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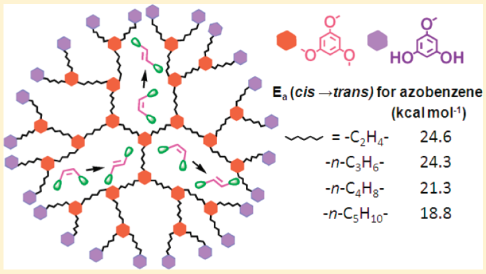
Dynamic Internal Cavities of Dendrimers as Constrained Media. A Study of Photochemical Isomerizations of Stilbene and Azobenzene Using Poly(alkyl aryl ether) Dendrimers

Baskar Natarajan,[†] Shipra Gupta,[‡] Nithyanandhan Jayaraj,[‡] V. Ramamurthy,*[,‡] and Narayanaswamy Jayaraman*[,†]

[†]Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India
[‡]Department of Chemistry, University of Miami, Coral Gables, Florida 33124, United States

ABSTRACT: Dendritic microenvironments defined by dynamic internal cavities of a dendrimer were probed through geometric isomerization of stilbene and azobenzene. A third-generation poly(alkyl aryl ether) dendrimer with hydrophilic exterior and hydrophobic interior was used as a reaction cavity in aqueous medium. The dynamic inner cavity sizes were varied by utilizing alkyl linkers that connect the branch junctures from ethyl to *n*-pentyl moiety (**C_2G3−C_5G3**). Dendrimers constituted with *n*-pentyl linker were found to afford higher solubilities of stilbene and azobenzene. Direct irradiation of *trans*-stilbene showed that **C_5G3** and **C_4G3** dendrimers afforded considerable phenanthrene formation, in addition to *cis*-stilbene, whereas **C_3G3** and **C_2G3** gave only *cis*-stilbene. An electron-transfer sensitized *trans*−*cis* isomerization, using cresyl violet perchlorate as the sensitizer, also led to similar results. Thermal isomerization of *cis*-azobenzene to *trans*-azobenzene within dendritic microenvironments revealed that the activation energy of the *cis*- to *trans*-isomer was increasing in the series **C_5G3** < **C_4G3** < **C_3G3** <**C_2G3**. With the change in the alkyl linker from C_5 to C_2, significant changes in the activation parameters were observed.



■ INTRODUCTION

The presence of multiple branch points through-out the interior of a dendrimer leads to the evolution of dynamic inner cavities of varying physical properties. The evolution of such cavities are seen more profoundly in the higher generation dendrimers, due to increased number of branch points and attendant increase in the number of peripheral groups, leading to more dense peripheries and less-dense interior cavities.[1−3] The monodispersed nature of these macromolecules and presence of dynamic inner cavities continue to prompt varied types of studies involving dendrimers.[4,5] Hydrophobic interior regions of the hydrophilic dendrimers provide an opportunity to conduct encapsulations[6−12] in a manner analogous to that inside hosts, such as micelles, liposomes, and various types of cavitands such as cyclodextrins, cucurbiturils, and octa acid.[13−17] We demonstrated previously that dendritic microenvironments of poly(alkyl aryl ether) based dendrimers[18] could mediate photochemical reactions, often with high regioselectivities.[19,20] The hypothesis that linkers connecting branch points in a dendrimer define the interfacial regions separating hydrophobic interior from exterior aqueous milieu was investigated through preparation of poly(alkyl aryl ether) dendrimers constituted with varying alkyl chain lengths.[21] On the basis of these studies, it was concluded that higher hydrophobic microenvironments emerge for a lower generation dendrimer constituted with longer alkyl chain lengths than a higher generation dendrimer constituted with more number of shorter alkyl chain linkers. Continuing the efforts to utilize dynamic inner cavities of dendrimers as reaction cavities in an aqueous medium, we undertook studies of photochemical isomerizations of azobenzene and stilbene, two well-investigated systems in solution.[22−31] Water-soluble dendrimers based on poly(alkyl aryl ether) dendrimers were utilized as reaction media. Thermal or photochemical activations of the double bond, followed by inversion or rotation, are the steps involved in the transition state during isomerization of azobenzene. Photochemical isomerization of stilbene proceeds via rotation of the C═C bond. Assessing thermodynamic parameters provides information on the transition state, including the role of solvations during thermal isomerization of azobenzene. Results of the study are presented herein.

