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Molecular Compasses and Gyroscopes. II. Synthesis and Characterization of Molecular Rotors with Axially Substituted Bis[2-(9-triptycyl)ethynyl]arenes

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Abstract: We have developed a simple convergent procedure for the synthesis of molecular rotors consisting of a central aromatic group coupled with two axially positioned ethynyltriptycenes. Molecular rotors with 1,4-phenylene (**1**), 1,4′-1,1′-biphenylene (**2**), 9,10-anthracenylene (**3**), and 2,7-pyrenylene (**4**) groups were prepared by Pd(0)-catalyzed coupling of ethynyl triptycenes with the corresponding dibromoarenes. Although compounds **1**−**4** were not expected to have free rotation in the solid state, the rotational potentials of **1** and **3** were analyzed by semiempirical methods and the crystal packing of **1** was analyzed to design the structures most likely to yield a functional rotor in the solid state. Semiempirical PM3 calculations predict compounds **1**, **2**, and **4** to have frictionless internal rotation even at temperatures as low as 25 K, while compound **3** is expected to have a barrier of ca. 4 kcal/mol.

1. Introduction[1]

Recent advances in communication technologies have stimulated much interest in the field of photonics.[2,3] The need for materials with tunable transmittance, refraction, polarization, and color poses new challenges and opportunities for organic materials chemistry.[2,4] While most research in this field falls in the areas of polymer chemistry[5] and liquid crystals,[6,7] we have recently begun a strong effort toward the realization of a new concept for the fabrication of photonics materials based on dipolar units that can reorient rapidly under the influence of electric, magnetic, and optical stimuli. The desired compounds will take advantage of novel molecular architectures expected to have a function analogous to those of macroscopic *compasses and gyroscopes* (Figure 1).

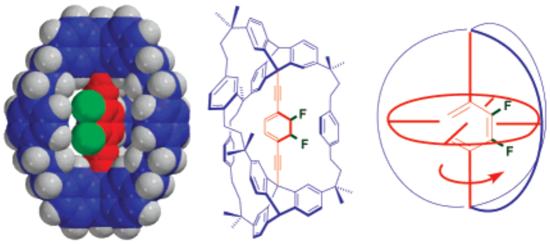

Figure 1. Space-filling model (left) and line formula (center) of a 1,4-bis[(9-triptycyl)ethynyl]-2,3-difluorobenzene illustrating the homeomorphism of the molecule with a macroscopic gyroscope shown on the right.

The structural elements required for a functional molecular compass, or molecular gyroscope, can be illustrated in the triply bridged 1,4-bis[(9-triptycyl)ethynyl]-2,3-difluorobenzene shown in Figure 1. In lieu of the magnetic dipole of a compass needle, or the moment of mass of a gyroscope rotor, the desired molecular rotors will have polar or polarizable groups that can respond to external fields.[8] This is illustrated with a 2,3-difluoro-1,4-phenylene rotor, shown in red, with fluorine atoms in green. We expect that rotation of aromatic rotors will be facilitated by the cylindrical symmetry of the two axial alkyne bonds, which will act as an axle. Since fast dynamics in the solid state will require shape- and volume-conserving motions, the reorienting phenylene should be sterically shielded from contact with other molecules in the environment. Shielding will be provided

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(1) Part I: Dominguez, Z.; Strouse, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 2393−2399.

(2) Salech, B. E. A.; Teich, M. C. *Fundamentals of Photonics*; Wiley-Interscience: New York, 1991.

(3) Photonics has been defined as "The technology of generating and harnessing light and other forms of radiant energy whose quantum unit is the photon". See: Laurin, T. C. *The Photonics Ditionary*, 45th ed.; Lauring Publishing Co.: Pittsfield, MA, 1999; p D-107.

(4) Burns, G. *Solid State Physics*; Academic Press: New York, 1985.

(5) (a) Nalwah, H. S. *Ferroelectric Polymers*; Marcel Dekker: New York, 1995. (b) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430−436.

(6) For some examples of recent research on crystalline photonics materials please see: (a) Liu, C.-Y.; Bard, A. J. *Acc. Chem. Res.* **1999**, *32*, 235−245. (b) Iverson, I. K.; Tam-Chang, S.-W. *J. Am. Chem. Soc.* **1999**, *121*, 5801−5802. (c) Wang, S. J.; Oldham, W. J.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695−5709.

(7) (a) Collings, P. J.; Hird, M. *Introduction to Liquid Crystals*; Taylor and Francis, Ltd.: London, 1997. (b) Blinov, L. M. *Electrooptic and Magneto-Optical Properties of Liquid Crystals*; Wiley: New York, 1983. (c) Guymon, G. A.; Dougan, L. A.; Martens, P. J.; Clarck, N. A.; Walba, D. M.; Bowman, C. N. *Chem. Mater.* **1998**, *10*, 2378−2388. (d) Walba, D. M.; Dyer, D. J.; Sierra, T.; Cobben, P. L.; Shao, R.; Clark, N. A. *J. Am. Chem. Soc.* **1996**, *118*, 1211−1212.

