ORGANIC LETTERS

2010
Vol. 12, No. 21
4784−4787

Arylene Ethynylene Macrocycles with Intramolecular $\pi-\pi$ Stacking

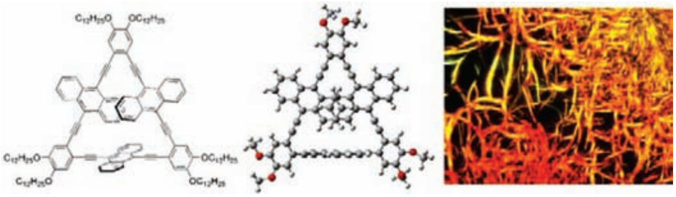
Shusen Chen, Qifan Yan, Tian Li, and Dahui Zhao*

Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry and Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

dhzhao@pku.edu.cn

Received August 13, 2010

ABSTRACT



Arylene ethynylene macrocycles containing 9,10-anthrylene or 1,4-naphthylene units were synthesized. In chloroform, significant resonance upfield shifting was observed with β-protons of anthrylene and naphthylene in NMR spectra. This was considered to result from partial stacking of these aromatic units intramolecularly, driven by attractive $\pi-\pi$ interactions. DFT calculations supported the proposed intramolecular stacking motif. Moreover, a liquid-crystal phase was exhibited by the anthrylene-containing macrocycle, by virtue of the unique discotic shape.

Despite its relatively weak strength, as an important type of noncovalent force $\pi-\pi$ stacking interactions ubiquitously influence crystal packing, molecular recognition, biomacromolecule conformations, and so on. Hence, considerable research has been conducted to explore the nature as well as applications of aromatic interactions.[1] Particularly, intermolecular $\pi-\pi$ stacking plays an important role in supramolecular self-assembly of polycyclic aromatic systems.[2,3] Electronic properties of the molecules are affected by $\pi-\pi$ interactions, resulting in exciton coupling, charge or energy transfer, excimer or exciplex formation, etc.[4,5] However, intramolecular $\pi-\pi$ stacking is employed for designing and creating synthetic architectures with higher order structures.[6]

Owing to the shape-persistent, planar geometry, arylene ethynylene macrocycles (AEMs) effectively harness $\pi-\pi$ interactions as the major driving force for intermolecular association and self-assembly.[7,8] Diverse supramolecular architectures have been realized by AEMs via self-assembly, including three-dimensional nanostructures,[9] extended tubular channels,[10] discotic liquid crystals,[11] host−guest complexes,[7b] and so forth. Recently, self-assembled AEMs were

---

[1] (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. (b) Grimme, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3430. (c) Wheeler, S. E.; Houk, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 10854. (d) Ringer, A. L.; Sherrill, C. D. *J. Am. Chem. Soc.* **2009**, *131*, 4574.

[2] Klosterman, J. K.; Yamauchi, Y.; Fujita, M. *Chem. Soc. Rev.* **2009**, *38*, 1714.

[3] Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491.

[4] Chen, Z.; Lohr, A.; Saha-Möller, C. R.; Würthner, F. *Chem. Soc. Rev.* **2009**, *38*, 564.

[5] Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718.

[6] (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893. (b) Saraogi, I.; Hamilton, A. D. *Chem. Soc. Rev.* **2009**, *38*, 1726. (c) Ni, B.-B.; Yan, Q.; Ma, Y.; Zhao, D. *Coord. Chem. Rev.* **2010**, *254*, 954.

[7] (a) Zhao, D.; Moore, J. S. *Chem. Commun.* **2003**, 807. (b) Höger, S. *Chem.—Eur. J.* **2004**, *10*, 1320. (c) Zhang, W.; Moore, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4416.

[8] For recent examples of AEMs, see: (a) Mössinger, D.; Chaudhuri, D.; Kudernac, T.; Lei, S.; De Feyter, S.; Lupton, J. M.; Höger, S. *J. Am. Chem. Soc.* **2010**, *132*, 1410. (b) Chan, J. M. W.; Tischler, J. R.; Kooi, S. E.; Bulović, V.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 5659. (c) Kissel, P.; Schlüter, A. D.; Sakamoto, J. *Chem.—Eur. J.* **2009**, *15*, 8955. (d) Tahara, K.; Fujita, T.; Sonoda, M.; Shiro, M.; Tobe, Y. *J. Am. Chem. Soc.* **2008**, *130*, 14339. (e) Ishikawa, T.; Shimasaki, T.; Akashi, H.; Toyota, S. *Org. Lett.* **2008**, *10*, 417. (f) Hartley, S. C.; Moore, J. S. *J. Am. Chem. Soc.* **2007**, *129*, 11682. (g) Becker, K.; Lagoudakis, P. G.; Gaefke, G.; Höger, S.; Lupton, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3450. (h) Toyota, S.; Goichi, M.; Kotani, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2248.