■ RESULTS AND DISCUSSION

Structures of third-generation poly(alkyl aryl ether) dendrimer series, utilized in the present study, are shown in Figure 1. In the series of first to third generations, the encapsulation abilities of third-generation dendrimers were found previously to be maximum,[21] leading to the choice of this generation for the present study. Within the series, cavity sizes were varied methodically by changing the *n*-alkyl linker from ethyl to *n*-pentyl, connecting the branch points (**C_2G3−C_5G3**). Although the alkyl chain length of the linker varied, the number of phenolic groups at the periphery and the aromatic rings remained the same in this series of dendrimers. Dendrimers **C_2G3−C_5G3** are soluble in aqueous solutions at pH ∼10. Prior to isomerization studies, the

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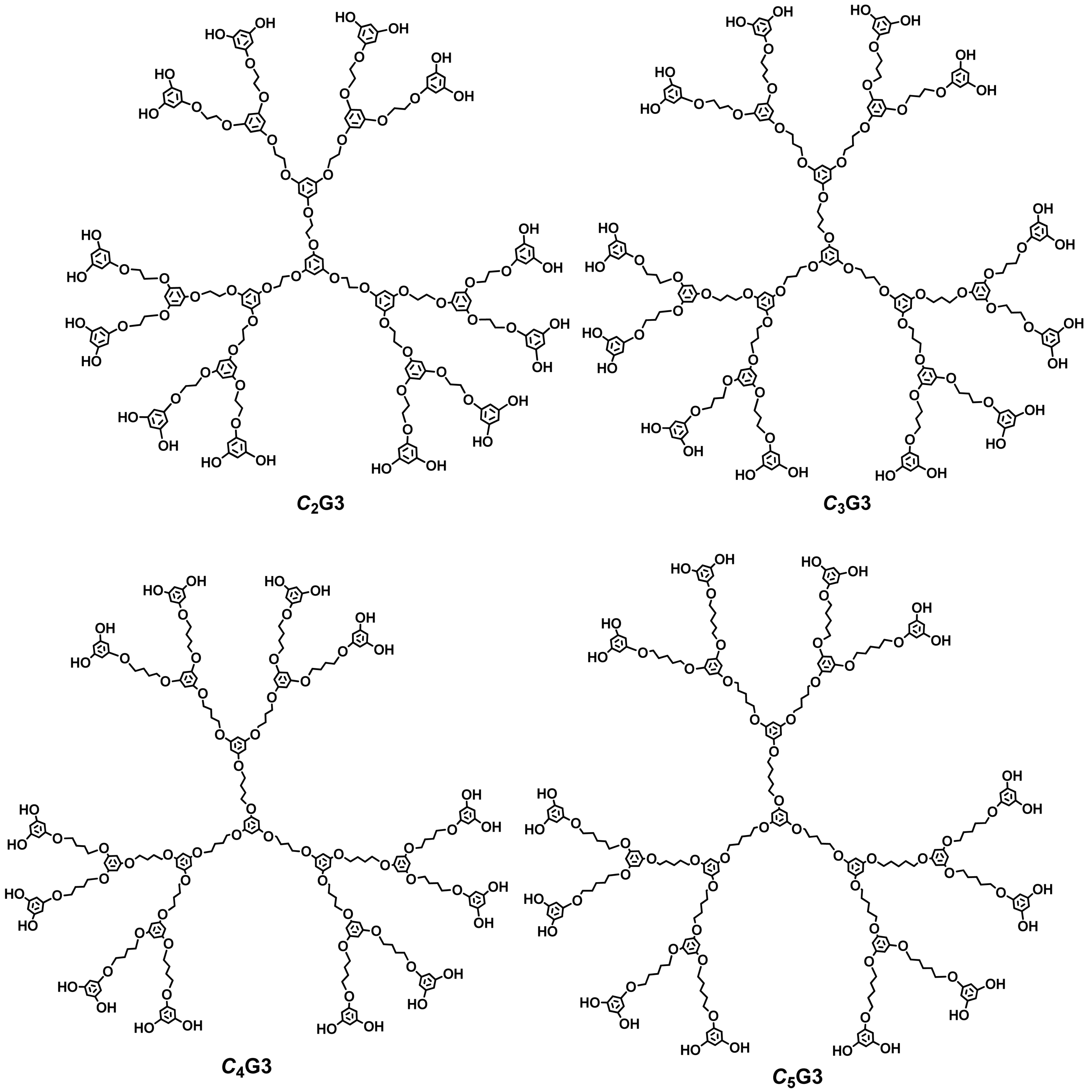


