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Synthesis and trans–cis isomerization of azobenzene dendrimers incorporating 1,2-isopropylidenefuranose rings

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Abstract—Azobenzene dendrimer **2** was synthesized from a known dendritic azo-tetracarboxylic acid and a dendritic amine incorporating 1,2-isopropylidenefuranose rings, and its trans–cis isomerization was studied by UV–vis absorption spectroscopy.

The area of dendrimers has attained great significance due to the unusual architectural features of the dendrimer structure coupled with their interesting properties.[1] The importance of azobenzene dendrimers stems from the facile cis–trans isomerization of the azobenzene moiety, a property which may be useful for the construction of photoswitchable devices.[2] Introduction of diversity in dendrimer structures is an important task, because future applications of dendrimers will also be dependent on the structural characteristics of the dendrimers. We recently introduced chiral dendrimers incorporating furanose ring substituted phenyls as branching units.[3] Apart from introducing chirality, these branching units would allow future functionalization of the exterior and the interior of the dendrimer. We report herein the synthesis and the study of the trans–cis isomerization of dendritic molecules **1** and **2** (Fig. 1) based on an azobenzene core and 1,2-isopropylidenefuranose branching units.

The azobenzene derivative **1** has recently been used in the synthesis of dendritic azobenzene hydrogelator **3**.[4] Amine **4** proved to be a useful branching unit for the synthesis of novel carbohydrate derived dendrimers.[3a] It appeared to be a worthwhile exercise to attempt a coupling of the tetraacid **3** and with the amine **4** in order to prepare the novel azodendrimer **2**. Toward this end, treatment of **3** and **4**, both prepared according to the literature procedures,[3a,4] in the presence of HATU and diisopropylethylamine at 25 °C for 96 h followed by purification by HPLC led to the formation of the desired dendrimer **2** in 73% yield (Scheme 1).[5] The structure of **2** was established on the basis of NMR and mass spectral analyses. Single sets of peaks due to the symmetry related protons and carbon atoms in the ^{1}H and ^{13}C NMR spectra clearly indicated the C_2-symmetric nature of **2.** The four-proton doublet at δ 6.09 due to the symmetry related interior furanoside protons served as a reference for the introduction of the desired number of branches. The appearance of integrations of one of the two sets of core aromatic protons (2H singlet at δ 7.37), interior furanoside anomeric protons (4H doublet at δ 6.09), peripheral furanoside anomeric protons (8H doublet at δ 5.87), and one of the two sets of peripheral aromatic protons (8H singlet at δ 7.52) in the ratio of 1:2:4:4 lent ample support to the structure of **2**. This rapid check for the introduction of the correct number of branch units was a useful feature of the characterization process. The ESI mass spectrum of **2** exhibited the molecular ion peak at $m/2z$ 1784.82 corresponding to the doubly charged species (M+2Na) as expected for the structure of the dendrimer.[5]

The UV–vis absorption spectrum of **1** in acetonitrile (MeCN) exhibited two π–π^* bands at 325 nm due to the trans isomer and at 237 nm due to the cis-isomer

