in 20° C—similar to low-molecular weight azobenzenes. In addition, the activation energy (E_{act}) for the *cis* to *trans* reversion is *independent of dendrimer size*. This is illustrated by not only the invariance of the data in Table 1 for dendrimers **1a-c**, but also for fourth generation dendrimers **4** and **5**. The results of these measurements lead to the following two conclusions. First, the relative invariance of the first order rate constants and activation energies (E_{act}) of **1a-c**, **4**, and **5** indicates no strong steric influence on the *cis-trans* thermal isomerization. Second, the magnitude of the same data indicates no alteration of the photoresponsive behavior of azobenzene by incorporation into dendritic architecture.[16,17)]

Conclusions

Several new dendrimers with azobenzene central linkers have been prepared and their photoresponsive behavior demonstrated. The rates and activation energies of the thermal *cis-trans* isomerization of a series of dendrimers of increasing size illustrates the insensitivity of the photoresponsive behavior of the azobenzene with respect to the nature of the attached dendritic fragment.

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