(8) The collective behavior of a lattice of reorienting dipoles depends on symmetry, dimensions, temperature, and the magnitudes of the dipole and the external field. See: (a) Adams, D. J.; McDonald, I. R. *Mol. Phys.* **1976**, *32*, 931. (b) Papazyan, A.; Maroncelli, M. *J. Chem. Phys.* **1991**, *95*, 9219−9241.

10.1021/ja012550i CCC: $22.00

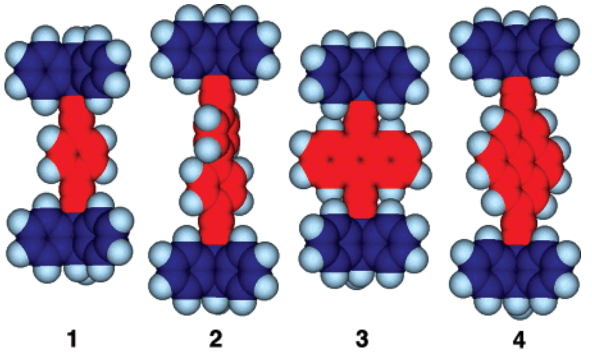

Figure 2. Space-filling models of phenylene-, biphenylene-, anthracenylene-, and pyrenylene-based molecular rotors **1**−**4**.

by a triply bridged framework, as shown in the bis(triptycyl) structure in Figure 1, or by frameworks with open topologies with bulky substituents.[9] To realize and optimize the desired molecular assemblies, one will need convenient synthetic procedures, a detailed analysis of their packing preferences, and the implementation of practical strategies to determine their solid-state rotational dynamics. In this paper, we report the synthesis and characterization of four model compounds with benzene, 1,1′-biphenyl, anthracene, and pyrene rotors (**1**−**4**, Figure 2). Although the aromatic groups of compounds **1**−**4** are not expected to have rapid rotation in the solid state, we have chosen this set to test a simple convergent procedure, to analyze their gas-phase rotational potential, and to explore their crystallization behavior and thermal properties.

2. Experimental Section

General. IR spectra were acquired on a Perkin-Elmer Paragon 1000 FT-IR instrument. The ^{1}H[^{13}C] NMR spectra were obtained on a Bruker NMR spectrometer operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C in $CDCl_3$ or $C_2D_2Cl_4$ with TMS as internal standard. Gas chromatography (GC) analyses were recorded on a Hewlett-Packard 5890 Series II capillary instrument equipped with a flame ionization detector. Melting points were determined with a Fisher-Johns melting point apparatus.

4-(9-Anthryl)-2-methyl-3-butyn-2-ol (5): Compound **5** was prepared by $Pd(PPh_3)_2Cl_2$-catalyzed coupling of 9-bromoanthracene and 2-methyl-3-butyne-2-ol in refluxing piperidine as described in a recent communication.[10]

4-(9-Triptycyl)-2-methyl-3-butyn-2-ol (6): 4-(9-Anthryl)-2-methyl-3-butyn-2-ol **5** (0.14 g, 0.397 mmol) was dissolved in 25 mL of benzene in a three-neck round-bottom flask and brought up to reflux. Anthranilic acid (0.32 g, 2.3 mmol) dissolved in 4 mL of 1,2-dichloroethane and isoamyl nitrite (0.3 mL, 2.2 mmol) dissolved in 4 mL of 1,2-dichloroethane were added dropwise and simultaneously. At the end of the addition and after cooling, the reaction mixture was washed with saturated $NaHCO_3$ (5 × 20 mL) and brine (2 × 20 mL) and dried over $MgSO_4$. Solvent was removed under vacuum and the product purified by column chromatography (hexanes:ethyl acetate 9:1 by volume) to afford 0.09 g (67%) of **6** as a white solid. Anal.: mp 248.7−250.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 1.89 (s, 6H, $-CH_3$), 2.26 (s, 1H, OH), 5.40 (s, 1H, bridgehead H), 7.03 (m, 6H, Ar), 7.37 (m, 3H, Ar), 7.66 (dd, $J = 7.2$, 1.5 Hz, 3H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$, TMS) δ 32.1, 52.6, 53.1, 65.8, 97.8, 122.4, 123.3, 125.0, 125.6, 144.1, 144.3; IR (KBr) 3771.2, 3443.0, 3068.4, 2978.1, 1456.6, 1332.0, 1165.6, 748.2 cm^{-1}; MS (70 eV) *m/z* (%) 336.1508 (100, M$^+$), 303.1 (57), 276.1 (31), and 321.1 (24).