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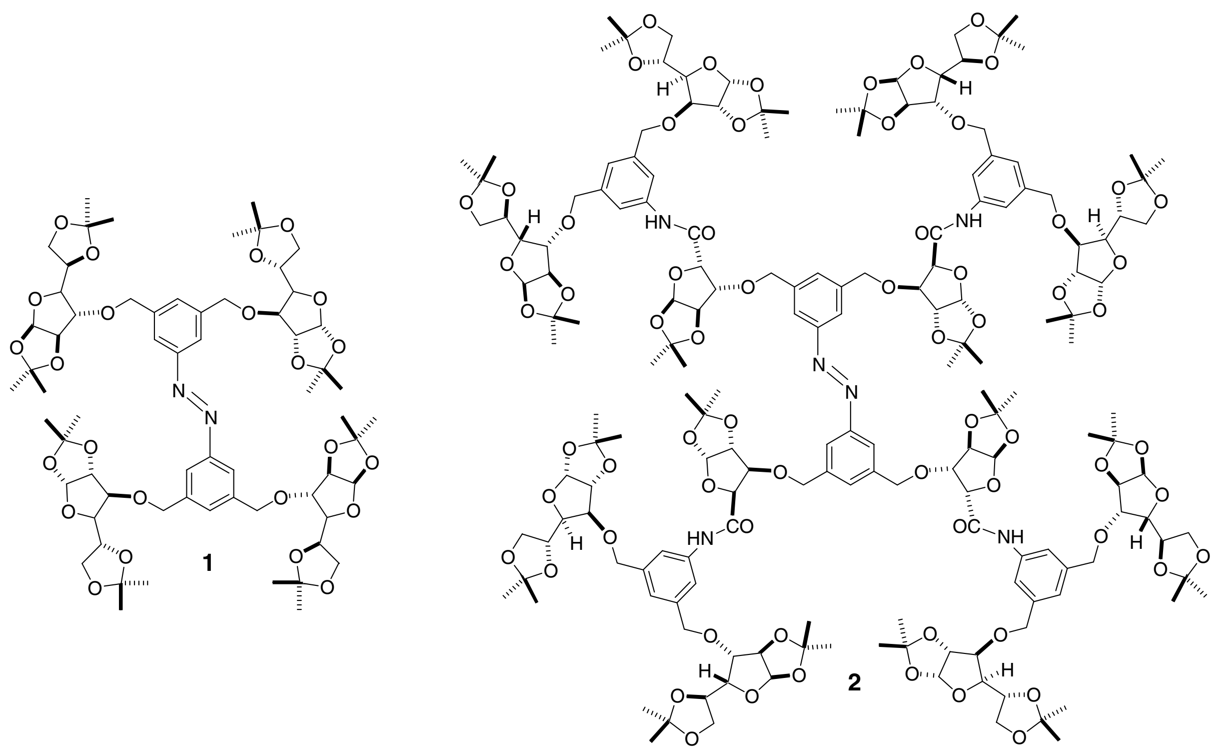
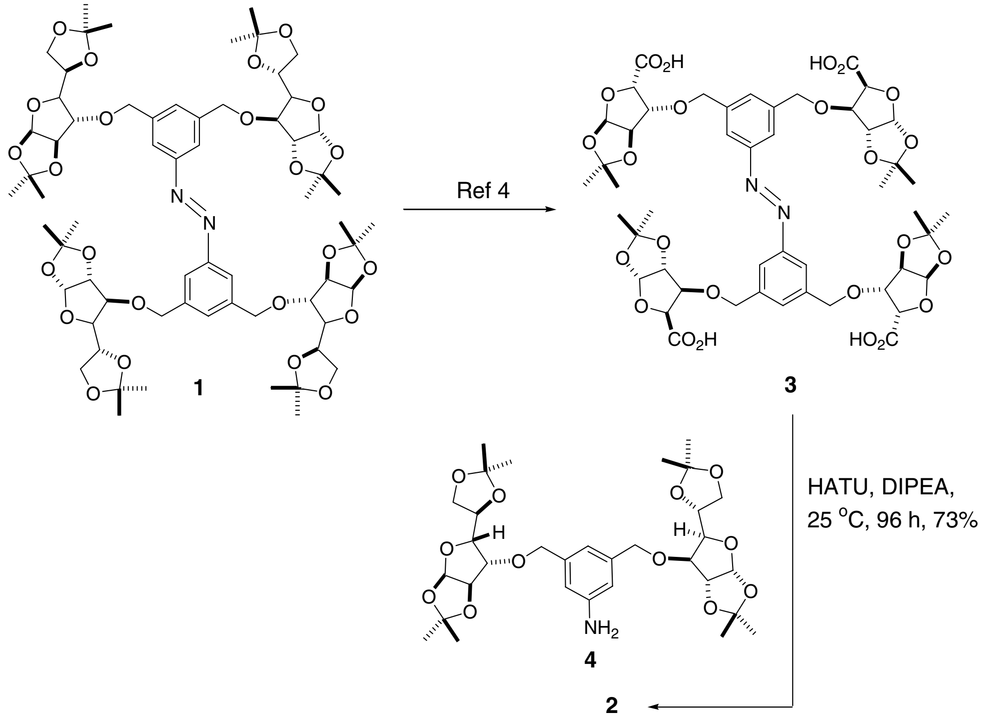


1 **2**

Figure 1. Azobenzene dendrimers **1** and **2** incorporating 1,2-isopropylidene-furanose rings.



1 **3** **4** **2**

Scheme 1. Synthesis of the azobenzene dendrimer **2** from **1**.

