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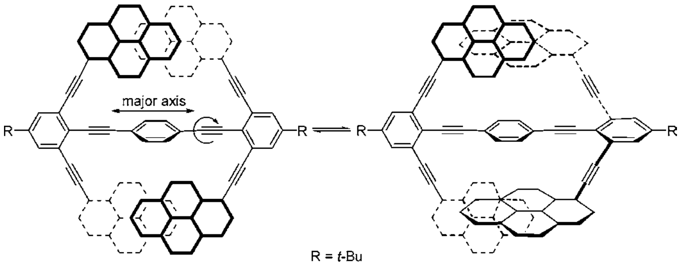
Intramolecular π-Stacking Interaction in a Rigid Molecular Hinge Substituted with 1-(Pyrenylethynyl) Units[‡]

Ritesh Nandy,[†] Mahadevan Subramoni,[§] Babu Varghese,[§] and Sethuraman Sankararaman*,[†]

Department of Chemistry and Sophisticated Analytical Instrument Facility, Indian Institute of Technology Madras, Chennai 600036, India

sanka@iitm.ac.in

Received October 19, 2006



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Synthesis of a tetrakis(1-pyrenylethynyl)-substituted rigid hinge-like molecule (**1**) is described. The intramolecular π-stacking interaction of the pyrene units is studied by ^{1}H NMR and fluorescence spectroscopy. Due to intramolecular π-stacking interactions, chemical shifts of the pyrene protons in **1** are highly shielded in the NMR spectrum. Fluorescence from the static excimer state is observed due to π-stacking interactions among the pyrene units in the ground state of **1**. Based on the spectroscopic evidence, conformations and dynamics of **1**, arising from the hindered rotation of the major axis, are proposed.

Introduction

Among weak molecular interactions, the π−π interaction is very important. In biomolecules, π-stacking interactions among aromatic units play a major role in DNA stacking,[1] protein folding,[2] and molecular recognition.[3] In chemistry, π-stacking interactions of aromatic π systems influence the supramolecular assembly of molecules in solution and solids[4] and at the interfaces.[5] Electronic properties of organic molecules are affected by π-stacking interactions, resulting in efficient intermolecular electron transfer, improved electrical conductivity, and emission at longer wavelengths.[6] π-Stacking interactions of aromatic pendent units attached to a polymer backbone have been studied in many systems.[7] Supramolecular aggregation through intermolecular π−π interactions is well-known in many polycyclic aromatic hydrocarbons and superacenes, resulting in

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[‡] Dedicated to Professor Alfred Fischer on the occasion of his 75th birthday.

[*] To whom correspondence should be addressed. Phone: +91 44 2257 4210. Fax: +91 44 2257 0545.

[†] Department of Chemistry.

[§] Sophisticated Analytical Instrument Facility.

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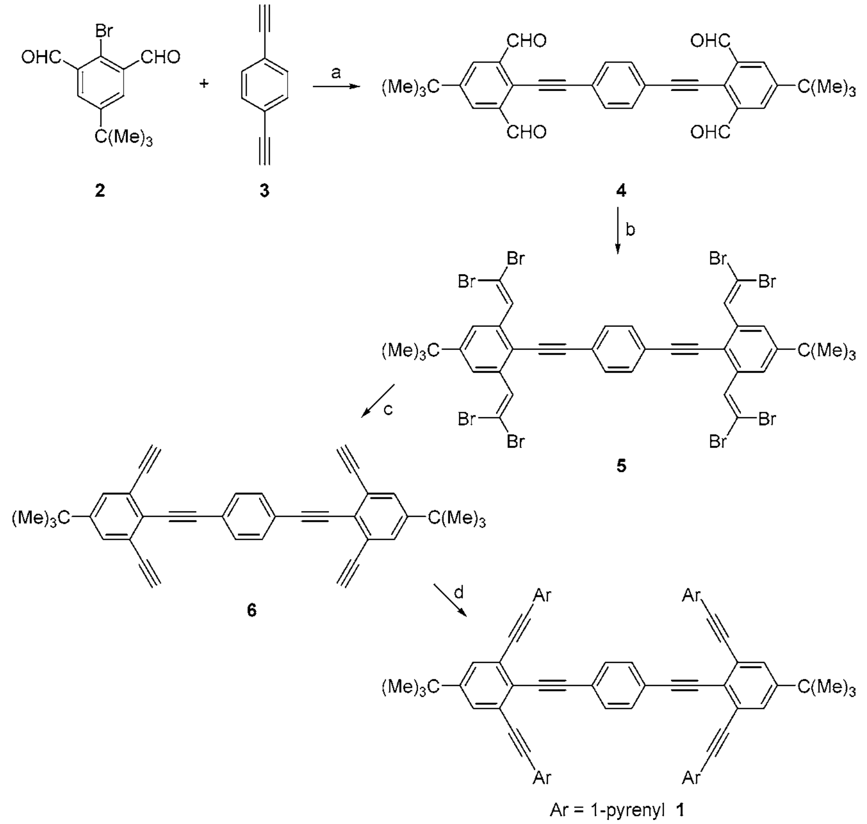
10.1021/jo062173y CCC: $37.00

