

quartet at δ 4.09,¹⁹ indicating the magnetic equivalence of these two protons. The two methylene protons next to the carboxylate group in compound IV were also found to be magnetically nonequivalent in their appearance as two multiplets at δ 3.98 and 3.87. As a result of irradiation at δ 1.62 (identified for $\text{COOCH}_A\text{H}_B\text{CH}_2\text{CH}_2$), these two multiplets were found to collapse into two doublets with $J_{AB} = 10.5$ Hz, resembling the two at δ 5.33 and 5.56 observed in compound III. In short, pyrenyl groups attached to bicyclooctene ring in an all-exo configuration are subject to hindered rotation. In contrast, as pyrenyl rings are attached to cyclohexane in a 1-axial 2-equatorial configuration, they seem to be capable of free rotation. These same observations were also made in compounds V and VI, in which carbazolyl groups are connected to the two ring systems via a propylene spacer. Specifically, in compound V the methylene protons next to the carboxylate group yield two triplets at δ 4.15 and 4.20 with integrations in the ratio 2:1, signifying a 2-equatorial 1-axial configuration. In compound VI with an all-exo configuration, the same methylene protons appear as two overlapping multiplets centered at δ 4.03, instead of a triplet as expected on the basis of a neighboring methylene group at δ 2.12 (identified for $\text{COOCH}_A\text{H}_B\text{CH}_2\text{CH}_2$). Upon irradiation at δ 2.12, the multiplet at δ 4.03 was found to collapse into two doublets with $J_{AB} = 11.1$ Hz. Thus, the ability of the pendant rings to undergo free rotation is determined primarily by the stereochemistry imposed by the central core.

Let us look into the implication of the rotation of pendant pyrenyl and carbazolyl groups, as revealed by proton NMR spectroscopy, on excimer formation as detected by fluorescence spectroscopy. Shown in Figure 4 are the fluorescence spectra, with an excitation wavelength, λ_{ex} , at 344 nm, of 1-pyrenylmethanol as well as compounds I–IV and VII in methylene chloride at concentrations ranging from 5×10^{-6} to 1×10^{-4} M (in pyrenyl groups). The spectrum of 1-pyrenylmethanol is attributed to emission from monomeric pyrene,²⁰ indicating the absence of chromophoric interaction leading to excimer formation. On the other hand, there is an increasing trend in excimer formation between pendant pyrenyl groups as they are attached to the adamantane, cyclohexane, and bicyclooctene cores as evidenced by the intensity of the broad peak centered at 475 nm²⁰ relative to that of monomer emission. Thus, the extent of excimer formation does not seem to simply correlate with the restricted rotation of pyrenyl groups detected in the ground state. The facts that no excimer emission was observed in 1-pyrenylmethanol and that the emission spectra for all pyrene-containing compounds are independent of concentration suggest the intramolecular nature of excimer formation in compounds I–IV and VII. In contrast, pendant carbazolyl groups exhibit a different fluorescence behavior. Shown in Figure 5 are the fluorescence spectra, with a λ_{ex} of 294 nm, of compounds V and VI in addition to 3-(*N*-carbazolyl)propanol and *N*-ethylcarbazole in methylene chloride at concentrations ranging from 1×10^{-6} to 1×10^{-3} M (in carbazolyl groups) at room temperature. Practically the same set of spectra was obtained with a λ_{ex} of 320 nm. The relative intensity of the two emission

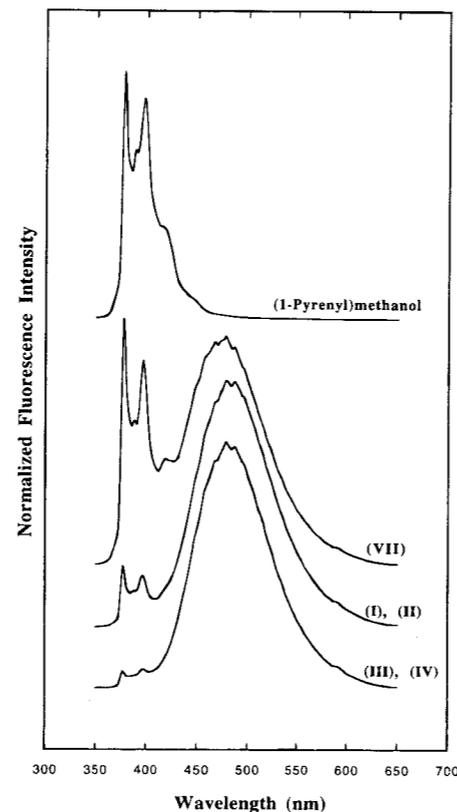


Figure 4. Fluorescence spectra (with $\lambda_{\text{ex}} = 344$ nm) of 1-pyrenylmethanol, compounds I–IV and VII in methylene chloride at room temperature and at concentrations from 5×10^{-6} to 1×10^{-4} M in pyrenyl groups.