Figure 1. Structures of various spacered third-generation poly(alkyl aryl ether) dendrimers.

extent of solubilization of sparingly water-soluble azobenzene and stilbene was assessed. For this purpose, a defined amount of the guest molecule was added to an aqueous basic solution of dendrimers, stirred for 12 h in the dark, and filtered, and the concentration of guest molecule solubilized was estimated by UV−vis absorption spectroscopy. Table 1 provides the maximum amount of guest molecules that could be solubilized in aqueous solutions containing defined amounts of dendrimers. As the linker changed from an ethyl to an *n*-pentyl group, an increase in the solubilization of guest molecules was noticed. Similar observations were noted previously for other guest molecules, such as pyrene and coumarin.[21] A 2.5−3 times increase in guest molecule solubilization occurred when the linker length was changed from an ethyl to an *n*-pentyl group. Progressively increasing solubilization indicated higher hydrophobicities of internal cavities as the alkyl chain length increased, even when the number of branches and the peripheral groups remained identical across the series C_2G3−C_5G3.

Table 1. Solubilization of *trans*-Stilbene and *trans*-Azobenzene in Aqueous Dendrimer Solutions

aq solution of dendrimer (100 μM) (pH ~10)	solubilized stilbene (μM)	solubilized azobenzene (μM)
C_2G3	17	15
C_3G3	26	22
C_4G3	33	41
C_5G3	42	48

Subsequent to evaluation of solubilization abilities, isomerization studies of stilbene and azobenzene were undertaken.

The experiments were performed in aqueous dendrimer solutions (pH ~10, aq NaOH) upon encapsulation of stilbene as described for the solubilization experiments. After purging with N_2(g) for 30 min, the solutions in Pyrex test tubes were irradiated using a medium-pressure Hg lamp for 6 h and extracted with diethyl ether, and the products were analyzed by gas chromatography. As a comparison, irradiations were also conducted in ethanol solution in the absence of the dendrimer. As shown in Table 2, in aqueous solutions containing dendrimers, conversion of *trans*-isomer to *cis*-isomer was complete. In addition to *cis*-isomer, a considerable amount of phenanthrene was formed with C_5G3 and C_4G3 dendrimers as well as in EtOH solution. Although stilbene dimerization in aqueous solutions, probably due to aggregation, to afford cyclobutane was known previously,[32] in none of the irradiations did tetraphenylcyclobutane, resulting from [2 + 2] cycloaddition, formed. The absence of dimers suggested that stilbene molecules were confined to the hydrophobic interior of dendrimers. Exclusive formation of only the *cis*-isomer within **C_3G3** and **C_2G3** dendrimers suggested that the *cis*-isomer was not favored to isomerize to the *trans*-form or cyclize to phenanthrene. This may also be an indication of the *cis*-isomer being more easily accommodated than the *trans*-isomer within the dendritic hydrophobic cavities. Formation of phenanthrene in solutions containing **C_5G3** and **C_4G3** dendrimers suggested that cyclization was becoming facile as the linker lengths constituting the dendrimer increased. Thus, among *cis*- and *trans*-isomers and phenanthrene, *cis*-isomer appeared to be the preferred resting state inside dendrimer cavities, followed by phenanthrene. The dominant role of cavity sizes in photoisomerization could thus be observed within a dendrimer generation by varying linkers connecting the branch points.