(Fig. 2), which were in agreement with assignments made earlier for reported azobenzene systems.[6] Photoirradiation of the dark incubated MeCN solution of **1** at 325 nm resulted in a gradual decrease in absorbance at 325 nm with a concomitant increase in absorbance at 237 nm with increased time (Fig. 2, top). This observation was consistent with trans–cis isomerization on photoirradiation. The UV–vis absorption spectrum of the larger dendrimer **2** exhibited a band at 325 nm due to a π–π^* transition of the trans azobenzene chromophoric unit and a weak band at 430 nm region due to the n–π^* transition of the corresponding cis form

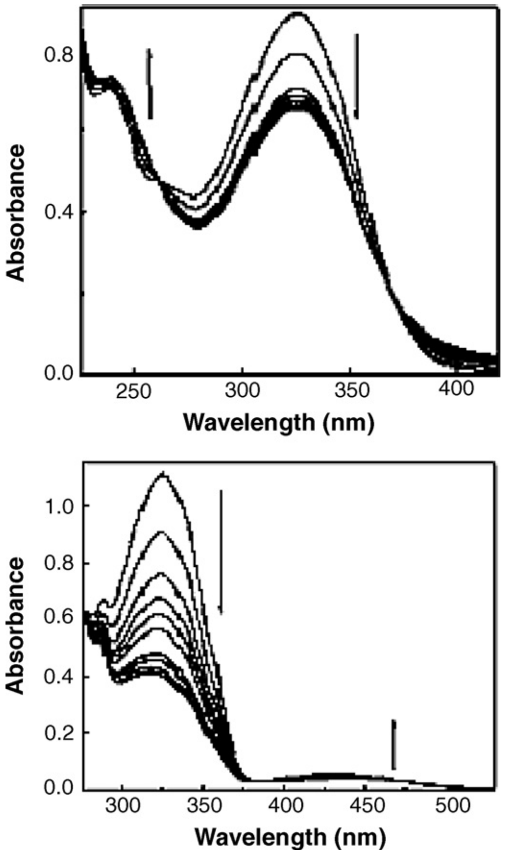


Figure 2. UV–vis absorption spectral changes in trans to cis conversion of **1** (top) and **2** (bottom) in MeCN.

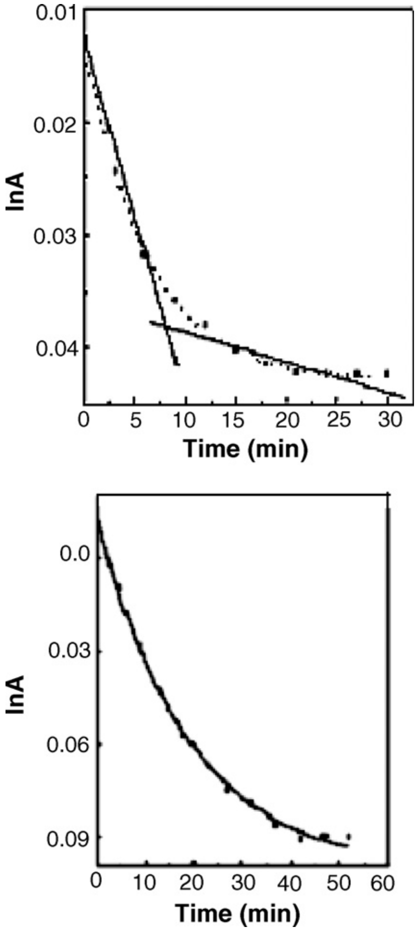


Figure 3. ln A versus time plot for absorbance change at 325 nm of **1** (top) and **2** (bottom).

Table 1. Rate constants (k_1, k_2) associated with fractional contributions ($f1$, $f2$) for photochemical isomerization from trans to cis at 325 nm for **1** and **2** in MeCN at 298 K

Dendrimer	k_1	k_2	$f1$	$f2$
1	2.7×10^{-3}	2.9×10^{-6}	0.01	0.99
2	8.7×10^{-4}	1.1×10^{-6}	0.01	0.99

(Fig. 2, bottom). On irradiation of the incubated solution of **2** in MeCN at 325 nm, changes similar to those observed in the case of **1** occurred in the absorption pattern.