1,4-Bis[2-(9-triptycyl)ethynyl]benzene (1): Alcohol **6** (0.20 g, 0.59 mmol) and 1,4-diiodobenzene (0.99 g, 0.30 mmol) were dissolved in 46 mL of deaerated toluene and 1.6 mL of Et_3N. Copper iodide (0.11 g, 0.58 mmol), KOH (0.81 g, 14.4 mmol), $(Bu)_4NI$ (1.1 g, 2.98 mmol), PPh_3 (0.18 g, 0.69 mmol), and $(PPh_3)_2PdCl_2$ (0.05 g, 0.071 mmol) were added under Ar at room temperature. The reaction mixture was magnetically stirred and heated in an oil bath at 100 °C for 24 h. The crude mixture was washed with brine and the organic layer was dried over $MgSO_4$. Solvent was removed under vacuum and the product purified by column chromatography (hexanes:CH_2Cl_2 3:1 by volume) to afford pure **1** in 20% yield. Coupling reactions carried out with alkyne **7** proceeded in 84% yield. The main byproduct under those conditions was identified as 1,4-bis(9-triptycyl)butadiyne.[11] Anal.: mp >400 °C dec; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, TMS) δ 5.51 (s, 2H, bridgehead H), 7.14 (m, 12H, triptycyl-Ar), 7.47 (dd, $J = 6.0$, 1.2 Hz, 6H, triptycyl-Ar), 7.86 (dd, $J = 7.0$, 0.9 Hz, 6H, triptycyl-Ar), 7.92 (s, 4H, Spacer-phenyl); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, TMS) δ 53.3, 53.8, 85.9, 92.7, 123.0, 123.5, 124.2, 125.6, 126.3, 132.6, 144.5, 144.7; IR (KBr) 3070.5, 3015.9, 2956.5, 1455.6, 1332.0, 745.0 cm^{-1}; MS (70 eV) *m/z* (%) 630.2 (34, M$^+$), 525.0 (5), 252.1 (6), 252.1, (20); HRMS (EI) calcd for $C_{50}H_{30}$ 630.2348, found 630.2337.

1,4′-Bis[2-(9-triptycyl)ethynyl]-1,1′-biphenyl (2): Rotor **2** was obtained as shown above for rotor **1** in 17% isolated yield. Anal.: mp >400 °C dec; ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, TMS) δ 5.39 (s, 2H, bridgehead H), 7.03 (m, 12H, triptycyl-Ar), 7.37 (dd, $J = 7.1$, 0.97 Hz, 6H, triptycyl-Ar), 7.76 (d, $J = 8.3$ Hz, 4H, biphenyl), 7.78 (dd, $J = 8.3$, 1.2 Hz, 6H, triptycyl-Ar), 7.91 (m, 4H, biphenyl); ^{13}C NMR (125 MHz, $C_2D_2Cl_4/CS_2$, TMS) δ 53.4, 53.5, 85.1, 92.4, 122.4, 122.5, 123.4, 125.1, 125.6, 127.1, 132.7, 140.4, 144.1, 144.2; IR (KBr) 3069.1, 3001.0, 2956.9, 1494.7, 1455.4, 822.6, 744.9, 640.8 cm^{-1}; MS (70 eV) *m/z* (%) 706.3 (5, M$^+$), 317.0 (20), 217.0, (28), 162 (32), 124 (100); HRMS (EI) calcd for $C_{56}H_{34}$ 706.2661, found 706.2657.

9,10-Bis[2-(9-triptycyl)ethynyl]anthracene (3): Rotor **3** was prepared as shown above for rotor **1** in 12% yield. Anal.: mp >400 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 5.53 (s, 2H, bridgehead H), 7.11 (m, 12H, triptycyl-Ar), 7.74 (dd, $J = 6.8$, 3.1 Hz, 6H, triptycyl-Ar), 8.03 (d, $J = 7.3$ Hz, 6H, triptycyl-Ar), 9.00 (dd, $J = 6.6$, 3.2, Hz, 6H, triptycyl-Ar); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, TMS) δ 56.7, 57.6, 92.4, 100.0, 121.6, 126.6, 127.0, 127.2, 128.5, 129.7, 147.6, 147.6; IR (KBr) 3067.8, 2923.7, 2852.7, 1455.6, 750.2 cm^{-1}; MS (70 eV) *m/z* (%) 730.3 (5, M$^+$), 629.0 (25), 510.2 (45), 252.1, (100); HRMS (EI) calcd for $C_{58}H_{34}$ 730.2661, found 730.2670.

2,7-Bis[2-(9-triptycyl)ethynyl]pyrene (4): Rotor **4** was prepared as shown above for rotor **1** in 36% yield. Anal.: mp >400 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, TMS) δ 5.47 (s, 2H, bridgehead H), 7.08 (td, $J = 7.2$, 1.0 Hz, 6H, triptycyl-Ar), 7.13 (td, $J = 7.3$, 0.99 Hz, 6H, triptycyl-Ar), 7.43 (d, $J = 7.1$ Hz, 6H, pyrene), 7.93 (d, $J = 7.5$ Hz, 6H, triptycyl-Ar), 8.19 (s, 4H, pyrene), 8.60 (s, 4H, pyrene); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, TMS) δ 53.4, 53.9, 84.6, 93.5, 121.1, 123.2, 124.2, 124.4, 125.7, 126.3, 128.2, 129.0, 131.7, 144.6, 144.7; IR (KBr) 3039.3, 1945.3, 1915.8, 1602.9, 1455.1, 882.7, 749.6, 639.9 cm^{-1}; MS (70 eV) *m/z* (%) 754.3 (55, M$^+$), 579.0 (70), 525.0, (35), 151 (100); HRMS (EI) calcd for $C_{60}H_{34}$ 754.2661, found 754.2659.

