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Conformational Isomers from Rotation of Diacetylenic Bond in an Ethynylpyrene-Substituted Molecular Hinge

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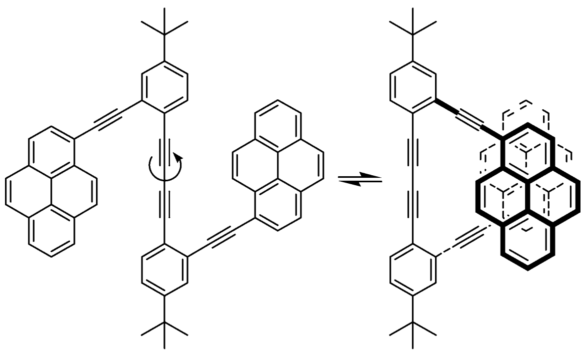
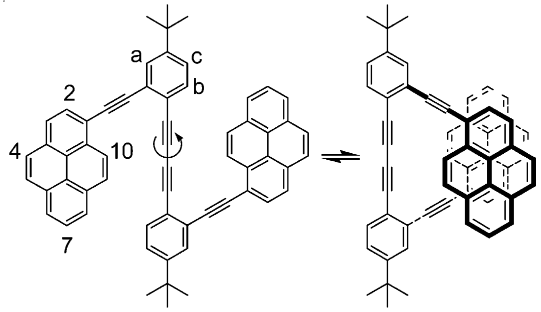


1a open conformer **1b** closed conformer

The first example of isolation and X-ray crystallographic structural characterization of two conformers arising from rotation along a diacetylenic bond is reported. In both the conformers extensive $\pi-\pi$ interactions are observed in the solid state. VT-NMR and fluorescence spectroscopic studies in solution suggest that the closed and open conformers are in equilibrium and that the closed conformer is the predominant species at room temperature.

SCHEME 1. Interconversion of Open (1a) and Closed (1b) Conformers by Rotation of the Diacetylenic Bond



1a open conformer **1b** closed conformer

Construction of molecular assemblies in the solid state through face-to-face π-stacking interaction of aromatic units is important in the field of organic molecular electronics and photonics.[1] Among the aromatics pyrene is capable of undergoing π-stacking interaction in the ground and excited states.[2] Some of the derivatives of pyrene have been shown to be potentially useful as molecular electronics and photonics materials.[3] Herein, we report the synthesis of a simple butadiynyl bridged molecular hinge (**1**) bearing pendent ethynylpyrene units. In **1**, rotation along the diacetylenic axis as indicated by the arrow should not have any barrier, and the open (**1a**) and closed forms (**1b**) are two extreme conformers arising from such a rotation. In the open form (**1a**), the two ethynylpyrene units are far away from each other, whereas in the closed conformation (**1b**) they can come in contact within the van der Waals distance (Scheme 1). Although entropic factor might favor the open form, the more organized closed form could derive stabilization from the π-stacking interaction between the two pyrene units. Although a very weak interaction ($<$2 kcal mol^{-1}), $\pi-\pi$ interaction could lead to the stabilization of certain molecular conformations. From a different perspective, **1** is useful for the understanding of the rotation of the triple bond. Restricted rotation of acetylenic bonds is important from the point of view of molecular chirality of exploded biphenyls. Earlier examples of restricted rotation of acetylenic bond in diphenylethyne derivatives deal with steric (*repulsive*) interactions among the bulky silyl and aryl substituents placed in the ortho positions of the phenyl groups. Vollhardt has reported hindered rotation in a exploded biphenyl bearing bulky dimethylthexylsilyl as the end groups.[4] Toyota has demonstrated hindered rotation of the acetylenic bond in the substituted derivatives bis(9-anthryl)ethyne and bis(9-triptycyl)ethyne.[5] Rotational barrier of 15−18 kcal mol^{-1} has been reported for the C(sp^3)−C(sp) bond. Moore has reported molecular turnstiles with freely rotating and conformationally locked spindles connected by acetylenic bonds.[6] The question of whether or not acetylenic bond rotation be restricted by weak *attractive forces* such as $\pi-\pi$ or hydrogen-bonding interactions remains to be