SCHEME 1. Synthesis of 1[a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, 60 °C, 2.5 h, 63%; (b) CBr_4, PPh_3, CH_2Cl_2, rt, 16 h, 95%; (c) LDA, THF, −78 °C, 20 min, 75%; (d) 1-iodopyrene, $Pd(PPh_3)_4$, CuI, Et_3N, THF, 48 h, 25%.

discotic liquid crystalline properties in certain systems.[8] Many theoretical studies have been undertaken to understand the nature of orbital interactions, stabilization arising from weak $\pi-\pi$ interactions, and the potential energy surface of such systems.[9]

Pyrene is a prototypical polycyclic aromatic fluorescent molecule. Emission of excited-state pyrene from the monomer and excimer states is fairly well understood.[10] π-Stacking interactions between two pyrene units either in the ground state or in the excited state result in the excimer emission upon photoexcitation. Intramolecular interaction of two pyrene units in the ground state through $\pi-\pi$ stacking has been observed when pyrene units are attached to a conformationally rigid molecular framework.[11] In molecules with conformational flexibility, metal-ion-mediated conformational changes have resulted in bringing two pyrene units close to undergo a π-stacking interaction.[12] Such molecules find application in fluorescence-based sensors. Recently, we have reported a novel pyrene octaaldehyde that exhibited interesting cooperative $\pi-\pi$ and C−H···O interactions, resulting in aggregation in the solution and solid states.[13] Herein, we report the synthesis of a rigid acetylenic molecular hinge to which four 1-pyrenylethyne units are attached. The intramolecular π-stacking interaction and hindered rotation along the major axis are studied by variable-temperature fluorescence and ^{1}H NMR spectroscopy.

Results and Discussion

Synthesis. We have designed and synthesized a molecular hinge (**1**) that has a rigid rod-like central unit to which four 1-pyrenylethynyl units are attached. It was synthesized in four steps as shown in Scheme 1. The 2-fold Sonogashira coupling of dialdehyde **2** and 1,4-diethynylbenzene (**3**) gave tetraaldehyde **4** in 63% yield. The ^{1}H NMR spectrum of tetraaldehyde **4** showed four singlets in the integration ratio of 1:1:1:4.5, consistent with its structure. Treatment of **4** with CBr_4 and Ph_3P yielded octabromide **5** in 95% yield as a pale-orange crystalline solid. It was characterized by various spectroscopic methods, and the structure was confirmed by single-crystal X-ray crystal-

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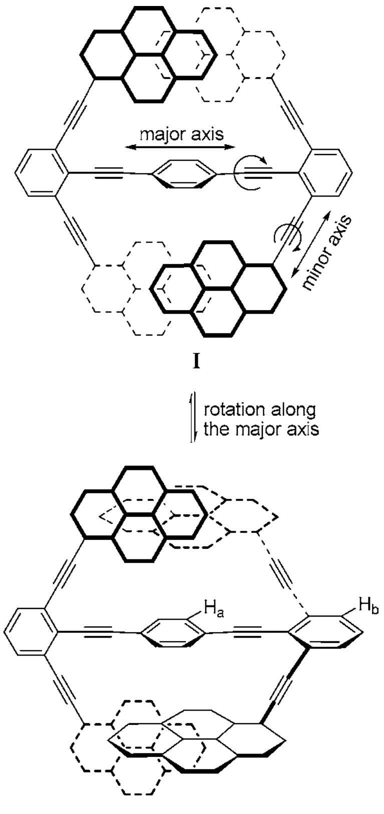
SCHEME 2. Dynamics of 1 Leading to π Stacking and Its Disruption at Higher Temperatures (*tert*-butyl groups are not shown)



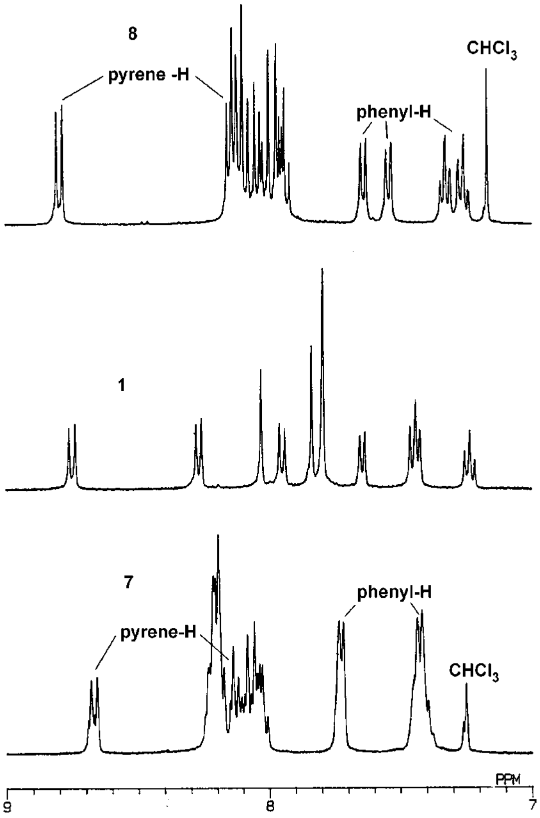


FIGURE 1. ^{1}H NMR spectra of **1** in $CDCl_2CDCl_2$, **7**, and **8** (in $CDCl_3$) at 25 °C.