Table 2. Isomerization of *trans*-Stilbene in Aqueous Dendrimer Solutions and in EtOH

	trans-stilbene (%)	*cis*-stilbene (%)	phenanthrene (%)
EtOH	15	56	29
C_5G3		72	28
C_4G3		91	9
C_3G3		99	trace
C_2G3		99	trace

Having established that the dendrimer interior favors the *cis*-isomer formation, we were curious whether such would be the case when the isomerization was prompted by a photoinduced electron-transfer process. It is well-known that photoinduced electron transfer of stilbene in organic solvents favors the *trans*-isomer.[33−35] We chose cresyl violet perchlorate (CVP) as the electron-transfer sensitizer (Scheme 1) for the following reasons: (a) CVP, a positively charged dye (Scheme 1), being polar in nature,[36] would prefer to be in the bulk aqueous solution and posed no competition to the encapsulation of *trans*-stilbene inside the dendrimers. Also, being positively charged, it was likely to interact with the negatively charged periphery of dendrimers. (b) The absorption spectra of *trans*-stilbene, *cis*-stilbene, CVP, and the CS-380 cutoff filter are shown in Figure 2.

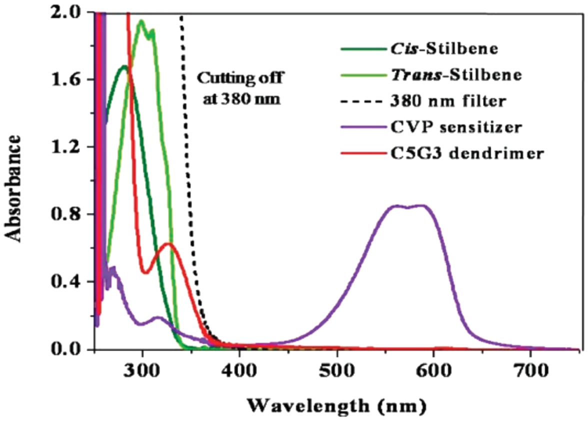


Figure 2. Absorption spectra of *cis*-, *trans*-stilbenes, **C_5G_3**, CVP, and 380 nm filter.

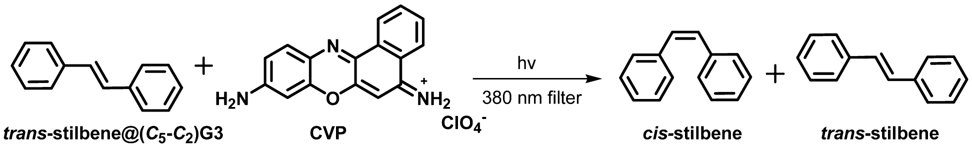
From the absorption spectra it is clear that CVP could be selectively excited in the presence of stilbenes. (c) Based on the known values of the oxidation and reduction potentials of the donor and the acceptor and the excitation energy of CVP, the photoinduced electron transfer is expected to be exothermic by −0.29 eV (E_{ox} [*trans*-stilbene] = 1.43 V vs SCE; E_{red} [CVP] = −0.46 V vs SCE; E_{S1} (Cresyl violet) = 2.118 eV (corresponding to 586 nm).

First, we established that CVP-sensitized isomerization of *trans*-stilbene in ethanol favors the *trans*-isomer. As indicated in Table 3, consistent with literature reports, CVP sensitization gave very little *cis*-isomer in ethanol without the presence of a dendrimer. For photoinduced electron-transfer studies in aqueous media, solubilization of *trans*-stilbene inside dendrimers was achieved similar to that during direct irradiation experiments. Selective excitation of the sensitizer in the presence of *trans*-stilbene[37] was conducted for 2 h using a Corning 380 nm filter. Similar to direct irradiation, CVP sensitization of *trans*-stilbene also led to *cis*-stilbene as the main product. Table 3 lists the relative percentages of *cis*- and *trans*-stilbenes encapsulated within **C_5G3−C_2G3** dendrimers,