9-(2-Phenylethynyl)triptycene (8): Compound **8** was prepared as shown above for rotor **1** in 70% yield. Anal.: mp 297.5−300.0 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$, TMS) δ 5.45 (s, 1H, bridgehead H), 7.06 (m, 6H, triptycyl-Ar), 7.40 (m, 3H, triptycyl-Ar), 7.48 (m, 3H, $-$Ph), 7.81 (m, 3H, triptycyl-Ar), 7.83 (m, 2H, $-$Ph); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, TMS) δ 53.3, 53.5, 83.8, 92.7, 122.5, 123.0, 123.4, 125.2, 125.7, 128.5, 128.7, 132.1, 144.4, 144.4; IR (KBr) 3063.5, 1455.7, 757.8, 640.9 cm^{-1}; MS (70 eV) *m/z* (%) 354.1 (100, M$^+$), 276.1 (25), 252.1, (35), 175.1 (13).

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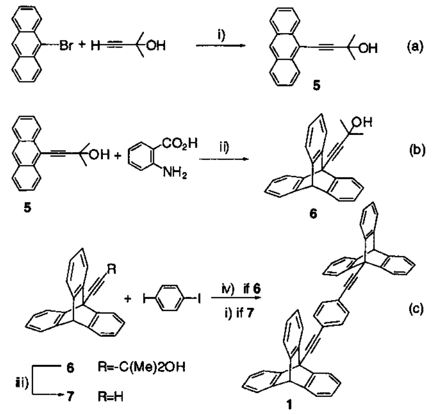
[9] Variations in the framework structure will help introduce steric barriers when hindered rotation is desirable.

[10] Dang, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 355−356.

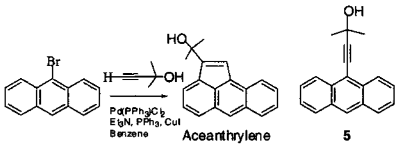
[11] Akiyama, S.; Ogura, F.; Masazumi, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*.

Scheme 1 [a]

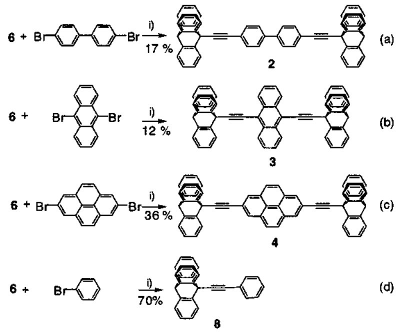


[a] Key: (i) Pd(PPh$_3$)$_2$Cl$_2$, piperidine, reflux; (ii) isoamyl-ONO, DCE, reflux; (iii) KOH, Bu$_4$NI, Ph-H, reflux; (iv) KOH, Bu$_4$NI, Ph-H, Pd(PPh$_3$)$_2$Cl$_2$, Et$_3$N, CuI, PPh$_3$, reflux.

Scheme 2

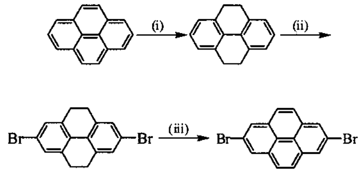


Scheme 3 [a]



[a] Key: (i) KOH, Bu$_4$NI, Ph-H, 2% Pd(PPh$_3$)Cl$_2$, Et$_3$N, CuI, PPh$_3$.

Scheme 4 [a]



[a] Key: (i) Pd/C(mol 10%), H$_2$ 45 psi, 6 days, 97% yield; (ii) Br$_2$/H$_2$O, 9% yield; (iii) Br$_2$/CS$_2$, quantitative.

3. Results and Discussion

3.1. Synthesis and Spectral Characterization. Molecular rotors **1**−**4** were prepared from 9-bromoanthracene by using the three-step procedure shown for the synthesis of 1,4-phenylene rotor **1** in Scheme 1. Initially, the preparation of the acetone-protected 9-anthrylacetylene **5** by Sonogashira coupling with copper cocatalyst[12] led to the unexpected formation of an isomeric aceanthrylene in 20−30% yield (Scheme 2).[13] However, reactions carried out with 10% (PPh$_3$)$_2$PdCl$_2$ in refluxing piperidine (Scheme 1a) yielded alcohol **5** in 70−75% isolated yields.

The preparation of 4-(9-triptycyl)-2-methyl-3-butyn-2-ol (**6**) was accomplished in 67% isolated yield via Diels−Alder addition of benzyne to anthracene **5** (Scheme 1b). Benzyne was formed in situ by diazotization of anthranilic acid with isoamyl nitrite.[14] Alcohol **6** is a stable, white solid with mp 249−250 °C that was characterized by conventional spectroscopic procedures. The structure of **6** was also confirmed by chemical correlation with the terminal alkyne **7** previously prepared by Akiyama[7] and by Stevens.[15] The deprotection of **6** was carried out in 87% yield with hydroxide ion in the presence of a phase-transfer catalyst in refluxing benzene (Scheme 1c).