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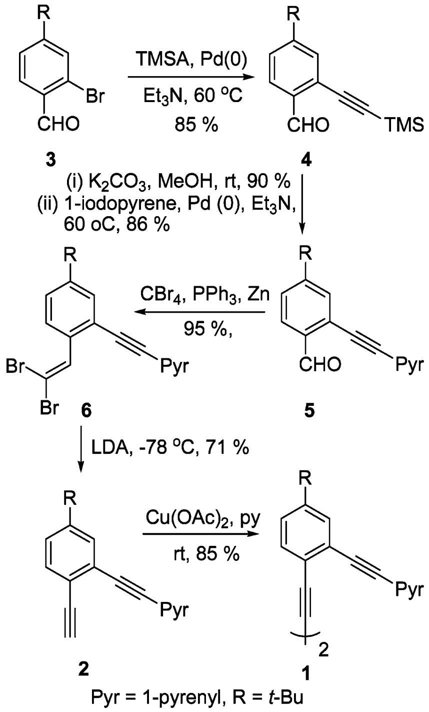
10.1021/jo7024724 CCC: $40.75

SCHEME 2. Synthesis of Target 1



addressed. Molecular hinges of the type **1** might be useful as a probe to investigate this interesting phenomenon. Recently, we have reported a tetrakis(ethynylpyrene)-substituted molecular hinge wherein the pyrene units are interlocked in $\pi-\pi$ interactions leading to restricted rotation of the central acetylenic molecular axis.[7]

Synthesis of 1. Target **1** was synthesized in six steps starting from 2-bromo-4-*tert*-butylbenzaldehyde (**3**) (Scheme 2). Sonogashira coupling of **3** with trimethylsilylacetylene gave **4**. Removal of the trimethylsilyl group from **4** followed by coupling with 1-iodopyrene resulted in the formation of **5**. Direct Sonogashira coupling of **3** with 1-ethynylpyrene gave **5** only in poor yield along with the oxidative dimer of 1-ethynylpyrene. Aldehyde **5** was converted to the corresponding dibromovinyl derivative **6**, which on treatment with LDA furnished the desired terminal acetylene precursor **2**. Oxidative dimerization of **2** yielded the target molecule **1** as a yellow crystalline solid (Scheme 2).

X-ray Crystallographic Studies. Crystallization of **1** from hexane yielded two types of crystals, colorless triclinic crystals corresponding to the open conformer (**1a**) and pale yellow orthorhombic crystals corresponding to the closed conformer (**1b**) (Figure 1). Crystals of **1a** were of good quality and suitable for single-crystal X-ray diffraction studies. Due to intermolecular π-stacking and C−H$\cdots\pi$ interactions, **1a** forms a one-dimensional chain in the crystal (Figure 2). Only one of the pyrene rings shows π-stacking interactions with a pyrene ring of the neighbor. The other pyrene ring shows only a C−H$\cdots\pi$ interaction. Crystallization of the closed conformer **1b** was very difficult. Crystals of **1b** were consistently of poor quality and small size.[8] Although the gross structure obtained is clearly consistent with the closed conformer (Figure 1), the quality of the X-ray reflections for higher angles were very poor. In **1b**, the two pyrene rings show intramolecular π-stacking interactions along with intermolecular $\pi-\pi$ interaction between the neighboring molecules (see the Supporting Information). In both structures, the π-stacking pyrene rings are nearly parallel but displaced lengthwise (Figure 2) with respect to each other.[9] The length of the butadiynyl bridge is optimal for such a displaced π-stacking interaction between the pyrene units.

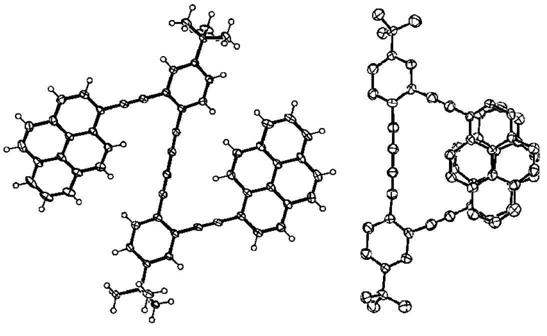


FIGURE 1. ORTEP representation of the structure of **1a** (left) and **1b** (right) in the crystal. **1a** has a center of symmetry (achiral), and **1b** has a C_2 axis of symmetry (chiral).