lographic data (Supporting Information). In the ^{1}H NMR spectrum of **5**, the vinylic protons appeared as a singlet at δ 7.77 ppm. Reaction of octabromide **5** with excess LDA yielded tetrayne **6** in 75% yield as a colorless solid. The ^{1}H NMR spectrum of tetrayne **6** showed four singlets in the integration ratio of 1:1:1:4.5, and the acetylenic protons appeared as a sharp singlet at δ 3.37 ppm, confirming the smooth conversion of **5** to **6**. The target molecule **1** was obtained in 25% yield by the 4-fold Sonogashira coupling of tetrayne **6** with 1-iodopyrene. The tetrakis(1-pyrenylethynyl) derivative **1** was obtained as a bright-yellow fluorescent solid. From the ^{1}H NMR spectral integration of **1**, it is evident that the relative ratio of the two different types of phenyl protons (H_a and H_b) (Scheme 2) and the pyrene protons is 1:1:9, confirming the presence of four pyrene units in the molecule. The MALDI−TOF MS of **1** confirmed its molecular weight.

^{1}H NMR Spectrum of 1. The ^{1}H NMR spectrum of **1** recorded in 1,1,2,2-tetrachloroethane-d_2 at 25 °C is shown in Figure 1. For comparison, the ^{1}H NMR spectra of 1-(phenylethynyl)pyrene (**7**) and 1-(2-ethynylphenylethynylpyrene) (**8**) recorded in $CDCl_3$ are also shown. The protons on the phenyl rings (H_a and H_b) (Scheme 2) in **1** appeared as two singlets of equal intensity at δ 8.01 and 7.86 ppm, respectively. The signals due to the protons on the pyrene rings in **1** are very well resolved in comparison to that in **7** and **8**. Assignment of the individual proton resonance in **1** is based on the ^{1}H−^{1}H COSY spectrum, which established the coupling partners. It is also evident that, for all of the protons in the four pyrene rings in **1**, there is only one set of signals observed in the spectrum. This is due to the highly symmetrical structure of **1** in which the proton of a particular position in each of the pyrene unit is under a chemically identical environment. The resolution of the signals of various pyrene protons of **1** in comparison to those of **7** and **8** is due to a π-stacking interaction and the anisotropic effect arising from the ring current of the pyrene rings. In the absence of any strong electronic effects due to functional groups, it is not possible to explain the spread of the aromatic proton signals in **1**. The spread of the chemical shifts to give a near first-order spectrum for all nine protons of the pyrene ring can only be due to the π-stacking interactions of pyrene rings in the ground state. Otherwise, polycyclic aromatic hydrocarbons generally show complex second-order multiplets that are poorly resolved (**7** and **8** in Figure 1). Moreover, the chemical shifts of the pyrene protons in **1** are relatively more shielded (7.2 to 8.7 ppm) compared to that in other ethynyl-substituted pyrene derivatives (typically 8.0 to 8.5 ppm). It is well-established that π-stacking interactions between aromatic rings result in the shielding of the protons due to the anisotropy of the ring current effect.[13,14] For example, the pyrene protons of [2,2]-2,7-pyrenophane are more shielded than that of 2,7-dimethylpyrene.[15] In the present case, π-stacking interactions of two pyrene rings on either side of the rigid hinge are not exactly parallel-superimposed (A in Figure 2), it is rather a parallel-displaced type of π stacking. With respect to the pyrene rings, it is the lengthwise displacement (C in Figure 2) which puts the H-7 proton of one pyrene

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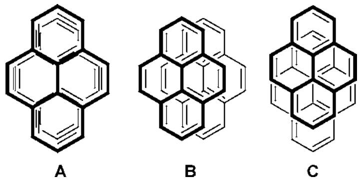

FIGURE 2. Various modes of π-stacking interactions between two pyrene units. (A) Parallel-superimposed. (B) Parallel-displaced breadthwise. (C) Parallel-displaced lengthwise.[16]

ring on the shielding zone of the ring current of the other pyrene ring.[16] The chemical shift of proton H-7 is unusually low, appearing at δ 7.24 ppm. Assignment of this signal at δ 7.24 ppm to proton H-7 is straightforward because H-7 is the only proton that has two ortho protons (H-6 and H-8) which couple and, hence, a triplet signal ($J = 7.6$ Hz). The most deshielded signal is a doublet at δ 8.75, and it corresponds to H-10. Typically, in ethynyl-substituted pyrene derivatives, proton H-10 is highly deshielded, and it appears at δ 8.8−9.0 ppm due to the anisotropic effect of the ethynyl group in the peri position.[17] The H-10 in **1** is located in the deshielding zone of the two ethynyl units. Due to the π-stacking interactions, the H-10 proton is relatively more shielded in **1** than it is in ethynylpyrene derivatives such as **7** and **8** in which the π-stacking interaction is absent (Figure 1).