Rotors **1**−**4** and compound **8** were prepared from alkynyl triptycene **6** by in situ deprotection using conditions similar to those reported by Pugh and Percec.[16] The reaction was carried out in refluxing benzene in the presence of KOH and Bu$_4$NI. The double coupling reaction proceeded with 2 equiv of **6** with respect to the dihaloarene using 10% Pd(PPh$_3$)$_2$Cl$_2$ in the presence of CuI, Et$_3$N, and PPh$_3$. Rotor **1** was prepared with 1,4-diiodobenzene (Scheme 1c). Molecular rotors **2** and **3** and compound **8** were prepared with commercial 4-(4-bromophenyl)bromobenzene, 9,10-dibromoanthracene, and bromobenzene (Scheme 3), respectively. Samples of 2,7-dibromopyrene for the synthesis of rotor **4** were prepared from pyrene by partial reduction, bromination, and rearomatization, as reported in the literature (Scheme 4).[17]

The complete disappearance of the starting materials under tandem deprotection and double Pd(0)-catalyzed coupling conditions was observed after 24−36 h. Pure samples of rotors **1**−**4** were obtained after repeated column chromatography in silica gel with a mixture of CH$_2$Cl$_2$:hexanes (3:2) as the eluant. The isolated yields of compounds **1**, **2**, **3**, and **4** under these conditions were 20%, 17%, 12%, and 36%, respectively. Besides reflecting the outcome of three consecutive reactions, these yields also reflect the solubility and ease of handling of each of the final products. We established that preparation of rotor **1** by stepwise deprotection and coupling reactions proceeds in higher overall yield (ca. 73%). Deprotection of **6** to give the terminal alkyne occurred in 87% yield and the double coupling reaction carried out with 2.5 equiv of the terminal alkyne **7** produced **1** in 84% yield. A drawback of the stepwise procedure was the formation of the nearly inseparable 1,4-bis(9-triptycyl)-butadiyne, which is formed by oxidative coupling of two terminal alkynes.[11] With only one coupling reaction and having a significantly higher solubility, compound **8** was obtained in 70% yield from the protected alkyne **6** and bromobenzene.

Rotors **1**−**4** were characterized by ^{1}H and ^{13}C NMR, EI-HRMS, and FT-IR spectroscopies. Although highly insoluble solids were obtained in all cases, only crystals of **1** grown from *m*-xylene were suitable for X-ray diffraction analysis (see below). All four solid samples decomposed without melting above 400 °C. High-resolution mass spectra obtained by electron impact ionization gave relatively abundant parent ions. As expected from the low polarity across the triple bond, infrared spectra exhibited unobservable (**1**−**3**) or extremely weak alkyne

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(12) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(13) Reaction conditions could be optimized to obtain aceanthrylene in better than 80% yield, see ref 10 and: Dang, H.; Levitus, M.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, In press.

(14) Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089−3092.

(15) Stevens, A. M.; Richards, C. J. *Tetrahedron lett.* **1997**, *38*, 7805−7808.

(16) Pugh, C.; Percec, V. *Polym. Bull.* **1990**, *23*, 177−184.

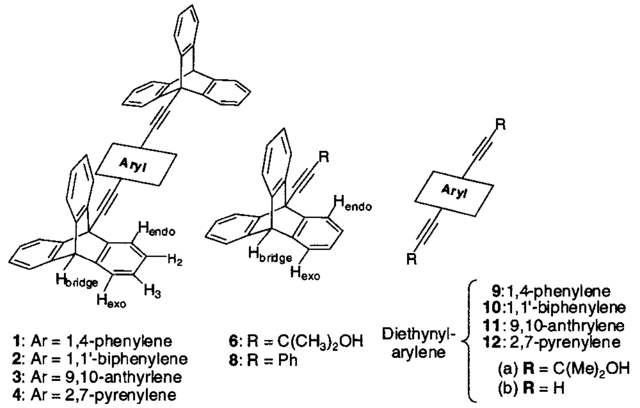
(17) (a) Coonor, D. M.; Allen, S. D.; Collar, D. M.; Litta, D. M.; Shiraldi, D. A. *J. Org. Chem.* **1999**, *64*, 6888−6890. (b) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1986**, *51*, 2847−2848.

Table 1. ^{1}H NMR Chemical Shifts of Rotors **1**−**4** and Several Model Compounds[a]

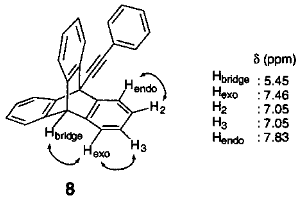
signal	1	2	3	4	8	6
H bridge	5.51	5.39	5.53	5.47	5.45	5.40
H_2, H_3	7.14	7.03	7.11	7.10	7.058, 7.060	7.03
H_{exo}	7.47	7.37	7.46	7.43	7.40	7.37
H_{endo}	7.86	7.76	8.03	7.93	7.81	7.66
H_{aryl}[b]	7.92	7.78, 7.91	7.70, 9.00	8.19, 8.60	7.48, 7.83	
diethynylarylene	(**9a**) 7.34[c]	(**10a**) n.a.[d]	(**11a**) 7.67, 8.59[e]	(**12a**) 8.00, 8.22[f]		