The energetically preferred trans configuration corresponding to the 325 nm band transformed gradually to the cis species as evidenced from the regular increment of the 430 nm band with time (Fig. 2, bottom) at the expense of the 325 nm band. The presence of isobestic points in the UV–vis absorption spectra of both **1** and **2** was also indicative of the conversion of trans to cis isomers. Plots of ln A versus time at 325 nm for **1** and **2** are shown in Figure 3 (top and bottom), respectively. From the decay it appears that initially a fast component of lifetime developed, but a slower component prevailed with increased time. Two first order rate constants (k_1 and k_2) for the decay were obtained by using biexponential fit (Table 1). As apparent from the decay, the computed fractional contribution ($f1$) associated with the faster component k_1 was found to be smaller (~0.01) and a much larger value (~0.99) was observed for the slower component k_2 (Table 1). This effective temporal decrease of the first order rate constant for the trans to cis isomerization was possibly due to a gradual increase of the more compact cis isomer. In the dark, the reverse isomerization from cis to trans was observed (Fig. 4) in the cases of both **1** and **2**. However, the rates associated with the reverse isomerization, as estimated by the reported procedure were found to be lower ($1.1 \times 10^{-6}\ \mathrm{s}^{-1}$ for **1** and 4.4×10^{-8} for **2**) than those observed for trans to cis transformation.[7] The presence of the isosbestic point, as shown in Figure 4, during the reversible isomerization pointed to the reversible conversion of the azobenzene moiety. No photodegradation was responsible for this change, because no significant shift of the band position was observed. The formation of the trans isomer of the dendrimer **2** was also apparent from the nature of absorbance recorded at 298 K, 308 K, and 318 K (Fig. 5). The values of the activation energy (E_a), estimated from the slopes of the Arrhenius plot (Fig. 6), are presented in Table 2. Contrary to expectation, the E_a for **2** (~37 kcal mol^{-1}) is nearly 2.5 times larger than that of **1** (14.8 kcal mol^{-1}). The reason for this unexpected observation is not known at present. It is possible that during the time of the measurements (~800 min), a substantial amount of the cis-form is present in the case of **2**.

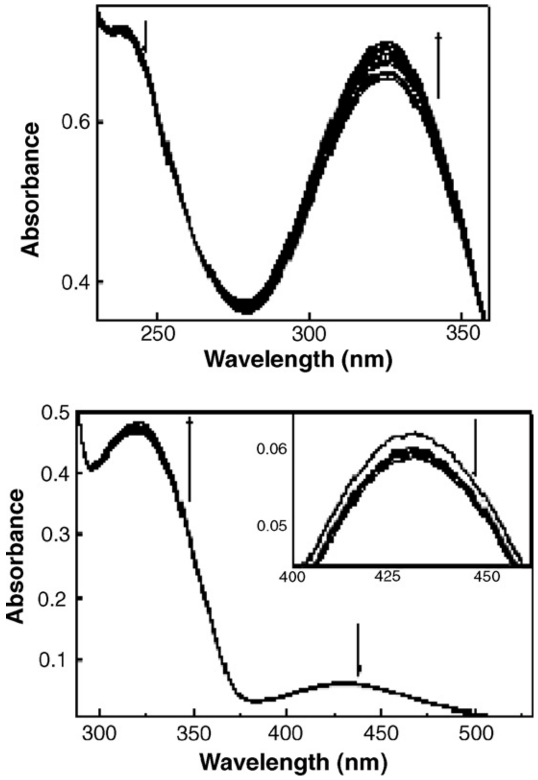


Figure 4. UV–vis absorption spectral changes in cis to trans conversion of **1** (top) and **2** (bottom) in MeCN.

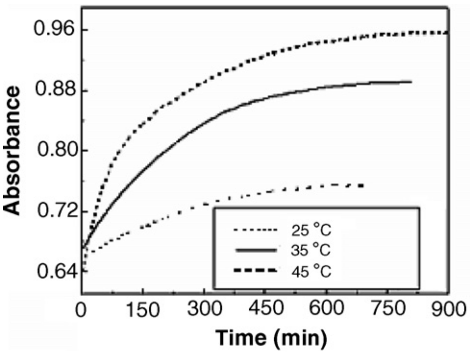


Figure 5. Absorbance versus time plot for the cis to trans conversion of **2** at different temperatures at ~325 nm.

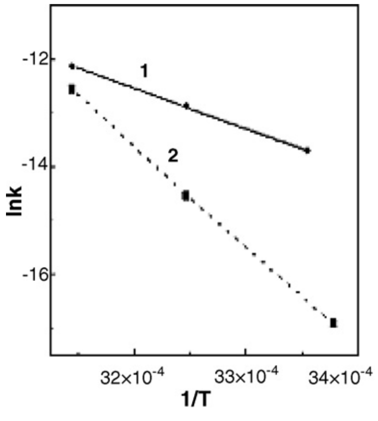


Figure 6. Arrhenius plots (ln k versus $1/T$) for **1** and **2**.