Table 3. Photo-isomerization of *trans*-Stilbene Encapsulated within C_2G3-C_5G3 Dendrimers, in the Presence of CVP as Electron-Transfer Sensitizer Dye, Using a 380 nm Filter and Irradiation for 2 h

dendrimer	*trans*-stilbene (%)	*cis*-stilbene (%)
ethanol	98	2
C_5G3	16	84
C_4G3	5	95
C_3G3	1	99
C_2G3	2	98

Scheme 1. Photoisomerization of *trans*-Stilbene@(C_5−C_2)G3 Dendrimers in the Presence of CVP as Electron-Transfer Sensitizer



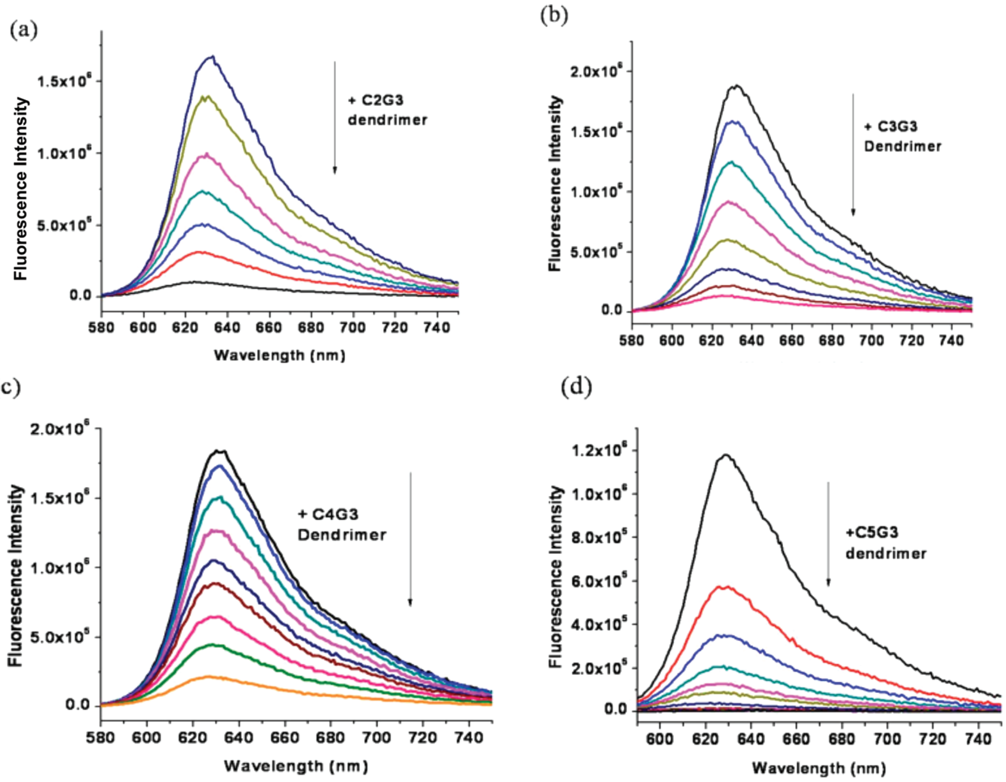


Figure 3. Fluorescence studies of CVP in presence of various (a–d) (**C_2G3–C_5G3**) dendrimers respectively. [CVP] = 3 × 10^{-5} M in water. [**C_nG3**] = 0.33 × 10^{-6} M to 1.7 × 10^{-4} M. λ_{ex} = 580 nm.

Table 4. Rate Constants (k), Activation Energies (E_a), and Thermodynamic Parameters of Thermal *Cis* → *Trans* Isomerization of Azobenzene in Aqueous C_nG3 Dendrimer Solutions

	rate constant k^a								
	x 10^5	x 10^4	x 10^4	x 10^4					
	318 K	323 K	328 K	333 K	$E_a{}^b$	log A	$\Delta H^‡$	$\Delta S^‡$	$\Delta G^{‡c}$
C_5G3	6.23	1.08	1.70	2.35	18.78	8.69	18.16	−20.81	24.79
C_4G3	5.72	1.02	1.65	2.58	21.26	10.35	20.49	−13.67	24.85
C_3G3	4.57	0.93	1.56	2.61	24.26	12.32	23.63	−6.23	25.61
C_2G3	4.30	0.84	1.59	2.40	24.61	12.53	23.97	−3.31	25.02