10.1021/ol101914f

shown to perform functions by virtue of their semiconductive properties, which has further enhanced their research values.[12,13] Here, we report an AEM that exhibited intramolecular $\pi-\pi$ stacking in solution and manifested a columnar liquid crystal (LC) phase.

Previously, we studied an AEM composed of alternative *o*-PE (phenylene ethynylene) and *p*-PE units which exhibited notable photoconductive properties.[13,14] Aimed to further exploit related functions, an analogous macrocycle **AEM-A** was designed (Figure 1). In addition to *o*-PE, this macrocycle accommodated 9,10-anthrylene units. The structure was accomplished via a multistep synthetic route. The final reaction was a one-pot intermolecular Sonogashira cross-coupling followed by intramolecular cyclization, carried out between diiodo-functionalized precursor **1-A** and a bis-acetylene terminated molecule.[14] The latter was obtained upon removing the isopropanol protective groups from **2-A** (see the Supporting Information for details). A similar reaction initially performed with a dibromo-substituted analogue of **1-A** was not successful, due to the lower reactivity of aryl bromide in the Sonogashira reaction. The dodecyloxy side chains on *o*-phenylenes conferred the target molecule and precursors sufficient solubility in common organic solvents, and allowed the use of flash column chromatography for purification. The structure and purity of **AEM-A** were fully characterized by ^{1}H and ^{13}C NMR, MALDI-TOF mass spectroscopy, and elemental analysis.

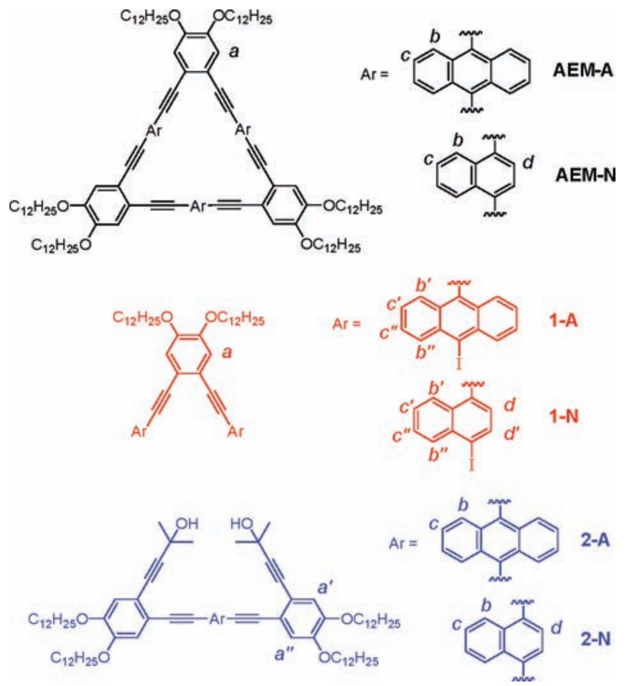


Figure 1. Chemical structures of studied AEMs and their synthetic precursors.

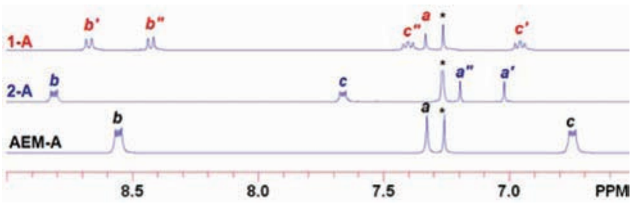


Figure 2. The aromatic region of ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1-A**, **2-A**, and **AEM-A** with resonance assignments (signals labeled *a*, *b*, *c*, etc. were assigned to protons with corresponding tags in Figure 1; signals with an asterisk were from residual $CHCl_3$ in $CDCl_3$).