peaks is determined by a significant reabsorption of the emission at 353 nm relative to that at 368 nm, as pointed out by Yokoyama et al.²¹ Specifically, the peak at 353 nm diminishes to a shoulder of the peak at 368 nm at a concentration of 10^{-3} M presumably because of the overwhelming reabsorption at the shorter wavelength. Moreover, the ratio of the intensities of these two emission peaks, I_{368}/I_{353} , was found to decrease to an asymptotic value of 0.80 as expected in the limit of high dilution. The peaks at 353 and 368 nm can be attributed to emission from monomeric carbazole, as concluded by both the steady-state and dynamic fluorescence experiments involving *N*-ethylcarbazole and *trans*-1,2-dicarbazolylcyclobutane in DMF at 10^{-4} M²² and *N*-ethylcarbazole in methylene chloride at the same concentration,²³ all performed at room temperature. On the contrary, intramolecular excimer formation was demonstrated for both 1,3-bis(*N*-carbazolyl)propane and poly(*N*-vinylcarbazole) under the same conditions.^{21–24} Therefore, while the extent of intramolecular excimer formation is determined, to some extent, by the stereochemistry imposed by the central core in pyrene-containing compounds, neither intramolecular nor intermolecular excimer formation is allowed in carbazole-containing counterparts. Apparently, a more stringent stereochemical requirement will have to be met for excimer formation involving pendant carbazolyl groups.

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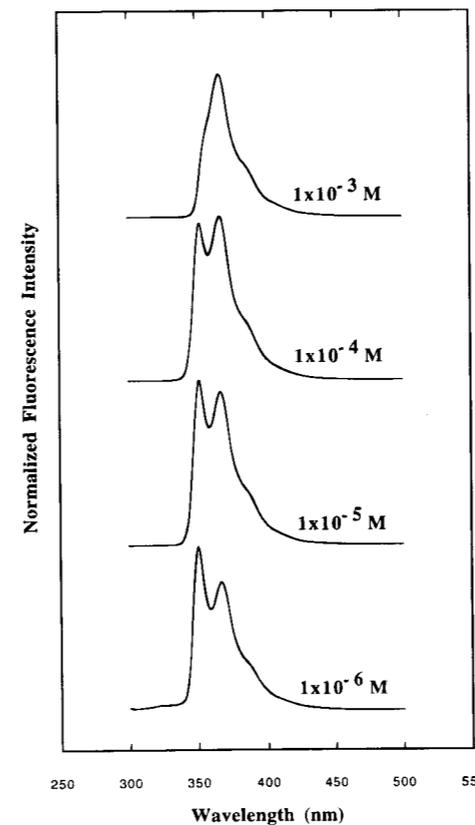


Figure 5. Fluorescence spectra (with $\lambda_{\text{ex}} = 294$ and 320 nm) of 3-(*N*-carbazolyl)propanol, *N*-ethylcarbazole, and compounds V and VI in methylene chloride at room temperature and at concentrations from 1×10^{-6} to 1×10^{-3} M in carbazolyl groups.