[a] Chemical shifts in $C_2D_2Cl_4$ except **2**, which was measured in a mixture of $C_2D_2Cl_4$:CS_2 = 3:1. [b] Hydrogens in aromatic rotor. [c] MacBride, J. A. H.; Wade, K. *Synth. Commun.* **1996**, *26*, 2309−2316. [d] Wu, X.; Dirlikov, S. K. *Polym. Mater. Sci. Eng.* **1989**, *60*, 762−766; NMR data not reported. [e] Schmieder, K.; Levitus, M.; Garcia-Garibay, M. A. *J. Phys. Chem.* **2002**, *106*, 1551−1556. [f] Inouye, M.; Itoh, M.-A. S.; Nakazumi, H. *J. Org. Chem.* **1999**, *64*, 9393−9398.

Scheme 5



Scheme 6



8

stretching bands (**4**, 2230 cm^{-1}). The NMR spectra were acquired in $C_2D_2Cl_4$ for **1**, **3**, and **4** and in mixtures of $C_2D_2Cl_4$:CS_2 (3:1) in the case of **2** (Scheme 5 and Table 1). Fast rotation about the aryl−alkyne single bonds in solution was deduced from the dynamically averaged 3-fold symmetry of the triptycyl groups and the 2-fold symmetry of the four aromatic rotors in all cases. Chemical shift assignments for compounds **1**−**4** were carried out by analogy with those of compound **8**. Hydrogen signals in the triptycyl group were assigned by 2D-NOESY taking advantage of the easily recognized bridgehead hydrogen (Scheme 6).

Carbon resonances were assigned by a 2D HMQC experiment by taking advantage of the previously assigned hydrogen signals. The alkyne substituents at the bridgehead position of the triptycene core change the spin system from AA′BB′ in the parent hydrocarbon to a more asymmetric ABMX pattern. The bridgehead hydrogen of **8** has a chemical shift of 5.45 ppm and signals corresponding to hydrogens at positions 2 and 3 of the triptycene core (H_2 and H_3 in Scheme 6) appear at δ 7.05. Signals corresponding to H_{exo} occur at δ 7.46 and signals of H_{endo} are deshielded to δ 7.83 (Scheme 6). Although a solvent effect is responsible for a systematic 0.1 ppm shielding in all the signals of **2**, a comparison of the ^{1}H chemical shifts of molecular rotors **1**−**4** indicates that significant differences occur only for the aromatic rotors and the *endo*-hydrogens. Variations in the chemical shifts of $H_{2,3}$ and H_{exo} from one compound to another are within 0.1 ppm. Analysis of the data shown in Table 1 shows that magnetic anisotropic effects from the alkyne and ring currents of the central aromatic rotor have a deshielding effect on the H_{endo} signal.[18] Assuming linearly additive effects, and based on the difference between the *endo*- and *exo*-hydrogens in ethynyl triptycene **6** (Scheme 5), one may conclude that the magnetic anisotropy of the triple bond alone causes a shift of −0.29 ppm. The ring current effect of the aromatic groups facing the triptycyl *endo*-hydrogens can be estimated by subtracting the chemical shift of the *endo*-hydrogen of **6** (δ 7.66 ppm) from that of the *endo*-hydrogen in each arylethynyltriptycene. For example, the field effect of a phenyl group in **1** can be estimated as $\delta H_{endo}(\mathbf{1}) - \delta H_{endo}(\mathbf{6}) = 7.86 - 7.66 = 0.2$ ppm. Similar arithmetics for **3** and **4** give values of 0.37 and 0.27 ppm, respectively. The larger field effects of anthryl and pyrenyl groups in **3** and **4** probably reflect their greater π-surface. The signals of the aromatic groups of **1**−**4** are also deshielded by the reciprocating field effect of the triptycenes. The value obtained by subtracting the chemical shift of the aromatic signals in **1**, **3**, and **4** from those of model arylalkynes **9a**, **11a**, and **12a** is 0.59 in all cases (Table 1). This suggests that the triptycyl group exerts the same field effect on all the aromatic rotors.

The ^{13}C NMR spectra of compounds **1**−**4** obtained at 125 MHz at ambient temperature were also consistent with a dynamically averaged structure. Triptycyl signals were also assigned by correlation with those of compound **8**. Carbon atoms in the two nonequivalent halves of the triptycenes were separated by ~0.5 ppm. Bridgehead carbons in **8** resonate at 53.55 and 53.29 ppm. Aromatic signals corresponding to C_2 and C_3 occur at 125.19 and 125.68 ppm. The signals corresponding to C_{endo} and C_{exo} appear at 122.53 and 123.42 ppm, respectively. Nonprotonated aromatic triptycyl signals resonate at 144.43 and 144.35 ppm. Similar shifts were observed for compounds **1**−**4**.