In examining the ^{1}H NMR spectrum of **AEM-A**, interesting observations emerged (Figure 2). With a highly symmetric structure, **AEM-A** exhibited only three resonances in the aromatic region. Two multiplets at about 8.6 and 6.7 ppm were assigned to protons *b* and *c* of the anthrylene unit, respectively. On the basis of previously published reports, chemical shifts of β protons (2-, 3-, 6-, and 7-positions) of anthracene, with 9- and 10-positions substituted with alkoxyphenylethynyl groups, should be in the range of 7.6 to 7.7 ppm.[15] Apparently, in **AEM-A** the resonance of protons *c* was significantly shifted upfield. Additionally, we noticed that in the spectrum of **1-A** protons *c′* also exhibited an unusual chemical shift of less than 7.0 ppm, although **2-A** gave a relatively normal value of ca. 7.7 ppm for its protons *c*. Moreover, the resonance of protons *a* on dialkoxy *o*-phenylene in both **AEM-A** and **1-A** appeared abnormally downfield at >7.3 ppm, although their usual chemical shift should be around 7.0 ppm, as observed in a previously synthesized macrocycle analogue.[14] Namely, the aromatic protons of **AEM-A** and **1-A** displayed atypical chemical shifts, while **2-A** showed relatively normal values. Evidently, the observed shifting cannot be fully justified by electronic effects imparted by chemical structures. Furthermore, since the chemical shifts and UV−vis absorption (Figure S2, Supporting Information) of **AEM-A** both exhibited concentration-independent properties within the investigated con-

---

(9) Kim, J. K.; Lee, E.; Kim, M. C.; Sim, E.; Lee, M. *J. Am. Chem. Soc.* **2009**, *131*, 17768.

(10) Ono, K.; Tsukamoto, K.; Hosokawa, R.; Kato, M.; Suganuma, M.; Tomura, M.; Sako, K.; Taga, K.; Saito, K. *Nano Lett.* **2009**, *9*, 122.

(11) Previous examples of AEM macrocycles exhibiting a liquid crystal state: (a) Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2655. (b) Höger, S.; Enkelmann, V.; Bonrad, K.; Tschierske, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 2268. (c) Höger, S.; Cheng, X. H.; Ramminger, A.-D.; Enkelmann, V.; Rapp, A.; Mondeshki, M.; Schnell, I. *Angew. Chem., Int. Ed.* **2005**, *44*, 2801. (d) Seo, S. H.; Jones, T. V.; Seyler, H.; Peters, J. O.; Kim, T. H.; Chang, J. Y.; Tew, G. N. *J. Am. Chem. Soc.* **2006**, *128*, 9264. (e) Shimura, H.; Yoshio, M.; Kato, T. *Org. Biomol. Chem.* **2009**, *7*, 3205.

(12) (a) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596. (b) Che, Y.; Yang, X.; Zhang, Z.; Zuo, J.; Moore, J. S.; Zang, L. *Chem. Commun.* **2010**, *46*, 4127.

(13) Luo, J.; Yan, Q.; Zhou, Y.; Li, T.; Zhu, N.; Bai, C.; Cao, Y.; Wang, J.; Pei, J.; Zhao, D. *Chem. Commun.* **2010**, *46*, 5725.

(14) Zhu, N.; Hu, W.; Han, S.; Wang, Q.; Zhao, D. *Org. Lett.* **2008**, *10*, 4283.

(15) (a) Nakatsuji, S.; Matsuda, K.; Uesugi, Y.; Nakashima, K.; Akiyama, S.; Fabian, W. *Perkin Trans. 1* **1992**, 755. (b) Schmidt, R.; Göttling, S.; Leusser, D.; Stalke, D.; Krause, A.-M.; Würthner, F. *J. Mater. Chem.* **2006**, *16*, 3708. (c) Valentini, L.; Bagnis, D.; Marrocchi, A.; Seri, M.; Taticchi, A.; Kenny, J. M. *Chem. Mater.* **2008**, *20*, 32.

centration range, the possibility was excluded that the shifting observed in ^{1}H NMR spectra was caused by intermolecular aggregation.