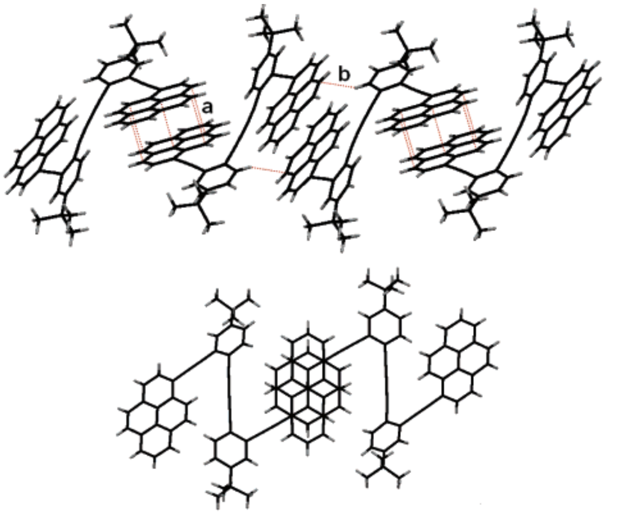


FIGURE 2. Packing of **1a** in the crystal. The short contacts are shown as dotted lines. The mean distance between the π-stacking planes of pyrene, a = 3.397 Å, and C−H$\cdots\pi$ distance, b = 2.761 Å. View perpendicular to the pyrene planes showing lengthwise displaced parallel π-stacking (bottom).

Precursor **2** with only one pyrene unit, and hence devoid of intramolecular π-stacking, was used as a model compound to compare the electronic absorption and emission properties and intramolecular π-stacking behavior of **1**.[10] A comparison of the UV−vis spectra of **1** and **2** (Figure 3) clearly revealed that the

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(8) After repeated attempts, crystals of **1b** of reasonable size for the structure determination could be obtained. The examination of the crystals with the polarizing microscope showed the crystals to have a poor degree of crystallinity (poor extinction). The quality of the reflections for higher angles was very poor, and there were only 1388 reflections with $I > 2\sigma(I)$ out of 3678 unique reflections. There are 301 least squares parameters and 199 restraints in the refinement. An R factor of 0.117 for reflections $I > 2\sigma(I)$ is reasonable for such data.

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(10) See the Supporting Information for the comparison of the ^{1}H NMR spectra of **1** and **2**.

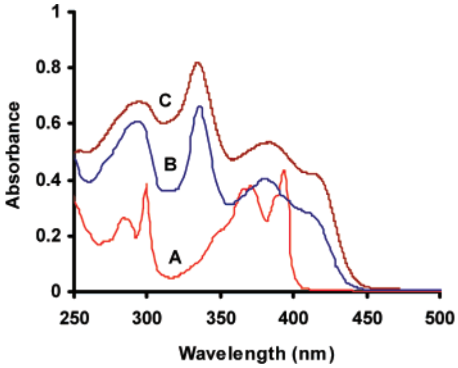

FIGURE 3. Absorption spectra of **2** (A) and **1** (B) in cyclohexane (1×10^{-5} M) and excitation spectrum of **1** (C) (λ_{em} 483 nm) in cyclohexane.

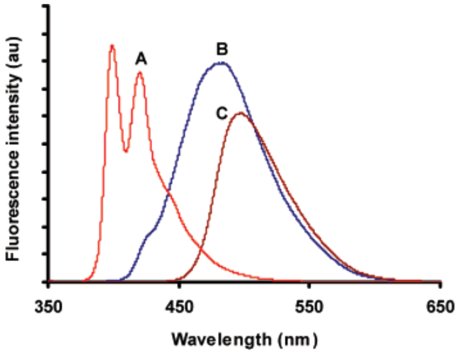

FIGURE 4. Fluorescence emission spectra of **2** (A, λ_{ex} 367 nm) and **1** (B, λ_{ex} 333 nm) in cyclohexane (1×10^{-5} M) and of **1** in the solid state as powder (C, λ_{ex} 333 nm).

absorption bands were broader in the case of **1** and were bathochromically shifted.[11]

The absorption cutoff was very sharp at 410 nm for **2**, whereas in **1** it was broad and extended up to 440 nm. The bathochromic shift is expected for **1** due to extensive conjugation in comparison to **2**. The broadness of the bands might also be due to many possible conformers of **1** in solution of which **1a** and **1b** represent two extreme cases. It is also well-known that π-stacking of pyrene units leads to broadening as well as bathochromic shift of the absorption bands.[7,11] The absorption spectrum of **1** in the solid state (as a thin film) was nearly identical to that in cyclohexane. The fluorescence spectra of **1** and **2** (Figure 4) were dramatically different. The emission spectrum of **2** showed vibrational fine structures [λ_{max} 401, 423, 445 (sh) nm], and it resembled the emission spectra of several ethynylpyrene derivatives.[12] It corresponds to the emission from the monomer excited state.[13]