3.2. Aryl Group Rotation. The space-filling models in Figure 2 suggest that the conformational space of molecular rotors **1**, **2**, and **4** should be uniquely determined by the energetics of rotation about sp−sp^3 and sp−sp^2 single bonds. In contrast, because of the close proximity between the two peripheral triptycenes and the central anthracene, some steric hindrance may be expected in the case of compound **3**. In contrast to the well-documented rotation about single bonds involving sp^3- and sp^2-hybridized carbon atoms,[19] little is known about the energetics of rotation about single bonds involving sp-hybridized carbons. A handful of experimental and computational studies

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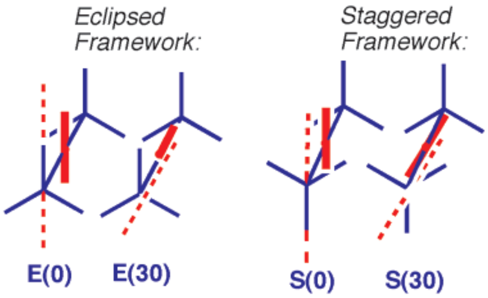
(18) Günther, H. *NMR Spectrosocopy. Basic Principles, Concepts, and Applications in Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1995; Chapter 4.

(19) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.

Scheme 7



reported in the past few years suggest that rotation of groups attached to carbon−carbon triple bonds should be essentially frictionless.[20] To gain some insight into the ground-state rotational potential of axially substituted diethynyl arenes, we analyzed compounds **1** and **3** with the semiempirical AM1 method.[21]

The conformational motions of compounds **1**−**4** can be defined in terms of the dihedral angles formed by the planes of the two triptycyls with respect to each other, and with respect to the plane of the central arylene group (Scheme 7). The relative position of the two triptycyls can be illustrated by projections along an axis connecting the two bridgehead carbons. These are shown in Scheme 7 with the tryptycene framework represented in blue and the arylene group in red. These projections reveal structures that are analogous to those of ethane. The triptycyl groups may be eclipsed E(Θ), staggered S(Θ), or have an infinite number of structures in between. One can define the orientation of the central rotor by a dihedral angle Θ, given by the planes of the arylene rotor and the plane of a benzene ring in the reference triptycene.

Calculations with the AM1 method in the case of compound **1** predicted remarkably flat energy surfaces. Minimizations that started with arbitrary dihedral angles between triptycyl and phenylene groups ended locally with energy differences of less than 0.05 kcal/mol. Varying the relative orientation of the two triptycyl groups made no difference on the calculated energies. Conformations E(0) and S(0) are predicted to be within 0.004 kcal/mol. The energy profile obtained by rotation of the phenylene group with a framework that has the two triptycenes eclipsed, E(Θ), is shown in Figure 3 along with marks that indicate the value of RT for $T = 300$ K. While the accuracy and resolution of these results must be questioned, rotation of the triptycyl and phenylene groups in the ground state should be essentially frictionless. These calculations predict that compound **1** should be a free rotor at temperatures as low as 25 K. Similar results were obtained for compounds **2** and **4**.

In contrast to compounds **1**, **2**, and **4**, which have an essentially flat rotational potential, AM1 minimizations with compound **3** lead to two structures with the triptycyl groups eclipsed [E(0), E(30)] and one with the triptycyls staggered [S(30)]. The energies of conformers S(30) and E(30) (Figure 4a,b) are indistinguishable from each other (374.77 kcal/mol), and only 0.74 lower in energy than that of conformer E(0) [Figure 4d]. The maximum point in the rotational surface, 3.93 kcal/mol above S(30) and E(30), is given by the structure of S(0) [Figure 4c]. This rotamer has the plane of the anthracene group aligned with one of the aromatic planes of the each of the periferal triptycyls, and experiences close contacts with both of them. These results are in good qualitative agreement with dynamically averaged ^{1}H NMR spectra measured in solution, which indicate a rapid conformational equilibrium.

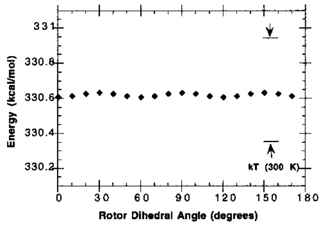


Figure 3. Changes in energy (AM1, kcal/mol) of rotor **1** as a function of phenylene rotation in a framework of eclipsed triptycyls. The minimum corresponds to E(0) and the maximum to E(30) (Scheme 7).

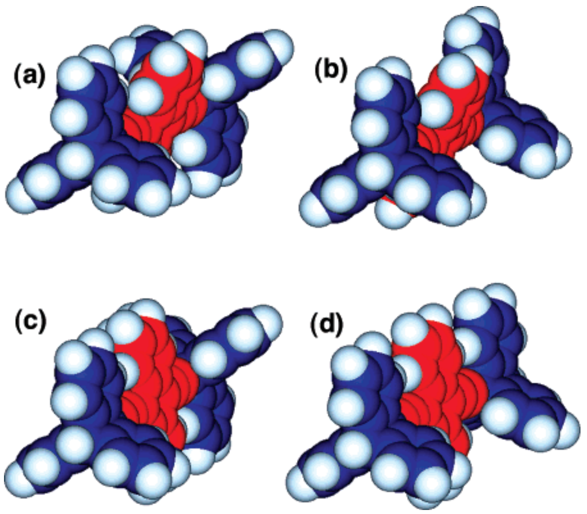


Figure 4. Space-filling models of rotamers of compound **3**: (a) S(30), (b) E(30), (c) S(0), and (d) E(0). Please see Scheme 7 for notation.