The above observations with chemical shifts led us to proposing that in $CDCl_3$ the anthrylene units of **AEM-A** partially stacked with one another intramolecularly. Such a hypothesis was put forward mainly for two reasons. First, the relative spatial distance and orientation of the anthrylene moieties in this molecule are confined by the *o*-PE linker, so they have to partially overlap with one another intramolecularly, unless adopting a significant dihedral angle with the *o*-phenylene units. However, the noncoplanar conformation disrupts π-conjugation and may thus be disfavored. More importantly, the observed chemical shifts served as supportive evidence for the overlapped conformation. When the anthracenes are intramolecularly stacked, certain β-protons on one anthrylene may fall in the shielded region imposed by the ring current of another anthrylene, thus exhibiting an upfield shift in the NMR spectrum.[16] In such an overlapping conformation, protons on the stacked, intraannular benzo-moieties should experience a different environment from those on the nonstacked, extraannular benzo-groups. However, at even −50 °C the NMR spectrometer did not distinguish these protons (Figure S5, Supporting Information). It implied that the anthrylenes were still undergoing rapid rotation around ethynylenes at such a low temperature and the NMR thus detected averaged chemical shifts. Precursor **1-A** contained a pair of anthrylene units positioned in a similar fashion with those in **AEM-A**. Due to the asymmetric substitution, the β-protons of anthrylene in **1-A** were differentiated into two sets (c' and c'') and both experienced upfield shifting, although to a different extent.

The overlapping conformation also explained the downfield shifting of protons *a* in **AEM-A** and **1-A**. When the anthrylenes were intramolecularly stacked, their aromatic rings were approximately in plane with the *o*-phenylene units. Consequently, their ring current exerted a deshielding effect on protons *a*, whereas in **2-A**, since no such $\pi-\pi$ interaction stabilized anthrylene to be in plane with *o*-phenylenes, the ring current entailed deshielding effect was less pronounced. This was consistent with the experimental observation that the resonance of a'' appeared at ca. 7.2 ppm.

Theoretical calculations were then conducted to help analyze and illustrate the intramolecular stacking motif of the anthrylenes. DFT-optimized conformations of **AEM-A** and **1-A** confirmed that the anthrylenes tended to stack with another anthrylene. Under such a conformation, protons *c* and c' were located on top of one of the benzene rings from the adjacent anthracene unit, where a strong shielding effect should operate (Figure 3). The model also predicted that in **AEM-A** two of the anthrylenes overlapped, while repelling the third anthrylene to be out of plane with *o*-phenylenes. Imaginably, at room temperature a rapid equilibration should exist among three equivalent conformers as depicted in Figure 3, resulting in averaged chemical shifts in NMR measurements.

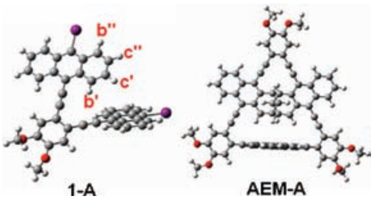


Figure 3. B3LYP/3-21G* optimized geometry of compounds **1-A** and **AEM-A**. Dodecyl chains were replaced by methyl groups in the calculations.

Regarding the driving force for such an intramolecularly stacked conformation, two possibilities were speculated. First, stacking of the anthrylenes was driven by attractive $\pi-\pi$ interactions. Alternatively, the interactions among anthrylenes are repulsive by nature but the steric repulsion was overwhelmed by the conjugation energy favoring the coplanar conformation of anthrylenes with respect to *o*-phenylenes, forcing the anthrylenes to stack. To delineate the origin of the stacking conformation, a new macrocycle, **AEM-N**, was synthesized. It differed from **AEM-A** only by three naphthylene units in place of anthrylenes. Since 1,4-naphthylene has only one benzene ring fused to the 1,4-phenylene, if the aromatic rings were repulsive to each other, the benzo-portion of naphthylenes may be flanked outside (extraannular) of the macrocycle, but still remain in plane with *o*-phenylene and nondisruptive to π-conjugation. On the other hand, if the aromatic units were attracted to each other, **AEM-N** would also display the stacked conformation. Hence, **AEM-N** would provide an unambiguous clue for the nature of interactions among these aromatic units.