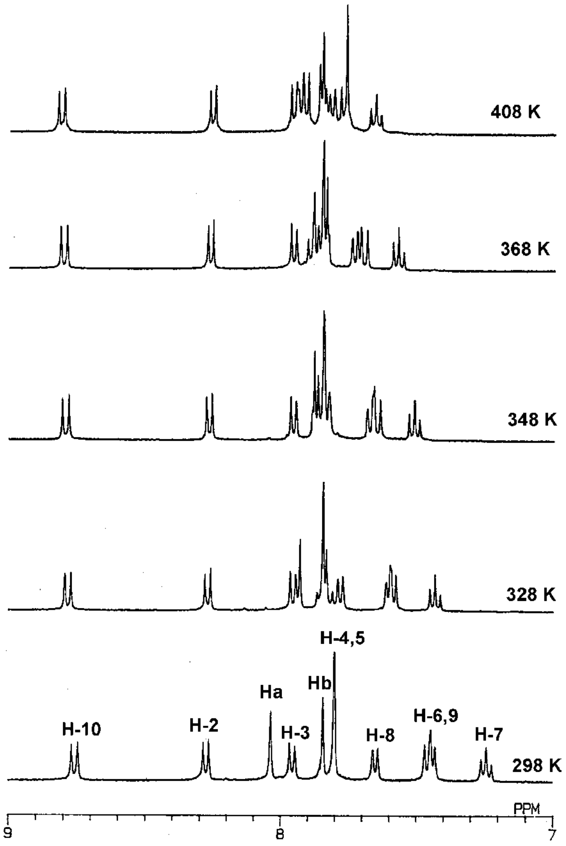

FIGURE 3. Variable temperature ^{1}H NMR spectra of **1** in $CDCl_2$-$CDCl_2$.

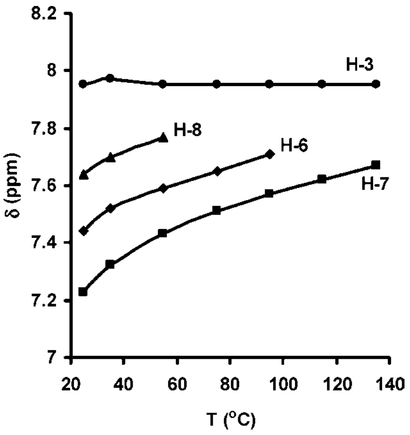

FIGURE 4. Effect of temperature on the chemical shift of various protons on the pyrene ring in **1**.

Variable-Temperature ^{1}H NMR Spectral Studies on 1. The effect of temperature on the chemical shift of various protons in **1** was investigated in the temperature range of 25 to 135 °C (Figure 3). With increasing temperature, the chemical shift of the protons (H_b) on the phenyl rings bearing the pyrene substituents was unaffected. However. protons (H_a) on the phenyl ring at the core of the molecule were gradually shifted to a lower δ value, from 8.03 ppm at 25 °C to 7.76 ppm at 135 °C. The H-2 and H-3 protons on the pyrene rings were also unaffected by temperature. However, there was a significant increase in the chemical shifts of the H-6, H-7, and H-8 protons with increasing temperature (Figure 4). There was a slight increase in the chemical shift of H-10 from 8.75 ppm at 25 °C to 8.81 ppm at 135 °C. π Stacking, being a weak interaction, can be broken at higher temperatures.[18] A rotation along the major axis can disrupt the π-stacking interaction in **1**, and this process is facilitated with increasing temperature. During the rotation along the major axis, the interplanar distances between the pyrene units become longer, resulting in varying degrees of the π-stacking interaction. As a result, the protons on the pyrene ring are gradually deshielded in going from conformer I to conformer II (Scheme 2). Conformer II is one extreme case where the pyrene rings are farthest away from each other. Further rotation along the major axis will bring the pyrene closer. Therefore, along the major axis, the molecule can only undergo an oscillatory motion and not a full rotation. In other words, there is a restricted rotation of the major acetylenic axis in **1** due to stabilizing π-stacking interactions between the pyrene units at room temperature. The pyrene units are interlocked due to π-stacking interactions. Earlier examples of hindered rotation of the triple bond of diphenylacetylene derivatives deal with repulsive steric interactions of bulky substituents present in the ortho positions of the aromatic ring.[19] Among the various protons, the ones at the core of the ring current effect will be relatively more deshielded (H-6, H-7, and H-8) as compared to the other protons (H-2 and H-3) which are located outside of the ring current effect of the pyrene rings. The experimental

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(16) Intermolecular $\pi-\pi$ interactions in benzene and naphthalene can occur through a T-shaped geometry. Calculations show that the minimum energy configuration is a T-shape. However, in polycyclic aromatic hydrocarbons such as pyrene and coronene and porphyrins, it is the displaced parallel stacking that is observed in the solid state. In such systems, the T-shaped geometry does not contribute to the π-stacking interactions. See refs 3a and 9c. See also: Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: Amsterdam, 1989; pp 92−96.