[a] k is expressed in s^{-1}. [b] E_a, $\Delta H^‡$, $\Delta G^‡$ are in kcal mol^{-1}, and $\Delta S^‡$ in cal mol^{-1} K^{-1}. [c] At 45 °C.

obtained after the photosensitized irradiation, in the presence of CVP. We observed that in going from C_5 to C_2 linker in the third-generation dendrimers, the percentage of *cis*-isomer increased. This supports the inference drawn from results of direct irradiation that a decrease in the size of inner cavities stabilizes *cis*-stilbene inside the dendrimers.

Given the closeness of the oxidation potential of the linker trialkoxybenzene units (E_{ox} [TMB = $G_3(OH)_{24}$] = 1.5 V vs SCE) with that of *trans*-stilbene, the linker units mediating the electron-transfer unit cannot be ruled out. To probe this possibility, the fluorescence of CVP was monitored with increased addition of dendrimers. As shown in Figure 3, addition of **C_2G3–C_5G3** dendrimers resulted in a decrease in CVP fluorescence intensity. Given that the excited singlet energy of the linker unit is higher than that of CVP, we believe that the quenching is likely to be due to electron transfer from linker units to excited CVP. The Stern–Volmer plot due to the above fluorescence quenching showed a nonlinear upward curve, indicating the quenching process to be under both dynamic and static mechanisms.

Following assessments of the photochemical behavior of stilbene in aqueous dendrimer solutions, a similar study was undertaken with azobenzene as the guest molecule. Photochemical isomerization of *trans*- to *cis*-isomer, followed by thermal reversal of azobenzene, is one of the most studied photoreactions of organic molecules in isotropic solutions and in constrained media.[28−31,38−40] Irradiation of azobenzene included within dendrimer was carried out for 20 min, by which time equilibria between *cis* and *trans* isomers were reached. Assuming that the *cis*-isomer does not absorb at 321 nm,[41] based on absorption intensity at this wavelength, the mixture was estimated to contain ∼70% of *cis*-azobenzene. Thermal reversal of *cis*- to *trans*-isomer was followed subsequently at room temperature, in order to assess the effect of dendritic microenvironments on the isomerization process. The rate of reversal process was monitored with increasing intensities of absorption at 321 nm, corresponding to the π–π* transition of *trans*-azobenzene. The first-order rate constants derived for each dendrimer solution at varying temperatures are given in Table 4. The rate constants of *cis*→*trans* isomerization were found to be generally lower for $\mathbf{C_2G3}$ and $\mathbf{C_3G3}$ solutions when compared to $\mathbf{C_5G3}$ and $\mathbf{C_4G3}$ solutions at 318 K and, to some extent, at 323 K. Such differences were not noticeable at higher temperatures. Associated energies of activation (E_a), determined by k vs $1/T$ plots, revealed differences more significantly for the *cis* → *trans* conversion at dendritic microenvironments. The activation energy was found to increase progressively with reducing alkyl chain linker, namely, C_5-, C_4-, C_3-, and C_2-linked dendrimers, indicating an effect of the microenvironments pertaining to each dendrimer. Associated activation parameters, namely, activation enthalpies ($\Delta H^{\ddagger}$), entropies ($\Delta S^{\ddagger}$), and free energies of activation ($\Delta G^{\ddagger}$) were evaluated with the aid of Eyring plots (Table 4). Striking differences could be noticed from these plots.