As shown in Figure 4, protons *c* of macrocycle **AEM-N** and c' of **1-N** exhibited similarly upfield-shifted chemical shifts of about 7.0 ppm. In comparison, the resonance of protons *c* appeared at nearly 7.7 ppm in **2-N**. This result suggested that in $CDCl_3$ naphthylenes in **AEM-N** and **1-N** also stacked intramolecularly. Reasonably, the downfield

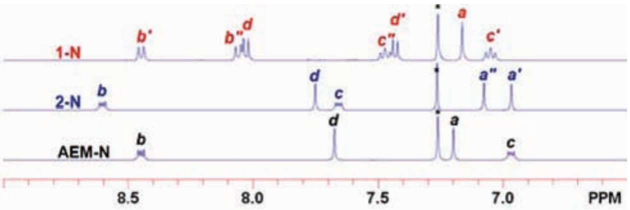


Figure 4. The aromatic region of ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1-N**, **2-N**, and **AEM-N** with resonance assignments (signals labeled *a*, *b*, *c*, *d*, etc. were assigned to protons with corresponding tags in Figure 1; signals with an asterisk were from residual $CHCl_3$ in $CDCl_3$).

---

[16] For other examples of molecules exhibiting resonance upfield shifting in ^{1}H NMR due to intramolecular $\pi-\pi$ stacking and/or ring current shielding effect in constrained structures, see: (a) Ting, Y.; Lai, Y. H. *J. Am. Chem. Soc.* **2004**, *126*, 909. (b) Mei, X.; Wolf, C. *J. Org. Chem.* **2005**, *70*, 2299. (c) Nandy, R.; Subramoni, M.; Varghese, B.; Sankararaman, S. *J. Org. Chem.* **2007**, *72*, 938.

shifting of protons *a* in **AEM-N** and **1-N** was less pronounced compared to that in **AEM-A** and **1-A**, appearing at ca. 7.2 ppm. Despite the intramolecular stacking conformation, in the absence of the extraannular benzo-units, the deshielding effect on protons *a* was evidently tempered in **AEM-N** and **1-N**. On the basis of the NMR spectrum of **AEM-N**, it was concluded that the intramolecular $\pi-\pi$ interactions were attractive forces in these systems, rendering both anthrylene and naphthylene units to stack intramolecularly in chloroform solution.

Interesting thermotropic behaviors were discovered for **AEM-A**, which were characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). The DSC traces were obtained at a scan rate of 5 deg min^{-1} and multiple transitions were detected for **AEM-A** (Figure 5).[17] With POM, an evident liquid-crystal (LC) texture with a strong birefringence was observed at elevated temperature, indicative of an LC phase of **AEM-A** (Figure 5). The existence of a mesophase phase was further confirmed by XRD analysis (Figure S1, Supporting Information). Further studies on this LC phase are being carried out and will be reported in due course.

In conclusion, we have synthesized two shape-persistent AEMs, **AEM-A** and **AEM-N**. Evidence from the ^{1}H NMR spectra suggested that the anthrylene and naphthylene units in the macrocycles partially stacked intramolecularly, favored by attractive $\pi-\pi$ stacking interactions. DFT calculations confirmed that the stacked conformation may confer through-space ring-current effect to bring about the experimentally observed proton resonance shifting. An LC phase was detected for **AEM-A**, which is believed to be pertinent to the unique intramolecularly stacked structure.

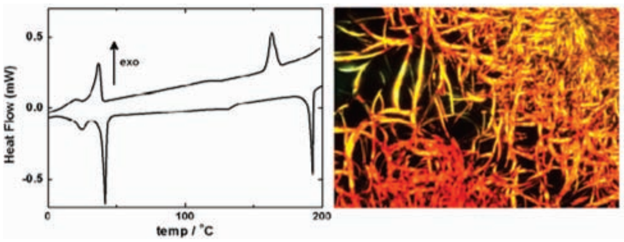


Figure 5. DSC trace and a POM image (taken at 153 °C) of **AEM-A**.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Projects 50603001 and 20774005), the Ministry of Science and Technology of China (No. 2006CB921600), and the Fok Ying-Tung Educational Foundation (No. 114008).

Supporting Information Available: Syntheses, optical spectroscopy, wide-angle X-ray diffraction of the LC phase, varied-temperature NMR spectra of **AEM-A**, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

OL101914F

---

(17) The DSC trace shown in Figure 5 is the first cooling and second heating scans; the first heating scan was neglected to exclude the influence of thermal history of the sample.