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observations described support this hypothesis. At room temperature, free rotation of the *p*-phenylene ring at the core of the molecule is perhaps not possible due to steric hindrance. Nevertheless, a sharp singlet is observed for all four protons (H_a) at 8.03 ppm at 25 °C. Upon increasing the temperature, the signal gradually shifted to lower δ values (7.76 ppm at 135 °C). This observation suggests that the *p*-phenylene ring at the core is perpendicular to the end phenyl rings at 25 °C, in the sterically least-hindered conformation. With increasing temperature, free rotation of the *p*-phenylene ring along the major axis is made possible, and as a result, the protons on this ring experience the ring current effect of the pyrene rings, causing the shielding of the H_a protons. From the detailed analysis of the ^{1}H NMR spectrum of **1** and its changes with temperature, we conclude that the molecule (**1**) exists in conformation I (Scheme 2) at room temperature and lower temperatures. Conformer I is stabilized by the π-stacking interactions between the pyrene rings. At higher temperatures, partial rotation along the major axis, as well as free rotation of the core *p*-phenylene ring, is possible, resulting in a change of conformation to II; perhaps a rapid equilibrium exsits at 135 °C, the highest temperature reached in this study. The spectrum at 135 °C resembles that of **7** and **8** in the aromatic region for the pyrene protons, suggesting that the π stacking is disrupted at higher temperatures. Although rotation along the minor axis can also disrupt the π stacking, such a process does not appear to be a major one because only one set of signals is observed for all of the pyrene protons, even at higher temperatures. Thus, the overall molecular symmetry must be retained. Moreover, the fact that the H_b protons are relatively insensitive to temperature supports this claim.

Absorption and Emission Spectra of 1. The pyrene chromophore is highly fluorescent. The fluorescence emission from the monomer and excimer states of pyrene is significantly different. Emission from the monomer state shows a vibrational fine structure and occurs at shorter wavelengths (λ_{em} 380 nm) in comparison to the broad, featureless emission of the excimer state that occurs at longer wavelengths (λ_{em} 480 nm).[20] In nonpolar solvents such as CH_2Cl_2 and cyclohexane, compound **1** showed several absorption bands with high extinction coefficients in the region of 200−410 nm (Figure 5). For comparison, 1-(5-*tert*-butyl-2-ethynylphenylethynyl)pyrene (**9**) is chosen as a model compound, and its absorption spectrum is also shown (C, Figure 5). It is evident from Figure 5 that the band intensities (and hence the extinction coefficients) of **1** are approximately four times that of the model compound **9** under identical concentrations. It is also evident that the absorption bands of **1** are broader and more red shifted by 14 nm than that of **9**, indicating the presence of π-stacking interactions in **1**.[15] In fact, the absorption spectrum of **1** corresponds to the π-stacked pyrene dimer chromophore rather than a pyrene monomer chromophore.

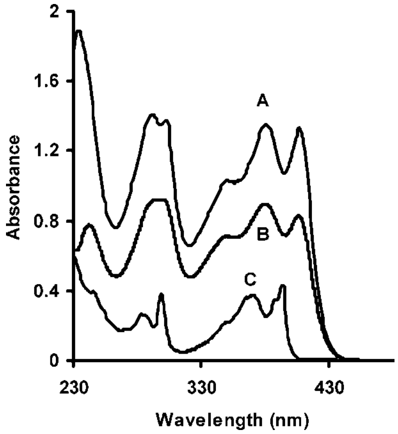

FIGURE 5. (A) UV−vis spectrum of **1** in CH_2Cl_2 (1×10^{-5} M). (B) Excitation spectrum in CH_2Cl_2 ($\lambda_{em} = 463$ nm, the *y*-axis in arbitrary scale). The spectrum of **9** (C) (1×10^{-5} M) is shown for comparison.