Progressively increasing $\Delta H^{\ddagger}$ values were countered by decreasing $\Delta S^{\ddagger}$ values as the linker lengths varied from *n*-pentyl to ethyl group. The more negative $\Delta S^{\ddagger}$ along with relatively lesser $\Delta H^{\ddagger}$ is indicative that the isomerization occurs through an inversion mechanism. On the other hand, larger activation enthalpy and positive activation entropy would indicate that the isomerization process occurs through a rotational mechanism.[28−31] The possibility of dendrimer microenvironments affecting shape changes at the transition state appears to be the most likely reason for the observed differences in the activation parameters. Drastically reducing negative activation entropies and increasing activation enthalpies in the present study indicate that isomerization in $\mathbf{C_5G3}$ and $\mathbf{C_4G3}$ differs from that in $\mathbf{C_3G3}$ and $\mathbf{C_2G3}$ dendrimers. The pre-exponential factors are seen to be within the range attributed for isomerization through either inversion or rotation mechanisms. Significant changes in the thermodynamic parameters among $\mathbf{C_{\mathit{n}}G3}$ dendrimers might be attributed either to the transition state proceeding through varying *cis*-conformers or to varying transition-state geometries. The free energy of activation decreased slightly with faster rate of isomerization with $\mathbf{C_5G3}$ and $\mathbf{C_4G3}$ dendrimers and vice versa with $\mathbf{C_3G3}$ and $\mathbf{C_2G3}$ dendrimers. The higher rate constant is also associated with larger negative entropy change. The effect of solvent polarity is that isomerization in polar solvents tends to exhibit positive entropy of activation and that in a nonpolar solvent exhibits negative entropy of activation.[29] Ordering of solvent molecules in the transition state would lead to negative entropy changes, and such ordering of solvents occurs in nonpolar solvents. Polar solvents decrease the tendency of solvent ordering around the transition state, thereby increase the entropy of activation. We envision a similar situation arising with dynamic internal cavities of dendrimers. The observed $\Delta S^{\ddagger}$ agree with the polarity differences of internal cavities in the $\mathbf{C_{\mathit{n}}G3}$ series, $\mathbf{C_5G3}$ being nonpolar and $\mathbf{C_2G3}$ being relatively polar. Progressively increasing $\Delta H^{\ddagger}$ and less negative $\Delta S^{\ddagger}$ indicate that both increasing polarities of interior cavities in the order from $\mathbf{C_5G3}$ to $\mathbf{C_2G3}$ and increasing cavity sizes from $\mathbf{C_2G3}$ to $\mathbf{C_5G3}$ affect the transition state during isomerization. The present study establishes periodic changes in isomerization kinetics achievable through dynamic interior cavities of dendrimers as new constrained media for photochemical reactions.

■ CONCLUSION

Dynamic internal cavities of poly(alkyl aryl ether) third-generation dendrimer series, with ethyl to *n*-pentyl linkers connecting the branch points, were utilized to study photochemical isomerizations of prototypical substrates, namely, stilbene and azobenzene, in an aqueous milieu. Dendrimers with *n*-pentyl and *n*-butyl linkers showed higher solubilities of hydrophobic dye molecules than those with *n*-propyl and ethyl groups, whereas dendrimers with C_5 and C_4 linkers allowed formation of the *cis*-isomer along with cyclized product, namely, phenanthrene, in significant proportion; those with C_3 and C_2 alkyl chains afforded exclusively the *cis*-isomer. Preliminary studies of electron-transfer-sensitized *trans-cis* isomerization of stilbene, using CVP, showed the extent of *trans*- to *cis*-isomerization was similar to that of direct irradiation. In the case of azobenzene isomerization at dendritic microenvironments, the rates and thermodynamic parameters were found to vary significantly between dendrimers with C_5, C_4 alkyl linkers and those with C_3, C_2 alkyl linkers. Assessment of the activation parameters showed significant changes in the ΔH and ΔS values for the iomerization as the linker alkyl chain varied from C_5 to C_2. The study establishes the properties of dendritic microenvironments to play a key role in mediating photochemical reactions of guests included within them.

■ EXPERIMENTAL METHODS

Solubilizations of Stilbene and Azobenzene in Aqueous Dendrimer Solutions. A solution of stilbene or azobenzene (5−7 mg) and $\mathbf{C_{\mathit{n}}G3}$ dendrimer[21] (100 μM) in THF (2 mL) was evaporated. The resulting residue was admixed aq NaOH solution (5 mL, pH >10), stirred for 12 h in dark at ambient temperature, and filtered (0.45 μm), and the concentration of solubilized guest molecule was analyzed by UV−vis spectroscopy (ε_{295} 29000 M^{-1} cm^{-1} for stilbene;[42] ε_{321} 19950 M^{-1} cm^{-1} for azobenzene[43]).