As indicated earlier, one of the objectives of this series of studies is to enable functional organic materials, such as highly crystalline pyrene ($T_m = 154$ °C) and carbazole ($T_m = 248$ °C), to form morphologically stable glassy films with a glass transition temperature, T_g , above the ambient. To assess the role played by the volume-excluding central core, the DSC thermograms of all three precursors to compounds I–VII, i.e. 1-pyrenylmethanol, 3-(*N*-carbazolyl)propanol, and 4-(1-pyrenyl)butanol were collected from the heating scans at 20 °C/min of the quenched samples (i.e., preheating the samples to 200 °C followed by quenching at -200 °C/min to -60 °C). Several observations were made of the DSC thermograms: (i) Quenched 1-pyrenylmethanol is crystalline with a T_m at 126 °C; (ii) quenched 3-(*N*-carbazolyl)propanol appears to be partially glassy and the amorphous melt undergoes recrystallization followed by a T_m at 104 °C; and (iii) quenched 4-(1-pyrenyl)butanol is glassy with a T_g at -12 °C and shows no evidence of recrystallization upon further heating. The DSC thermograms were then collected for compounds I–VII consisting of the three precursors attached to cyclohexane, bicyclooctene, and adamantane as the volume-excluding core. It was found that cooling of the melt of all seven model compounds resulted in vitrification without residual crystallinity. The resultant glass was then heated across T_g and up to 200 °C at a series of heating rates ranging from 0.2 to 20 °C/min in the DSC experiment as a way to assess the stability of the melt against thermally activated recrystallization. As shown in Figure 6, cyclohexane, bicyclooctene, and adamantane rings as central cores were

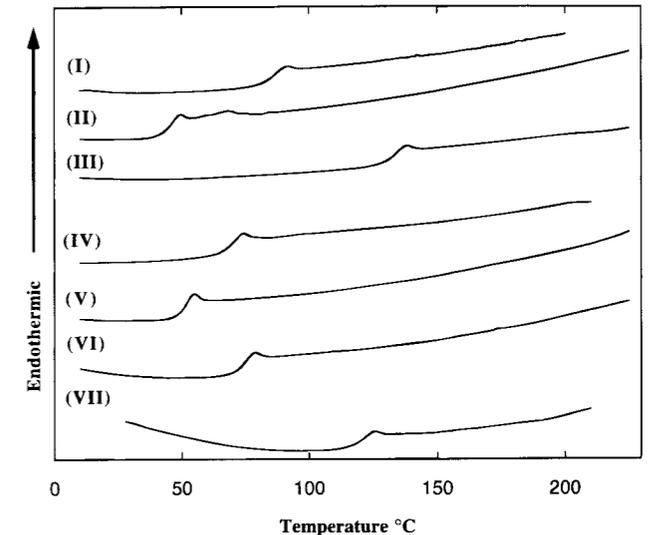


Figure 6. DSC heating scans (at 20 °C/min) of samples of compounds I–VII preheated to 200 °C followed by quenching at -200 °C/min. to -60 °C; same qualitative features were observed at a heating rate down to 0.2 °C/min.

found to promote both vitrification and morphological stability of all seven model compounds in comparison to their three precursors when subjected to identical thermal treatment. The observed values for T_g and ΔC_p , change of heat capacity across T_g , are included in Figure 1 in which chemical structures are depicted. A comparison of the thermal transition data of compounds I, III, and VII reveals that bicyclooctene gives rise to the highest T_g followed by adamantane and cyclohexane but with almost the same ΔC_p values, 0.24–0.28 J/g °C. It is also clear that a shorter spacer is capable of producing a significant elevation in T_g . An attempt was also made to quantitatively assess morphological stability through the measurement of linear spherulitic growth rate as a function of temperature, as was accomplished previously.¹⁸ However, no observable growth rate resulted from this effort, a further indication of the stability of the melt of these materials against thermally activated crystallization.

IV. Summary

Novel organic materials were synthesized by attaching pyrenyl and carbazolyl groups to cyclohexane with a 1-axial 2-equatorial configuration, bicyclooctene with an all-exo configuration, and adamantane. The NMR spectral data suggest that the rotation of the substituent groups on the bicyclic ring is restricted presumably because of steric hindrance. In contrast, free rotation seems to prevail in the case of cyclohexane and adamantane as central cores. Fluorescence spectra in methylene chloride solutions were collected to investigate the tendency for excimer formation as affected by the nature of the chromophore and by the structure of the central core. In the case of pyrene-containing compounds, the extent of intramolecular excimer formation was found to follow the order bicyclooctene > cyclohexane > adamantane with no evidence for intermolecular excimer formation up to a concentration of 10^{-4} M. In carbazole-containing compounds, no evidence was found for excimer formation presumably because of the more stringent requirements of interchromophoric distance and orientation, that were met in poly(*N*-vinylcarbazole) and 1,3-bis(*N*-carbazolyl)pro-

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