The excitation spectrum of **1** is nearly identical to that of its absorption spectrum in CH_2Cl_2. The fluorescence emission in these two solvents was broad and devoid of any vibrational fine structure. The fluorescence emission was independent of the wavelength of excitation in both of these solvents. The broad, featureless emission bands at λ_{max} 460 nm in CH_2Cl_2 and at 485 nm in cyclohexane correspond to emission from the excimer state. The monomer emission of pyrene and its derivatives invariably shows vibrational fine structure.[10,12] The fluorescence spectrum of the model compound (**9**) in which the π-stacking interaction is absent shows vibrational fine structure, and its emission maxima are 400 and 421 nm in cyclohexane. A large Stokes shift of 55−77 nm for **1** is consistent with the emission being from the excimer state. Alternatively, the observed red shift of the emission spectrum of **1** and its broad, featureless nature compared to that of the model system **9** could be due to the extensive through-bond π conjugation of the four pyrene units in the molecule and not due to through-space $\pi-\pi$ interactions. However, this explanation can be ruled out because the ^{1}H NMR spectrum of **1** very clearly indicates a $\pi-\pi$-stacking interaction in the ground state itself (vide supra). Otherwise, the spread of the NMR signals, the unusual shielding of H-7, and the observed gradual deshielding of H-6, H-7, and H-8 with increasing temperature cannot be explained satisfactorily. The Stokes shift in **1** is smaller than that of the pyrene excimer emission (100 nm). The emission maximum (and hence the Stokes shift) will depend on the extent of the π-stacking interaction. In case of pure pyrene, the π-stacking interaction is of the type A (Figure 2). However, in a constrained system such as **1**, type A π stacking is not possible. The excimer emission arises from type C π stacking in **1**, and hence, the excimer emission maximum is blue shifted compared to that of the pure pyrene excimer emission. An excimer emission maximum in the range of 460−480 nm is consistent with earlier reports for various pyrene derivatives.[12] In compound **1**, an excimer emission arises due to the intramolecular π-stacking interactions of the pyrene rings in the ground state. Such an excimer is termed as a static excimer as opposed to a dynamic excimer, which is formed by the diffusion of an excited-state molecule and a ground-state molecule.[21] The fluorescence emission maximum in CH_2Cl_2 (λ_{max} 460 nm) was invariant with the concentration of **1** in the range of $10^{-5}-10^{-9}$ M, indicating that the emission is arising from a static excimer due to the intramolecular π stacking and is not arising from a dynamic

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(19) For hindered rotation of a triple bond, see: (a) Toyota, S.; Yamamori, T.; Makino, T. *Tetrahedron* **2001**, *57*, 3521−3528. (b) Toyota, S.; Makino, T. *Tetrahedron Lett.* **2003**, *44*, 7775−7778. (c) Toyota, S.; Iida, T.; Kunizane, C.; Tanifuji, N.; Yoshida, Y. *Org. Biomol. Chem.* **2003**, *1*, 2298−2302. (d) Miljanic, O. S.; Holmes, D.; Vollhardt, K. P. C. *Org. Lett.* **2005**, *7*, 4001−4004. (e) Miljanic, O. S.; Han, S.; Holmes, D.; Schaller, G. R.; Vollhardt, K. P. C. *Chem. Commun.* **2005**, 2606−2608.

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(21) (a) Choi, J. K.; Kim, S. H.; Yoon, J.; Lee, K.-H.; Bartsch, R. A.; Kim, J. S. *J. Org. Chem.* **2006**, *71*, 8011−8015. (b) Jun, E. J.; Won, H. N.; Kim, J. S.; Lee, K.-H.; Yoon, J. *Tetrahedron Lett.* **2006**, *47*, 4577−4580.

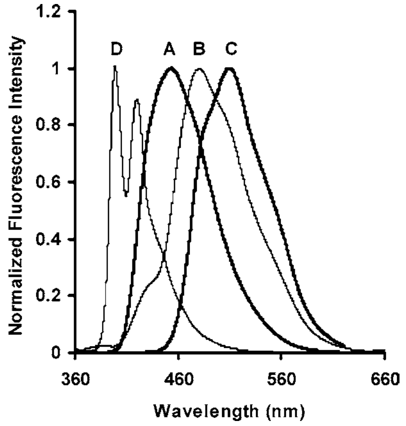

FIGURE 6. Fluorescence spectra of **1** (1×10^{-5} M, $\lambda_{ex} = 353$ nm) in cyclohexane (A), CH_2Cl_2 (B), and the solid state (C) ($\lambda_{ex} = 347$ nm). The fluorescence spectrum of **9** in cyclohexane (D) (1×10^{-5} M, $\lambda_{ex} = 367$ nm) is shown for comparison.