Isomerization of Stilbene in Aqueous Dendrimer Solutions. A solution of stilbene (10 mg) and C_nG3 dendrimer (1 mM) in THF (5 mL) was evaporated. The resulting residue was admixed aq NaOH solution (10 mL, pH >10), stirred for 12 h in the dark at ambient temperature, and filtered (0.45 μm). The filtrate was purged with N_2 (g) for 30 min and subjected to irradiation in a Pyrex tube under a high-pressure Hg lamp (400 W) for 6 h. The solution was extracted in Et_2O (3 × 10 mL), dried (Na_2SO_4), concentrated, and analyzed by gas chromatography, using a fused silica column. Peaks were identified by coinjecting with authentic samples.

Isomerization of Stilbene in Aqueous Dendrimer Solutions in the Presence of CVP. *trans*-Stilbene was dissolved in $CHCl_3$, and a known amount was added to a test tube (to make up a final concentration of 4×10^{-4} M). $CHCl_3$ was carefully removed, and to this 2−5 mL of a solution of $\mathbf{C_{\mathit{n}}G3}$ dendrimer (1×10^{-3} M) was added. This solution was stirred in dark for 12 h, while continuously purging N_2, and then it was filtered through an Acrodisc filter to remove any floating particles. One milliliter of 1 mM CVP solution in water was added to the above solution. The solution was irradiated while purging N_2 in a Pyrex tube with a 450 W medium-pressure Hg lamp for 2 h. The solution was extracted in Et_2O (3 × 10 mL), dried (Na_2SO_4), concentrated, and analyzed by gas chromatography on a gas chromatograph fitted with an HP-5 column. Peaks in the GC trace were identified by coinjectiion with authentic samples, which are commercially available.

Isomerization of Azobenzene in Aqueous Dendrimer Solutions. A solution of *trans*-azobenzene (2 mg) and $\mathbf{C_{\mathit{n}}G3}$ dendrimer (50 μM) in THF (2 mL) was evaporated. The resulting residue was admixed aq NaOH solution (10 mL, pH >10), stirred for 12 h in the dark at ambient temperatur, and filtered (0.45 μm). The filtrate was irradiated for 20 min by using a 200 W high-pressure mercury lamp with a 360 nm cutoff filter, by which time *trans*- and *cis*-isomers reached a photostationary-state (PSS) equilibrium. *Cis* → *trans* isomerization was followed by time course increase in the absorption at 321 nm, under dark conditions and at varying temperatures. The rate of thermal *cis* → *trans* reaction was calculated by plotting changes of absorbance, namely, $\ln [A_\infty - A_o/(A_\infty - A_t)]$, where A_∞ is the absorbance at the end of the reaction, A_o, the absorption at PSS; A_t, the absorption at the particular time, vs time, and by determining the slope of the corresponding straight line.

The energy of activation and thermodynamic parameters were derived by performing *cis* → *trans* isomerization kinetics at varying temperatures and fitting the data in the Arrhenius and Eyring equations as follows:

$$\ln k = \ln \mathrm{A} - E_{\mathrm{a}}/RT$$

$$\ln(k/T) = -\Delta H^{\ddagger}/RT + \ln(k'/h) + \Delta S^{\ddagger}/R$$

where k is the rate constant; T, temperature; $\Delta H^{\ddagger}$, enthalpy of activation; $\Delta S^{\ddagger}$, entropy of activation; R, molar gas constant; k', Boltzmann constant; h, Planck constant.

The activation free energy ($\Delta G^{\ddagger}$ was obtained by following equation

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

AUTHOR INFORMATION

Corresponding Author

*E-mail: (N.J.) jayaraman@orgchem.iisc.ernet.in, (V.R.) vramamurthy@mail.as.miami.edu.

Notes

The authors declare no competing financial interest.

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