Table 2. Rates (k) and activation energies (E_a) for thermal cis to trans isomerization of **1** and **2** (at 325 nm) in MeCN

Dendrimer	Temperature (K)	k (s^{-1})	E_a (kcal mol^{-1})
1	298	1.1×10^{-6}	
	308	2.5×10^{-6}	14.8
	318	5.4×10^{-6}	
2	296	4.4×10^{-8}	
	308	4.9×10^{-7}	37.2
	318	3.5×10^{-6}	

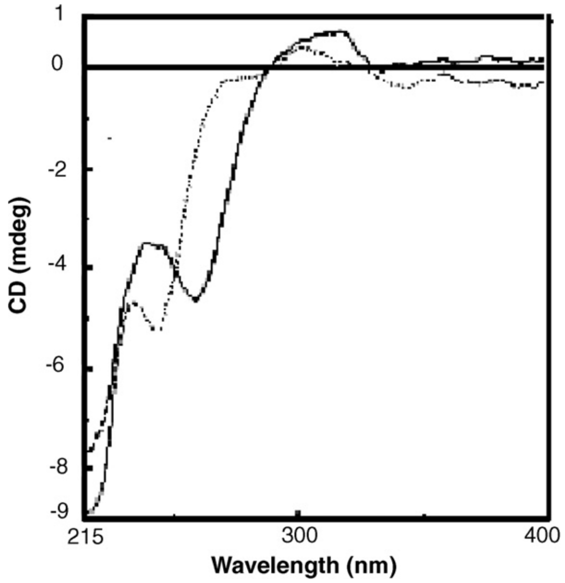


Figure 7. CD spectra of **1** (–) and **2** (···) in MeOH.

The dendrimer **2** incorporates an azobenzene chromophore embedded in a chiral environment. The CD spectrum of **2** in methanol exhibited a strong negative absorption at ~275 nm and a weak positive absorption at ~325 nm (Fig. 7). The CD spectrum of **1** was found to be similar in pattern, and it was evident that the larger dendritic environment in **2** had no pronounced effect on the chirality.

In conclusion, the above observations have revealed that both the dendrimers **1** and **2** are efficient photoswitchable systems, and the results are expected to be of importance for future applications in solar energy conversion devices.

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5. *Experimental procedure and spectral data for* **2**. HATU (0.035 g, 0.09 mmol) and DIPEA (0.04 mL, 0.23 mmol) were added to a well-stirred mixture of carboxylic acid **3**[4] (0.02 g, 0.02 mmol) and amine **4**[3a] (0.08 g, 0.12 mmol) in DMF (1 mL) at 0 °C, and stirring was continued for 96 h at 25 °C. After completion of the reaction as revealed by TLC, water (25 mL) was added to the mixture, which was then extracted with CH_2Cl_2. The organic layer was washed with water, dried, and concentrated to give a yellowish-orange liquid, which was chromatographed on Si-gel using EtOAc as eluent affording an orange foam. Further purification by HPLC on a C_{18}-column using MeCN as solvent yielded **2** (0.049 g, 73%) as an orange foam; $[\alpha]_D^{25}$ −38.2 (*c* 0.42, $CHCl_3$); IR (KBr): 3396, 2987, 1683 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, 4H), 7.69 (s, 4H), 7.52 (s, 8H), 7.37 (s, 2H), 7.08 (s, 4H), 6.09 (d, $J = 1.8$ Hz, 4H), 5.87 (d, $J = 3.2$ Hz, 8H), 4.83 (d, $J = 1.8$ Hz, 4H), 4.61–4.48 (m, 36H), 4.36–4.32 (m, 12H), 4.11–4.06 (m, 16H), 4.02–3.98 (m, 16H), 1.48 (s, 12H), 1.48 (s, 24H), 1.41 (s, 24H), 1.35 (s, 24H), 1.32 (s, 12H), 1.29 (s, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 (q), 152.6 (q), 139.1 (q), 139.0 (q), 137.4 (q), 129.6 (CH), 122.4 (CH), 121.6 (CH), 118.1 (CH), 113.0 (q), 111.8 (q), 109.0 (q), 105.6 (CH), 105.2 (CH), 82.8 (CH), 82.6 (CH), 82.3 (CH), 82.0 (CH), 81.3 (CH), 81.2 (CH), 72.5 (CH), 71.9 (CH_2), 67.3 (CH_2), 27.0 (CH_3), 26.8 (CH_3), 26.5 (CH_3), 26.3 (CH_3), 25.5 (CH_3); ESIMS (positive ion): *m*/2*z* 1784.82 (M+2Na), Calcd for $C_{176}H_{238}N_6O_{68}Na_2$, *m*/2*z* 1784.76. Anal. Calcd for $C_{176}H_{238}N_6O_{68}$: C, 59.96; H, 6.80; N, 2.38. Found: C, 59.83; H, 6.98; N, 2.10.
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