excimer due to intermolecular π stacking. Similar behavior was observed in cyclohexane with respect to a change of concentration from 10^{-5} to 10^{-9} M. In view of the results obtained from the variable-temperature ^{1}H NMR of **1**, the effect of temperature on the fluorescence emission was investigated in the temperature range from −10 to +70 °C in $CHCl_2CHCl_2$. The shape of the emission band and the intensity of fluorescence emission did not change significantly with increasing temperature. However, there was a gradual shift of the emission maximum from 467 nm at −10 °C to 457 nm at +70 °C. The observed blue shift of the pyrene excimer emission with increasing temperature is an indication of the π stacking being disturbed at higher temperatures.[8b,22] The blue shift of the excimer band and the distinct absence of any band due to monomer emission up to +70 °C indicates that there is rapid conformational equilibrium between I and II (Scheme 2). It is concluded that, within this temperature range, there is no significant change in the π-stacking behavior of **1**, resulting in a very minimal change in the emission behavior. The quantum efficiency of fluorescence emission of **1** was 0.8 (±0.03), measured using 9,10-diphenylanthracene as a reference.[23] Compound **1** is fluorescent in the solid state as well (Figure 6, D). In the solid state, the emission spectrum was broad and devoid of fine structures. The excimer emission maximum in the solid state is 512 nm (Stokes shift of 104 nm), and the emission maximum is independent of the excitation wavelength. In the solid state, besides intramolecular π stacking of the pyrene units, it is also possible that extensive intermolecular π stacking exsits in **1**.

Conclusions

We have designed and synthesized a molecular hinge (**1**) with four 1-pyrenylethynyl groups attached to it. Evidence from ^{1}H NMR and fluorescence spectroscopic studies suggests that there is an intramolecular π-stacking interaction among the pyrenyl units in **1**. The π-stacking interaction can be disrupted at higher temperatures, as is evident from the observed changes in the chemical shift of the pyrene protons in **1**. A similar conclusion is arrived at based on the temperature-dependent fluorescence study of **1**. Both in solution as well as in the solid state, **1** exhibits an excimer-type broad fluorescence emission. On the basis of all of this spectroscopic evidence, we have suggested that **1** exists in conformation I. At higher temperatures, rotation along the major axis of the hinge results in a change of conformation to II, resulting in equilibration between these two conformations. All of the experimental evidence presented herein fits this model well. Since π-stacking architecture is emerging as a powerful method to produce functional organic molecules that find application in sensors, molecular electronics, and photonics, study of molecules such as **1** will help in understanding the nature of $\pi-\pi$ interactions.

Experimental Section

Tetraaldehyde 4. A Schlenk flask was charged with bromodialdehyde[24] **2** (0.83 g, 3.1 mmol), $Pd(PPh_3)Cl_2$ (0.056 g, 0.08 mmol), PPh_3 (0.042 g, 0.16 mmol), CuI (0.017 g, 0.16 mmol), and degassed Et_3N (20 mL). The mixture was stirred and heated to 60 °C. A solution of diyne **3** (0.2 g, 1.59 mmol) in THF (5 mL) was added dropwise. After an hour, a copious amount of precipitate was observed and stirring was continued for another 1.5 h. The reaction mixture was cooled to rt and filtered. The yellow precipitate was dissolved in CH_2Cl_2 (100 mL), and the solution was washed with 5% aqueous HCl. The organic layer was dried over Na_2SO_4, and solvent was removed under reduced pressure at rt. The crude product was purified by column chromatography on silica gel using an ethyl acetate−hexane mixture (15:85 v/v) to yield the tetraaldehyde (**4**) as a yellow solid (0.5 g, 63%): mp 310 °C dec; IR (KBr) 2211, 1687 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.66 (s, 4H), 8.18 (s, 4H), 7.58 (s, 4H), 1.33 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.6, 153.1, 136.5, 131.9, 129.9, 126.1, 125.8, 122.8, 101.5, 35.4, 31.0; MALDI−TOF MS *m/z* 475 (M + 1 − CO), 503 (M + 1), 976 (dimer − CO), 1004 (dimer); ESI Q−TOF MS *m/z* 502 (10), 503 (55), 504 (20); HRMS calcd for $C_{34}H_{31}O_4$ [M + H$^+$], 503.2222; found, 503.2222.

Octabromide 5. A Schlenk flask was charged with CBr_4 (1.05 g, 3.2 mmol), PPh_3 (0.84 g, 3.2 mmol), and Zn powder (0.21 g, 3.2 mmol), and the mixture was dissolved in CH_2Cl_2 (70 mL) and stirred at rt for 4 h. Tetraaldehyde **4** (0.10 g, 0.2 mmol) was added in one lot, and stirring was continued at rt for 16 h. The mixture was filtered, and solvent was removed under reduced pressure in the rotary evaporator to obtain the crude product as an orange solid. It was purified by column chromatography on silica gel using 30% CH_2Cl_2−hexane (vol %) to yield **5** as a pale-orange crystalline solid (0.22 g, 95%): mp 210−212 °C; IR (KBr) 2962, 2917, 2849, 1593, 846, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 4H), 7.77 (s, 4H), 7.56 (s, 4H), 1.35 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.2, 137.4, 135.9, 131.6, 125.6, 123.1, 118.8, 99.9, 91.9, 87.4, 35.2, 31.0. Anal. Calcd for $C_{38}H_{30}Br_8$: C, 40.54; H, 2.68. Found: C, 41.37; H, 2.91.