In the case of **1**, the fluorescence emission appeared as a broad featureless band both in cyclohexane (λ_{max} 483 nm) and in the solid state (λ_{max} 498 nm), a very characteristic feature of emission from the excimer state.[7,11,13] In cyclohexane, the spectrum was invariant with respect to excitation wavelength as well as concentration in the range of 10^{-4}–10^{-8} M, indicating that the emission corresponds to the intramolecular excimer state (see the Supporting Information). These results suggest that at room temperature **1** exists predominantly in the closed form (**1b**) in cyclohexane. Alternatively, **1** could predominantly exist as **1a** in the ground state and convert to **1b** in the excited state before emission could take place. In such a case also, excimer emission would be expected from **1**. However this would require a substantial geometry change in the excited state on going from **1a** to **1b**. In such a case, the excitation spectrum is not expected to resemble that of the absorption spectrum. The excitation spectrum of **1** clearly resembled its absorption spectrum (Figure 3). The emission maximum in the solid state (in powder and in thin film samples of **1**) is bathochromically shifted (15 nm), and also the fwhm of the emission band is smaller (2333 cm^{-1}) compared to that in cyclohexane (3300 cm^{-1}). It is perhaps due to a more ordered π-stacked structure of **1** in the solid state. The fluorescence quantum yield of **1** in cyclohexane is 0.32.[14]

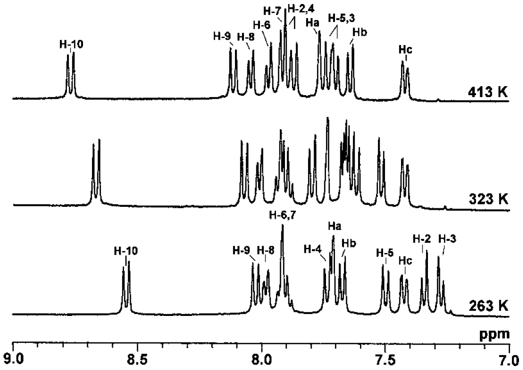

FIGURE 5. Temperature-dependent ^{1}H NMR spectra of **1** in $CDCl_2$-$CDCl_2$.

Variable-Temperature Spectral Studies. The absorption and emission spectra were measured in the temperature range of 278–343 K (see the Supporting Information). The λ_{max}, shape, and intensity of the absorption bands did not change significantly with increasing temperature. However, there was a small gradual blue shift of the emission maximum from 487 nm at 278 K to 480 nm at 343 K. It is concluded that the intramolecular π-stacking in **1b** is not significantly disturbed within the temperature range studied. The changes in the equilibrium in Scheme 1 might be small, and hence, it is not manifested in the absorption and emission spectra.

However, strong evidence for the equilibrium in Scheme 1 comes from ^{1}H NMR spectral studies of **1** in the temperature range of 263–413 K in $CDCl_2CDCl_2$. The proton chemical shift is very sensitive to even small changes in the π-stacking interactions of the aromatic rings.[15] Compared to the model compound **2**, the pyrene proton resonances in **1** are spread out (Figure 5).[10] The individual resonances of the pyrene ring protons could be assigned on the basis of the ^{1}H–^{1}H COSY spectrum of **1**. π-Stacking interactions among aromatic units result in shielding of the protons due to the ring current effect.[11] With increasing temperature, the equilibrium is shifted toward

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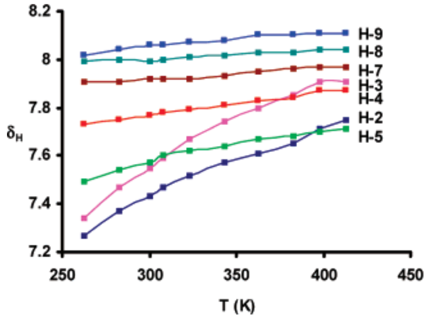

FIGURE 6. Effect of temperature on the chemical shift of various protons on the pyrene ring of **1** in $CDCl_2CDCl_2$.