Tetrayne 6. (Caution: During the determination of the melting point of **6**, violent decomposition with the formation of black soot was observed at 153 °C. Care should be taken not to heat this compound in large amounts). To a solution of octabromide **5** (0.1 g, 0.09 mmol) in THF (20 mL) stirred at −78 °C was added a solution of LDA [freshly prepared from diisopropyl amine (0.18 mL, 1.3 mmol) and *n*-BuLi (0.61 mL of 1.4 M solution in hexane, 1.3 mmol) in THF (10 mL) at −78 °C]. The mixture was stirred for 20 min at −78 °C and then quenched by adding a degassed saturated NH_4Cl solution (20 mL). It was allowed to attain rt. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layer was dried over Na_2SO_4, and solvent was removed under reduced pressure in a rotary evaporator. The crude product thus obtained was purified

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[22] A similar blue shift of the pyrene excimer emission with increasing temperature has been reported earlier; see: (a) Lou, J.; Hatton, T. A.; Laibinis, P. E. *Anal. Chem.* **1997**, *69*, 1262−1264. (b) See also ref 8b.

[23] Hamal, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83−89.

[24] Narayanan, V.; Sankararaman, S.; Hopf, H. *Eur. J. Org. Chem.* **2005**, 2740−2746.

by column chromatography on silica gel using 2% ethyl acetate in hexane (vol %). The tetrayne **6** was obtained as a colorless solid (0.032 g, 75%): mp 153 °C (violent decomposition); IR (neat) 2213 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.57 (s, 4H), 7.55 (s, 4H), 3.37 (s, 4H), 1.32 (s, 18H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 151.3, 131.7, 130.2, 125.9, 124.7, 123.4, 96.7, 88.6, 82.2, 80.9, 34.7, 30.9. Anal. Calcd for $C_{38}H_{30}$: C, 93.79; H, 6.21. Found: C, 92.89; H, 6.00.[25]

Tetrapyrenyl Derivative 1. A Schlenk flask was charged with iodopyrene[7b] (0.32 g, 0.95 mmol), Pd(PPh$_3$)$_4$ (19 mg, 0.016 mmol), CuI (6 mg, 0.032 mmol), degassed Et$_3$N (10 mL), and THF (10 mL). The mixture was stirred at 55 °C for 10 min. A solution of tetrayne **6** (80 mg, 0.16 mmol) in THF (5 mL) was added dropwise for 45 min, and stirring was continued for 2 days. After cooling to rt, the mixture was filtered, and yellow solid was repeatedly washed with CH$_2$Cl$_2$. It was recrystallized from a hot 1,1,2,2-tetrachloroethane: Yield 53 mg (25%); mp 292 °C; IR (neat) 2195 cm^{-1}; UV−vis (CH$_2$Cl$_2$) (log ϵ) 232 (5.268), 290 (5.145), 301 (5.136), 347 (sh, 5.005), 378 (5.125), 405 nm (5.116); ^{1}H NMR (CDCl$_2$CDCl$_2$, 400 MHz, 25 °C) δ 8.75 (d, 4H, J = 8.8 Hz), 8.26 (d, 4H, J = 7.8 Hz), 8.03 (s, 4H), 7.95 (d, 4H, J = 8.3 Hz), 7.83 (s, 4H), 7.80 (s, 8H), 7.64 (d, 4H, J = 7.8 Hz), 7.44 (m, 8H), 7.23 (t, 4H, J = 7.8 Hz), 1.56 (s, 18H); ^{13}C NMR (CDCl$_2$CDCl$_2$, 100 MHz, 25 °C) δ 151.6, 133.0, 132.3, 131.7, 130.8, 130.6, 130.2, 129.8, 129.1, 128.7, 127.2, 127.0, 126.0, 125.9, 125.6, 124.8, 124.5, 124.3, 123.9, 119.5, 117.5, 97.2, 94.6, 93.6, 90.9, 35.4, 31.6; MALDI−TOF MS *m/z* calcd for $C_{102}H_{62}$, 1287; found, 1287. Anal. Calcd for $C_{102}H_{62}$: C, 95.15; H, 4.85. Found: C, 89.22; H, 4.46.[25]

Acknowledgment. We thank SAIF, IIT Madras for the spectral data; CSIR, New Delhi for financial support; Dr. M. Vairamani, IICT for MALDI−TOF MS of **1**; and Mr. G. Venkataramana for the ^{1}H NMR spectrum of **8** and the UV−vis spectrum of **9**. We are grateful to one of the reviewers for thought-provoking comments and the revisions suggested.

Supporting Information Available: ^{1}H NMR, electronic absorption and fluorescence spectroscopic data of **1**, crystallographic data of **5** in CIF format, ^{1}H and ^{13}C NMR spectra of **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) In spite of repeated purification by recrystallization, elemental analysis of compounds **6** and **1** always gave lower values for the carbon content, presumably due to incomplete combustion of these carbon-rich molecules. Formation of black soot during the violent decomposition of **6** was evident during its melting point determination.