1a because π-stacking is a weak interaction.[7,15] As a consequence, all of the pyrene protons are shifted to higher δ values and that of the phenyl protons remained unaffected with increasing temperature. From Figure 6, it is clear that the effect of shifting the equilibrium is more dramatic on H-2 and H-3 compared to the other protons. It is due to the displaced parallel π-stacking of the pyrene rings which brings H-2 and H-3 in the shielding zone in **1b**. Hence, with increasing temperature they show a pronounced increase in their δ values. From the VT-NMR study, the equilibrium constant is estimated to be 4.5 ± 0.5 at 300 K (Scheme 1).[16]

In conclusion, we have demonstrated π-stacking in a novel pyrene derivative (**1**) in solution as well as in solid state. The two conformers **1a** and **1b** were crystallized and their structures determined by X-ray crystallography. Variable-temperature NMR studies established the equilibrium between **1a** and **1b** in solution, wherein **1b** appears to be the predominant species at room temperature.

Experimental Section

1-(5-*tert*-Butyl-2-ethynylphenylthynyl)pyrene (**2**). An oven-dried Schlenk flask was charged with **6** (0.4 g, 0.74 mmol) and dry THF (30 mL). It was cooled to −78 °C. LDA (2.95 mmol) [freshly prepared from 2.95 mmol each of *n*-BuLi (1.83 mL of 1.6 M solution in hexane) and diisopropylamine (0.4 mL) at −78 °C in THF] was added and stirring continued for 1 h. Upon completion of the reaction, it was quenched with saturated NH_4Cl at −78 °C. The reaction mixture was extracted with CH_2Cl_2 (30 mL). The organic layer was washed with water (2 × 40 mL) and dried over Na_2SO_4. Solvent was evaporated to dryness at rt under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane to yield **1** as a pale yellow solid (0.20 g, 71%): mp 85−87 °C; IR (KBr) 2950, 2189 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 9.3 Hz, 1H), 8.34−8.06 (m, 8H), 7.87 (d, J = 1.9 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.48 (dd, J = 8.3, 1.9 Hz, 1H), 3.62 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 132.5, 132.0, 131.2, 131.1, 130.9, 129.6, 128.8, 128.1, 127.1, 126.2, 126.1, 125.9, 125.5, 124.4, 124.4, 124.3, 124.1, 121.6, 117.7, 94.0, 92.2, 83.0, 80.6, 34.8, 31.0; MS (EI, 70 eV) *m*/*z* 383 (30, 382 (100, M^+), 326 (25), 170 (95); HRMS calcd for $C_{30}H_{22}$ 382.17215, found 382.17165.

1. $Cu(OAc)_2 \cdot H_2O$ (0.163 g, 0.82 mmol) was dissolved in a mixture of acetonitrile (12 mL) and pyridine (3 mL), and **2** (0.125 g, 0.327 mmol) was added. The reaction mixture was stirred at rt for 4 h. It was neutralized with 5% HCl and extracted with CH_2Cl_2 (25 mL). The organic layer was washed with water (30 mL) and dried over Na_2SO_4, and solvent was evaporated at rt under reduced pressure to dryness. The crude product was purified by column chromatography on silica gel using hexane to yield the dimer (**1**) as a yellow solid (0.106 g, 85%): temperature for onset of decomposition 255−259 °C; IR (KBr) 2957, 2196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 9.2 Hz, 2H), 8.0 (d, J = 8.8 Hz, 2H), 7.80−7.95 (m, 6H), 7.70 (m, 4H), 7.61 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.35−7.40 (m, 4H), 7.27 (d, J = 8.3 Hz, 2H), 1.37 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 133.0, 131.4, 130.9, 130.8, 130.3, 128.8, 128.6, 128.5, 127.3, 126.7, 125.6, 125.4, 124.7, 123.5, 123.4, 123.1, 121.5, 116.7, 93.6, 93.4, 82.4, 78.0, 35.0, 31.1; MS (EI, 70 eV) *m*/*z* 762 (100, M^+); HRMS calcd for $C_{60}H_{42}$ 762.32865, found 762.32740.

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Supporting Information Available: Synthesis, spectroscopic data for **1**−**6**, VT-NMR, absorption and fluorescence spectra for **1**, and crystallographic data (CIF) for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] The δ value of H-10 in **2** was taken as that of pure **1a** due to absence of π-stacking in **2**, and the δ value of H-10 at 263 K (Figure 5) was taken as approximately equal to that of pure **1b** to calculate the molar ratios **1a** and **1b**. Therefore, the equilibrium constant is only an approximate estimate.