3.3. X-ray Studies. Although molecular rotors **1**−**4** crystallize readily from a wide variety of solvents, only crystals of **1** have been of suitable quality for single-crystal X-ray diffraction analysis. The X-ray structure of **1** was solved and analyzed to obtain some insight into the packing preferences of molecular rotors with triptycene frameworks. Crystallographic parameters and refinement data are included in Table 2. ORTEP diagrams of the molecular and packing structures are included in Figures 5 and 6, and details of close-packing interactions are shown in Figure 7. Crystals grown from *m*-xylene incorporated solvent molecules in a 1:1 stoichiometry. Although crystals of **1** resisted melting up to 400 °C, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicated loss of *m*-xylene between 120 and 160 °C. The structure of the solvate was solved in the triclinic space group $P\bar{1}$ with two molecules per unit cell. Compound **1** crystallizes with the two triptycyls in a nearly eclipsed conformation with the plane of the phenylene group closely aligned with one of the aromatic planes of the flanking triptycenes. The point group of **1** deviates very slightly from C_{2v} to C_1 symmetry. Instead of being perfectly eclipsed, the aromatic planes of the two triptycyls form a dihedral angle of 0.6° and the two alkyne bonds deviate from collinearity by 1.1° (Figure 5).

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(20) (a) Saebo, S.; Almolof, J.; Boggs, J. E.; Stark, J. G. *J. Mol. Struct. (THEOCHEM)* **1989**, *200*, 361−373. (b) Abramenkov, A. V.; Almenningen, A.; Cyvin, B. N.; Cyvin, S. J.; Jonvik, T.; Khaikin, L. S.; Rommingin, C.; Vilkov, L. V. *Acta Chem. Scand.* **1988**, *A42*, 674−678. (c) Sipachev, V. A.; Khaikin, L. S.; Grikina, O. E.; Nikitin, V. S.; Traettberg, M. *J. Mol. Struct.* **2000**, *523*, 1−22.

(21) *Spartan*, V2−4.0; Wavefunction, Inc.: 18401 von Karman Ave., Suite 210, Irvine, CA 92715.

Table 2. Crystallographic Parameters for Phenylene Rotor **1**

empirical formula	$C_{50}H_{30}{\cdot}C_8H_{10}$
formula weight	630·106
crystal system	triclinic
space group	$P\bar{1}$
Z	2
size, mm^3	0.1 × 0.2 × 0.45
color, morphology	colorless prism
temperature, K	100(2)
unit cell dimensions	
a, Å	11.955(2)
b, Å	12.723(3)
c, Å	14.685(3)
α, deg	65.016(4)
β, deg	77.582(4)
γ, deg	84.540(4)
V, Å^3	1977.3(7)
D_c, Mg/m^3	1.193
total no. of reflcns	13165
no. of independent reflcns	9143
[R(int) = 0.0691], [$I > 2\sigma(I)$]	
$R1$	0.0705
$wR2$	0.1615

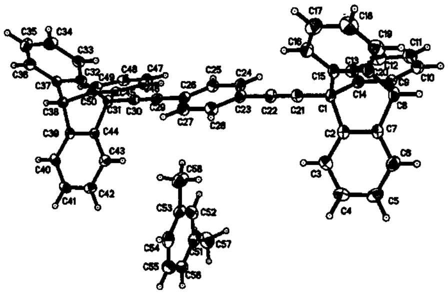


Figure 5. Ortep diagram of the asymmetric unit of rotor **1**, which includes one molecule of *m*-xylene.

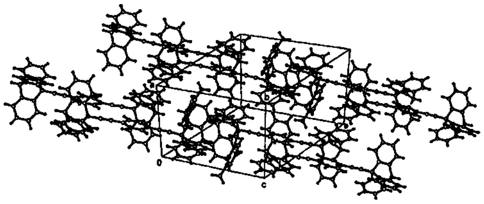


Figure 6. Packing diagram of rotor **1** illustrating a unit cell. All molecules of rotor **1** are aligned in the same direction.

As expected for a rigid, rodlike structure with a length-to-width ratio of ca. 2.2, the packing structure of rotor **1** is characterized by having all molecules aligned in the same direction (Figure 6). Adjacent molecules fit their voids and protuberances, or interdigitate very tightly, with solvent molecules acting as spacers (Figures 6 and 7). Although rotation in solution and in the gas phase may be essentially frictionless (vide supra), rotation of the phenylene group in the solid state is very strongly hindered. As illustrated by a projection along the molecular long axes in Figure 7a and by top space-filling views in Figure 7b, the rotational freedom of a reference phenylene R (shown in red in Figure 7) is restricted by the triptycyl groups from three close neighbors, labeled A, B, and C (all in blue), and the methyl group of a *m*-xylene molecule (in turquoise). The four close contacts of the reference rotor may be described as follows: (i) The plane of the phenylene group of R bisects the angle formed by two benzene rings of a triptycene in B. (ii) Phenylene R interdigitates with a triptycene of molecule C by aromatic face-to-face and edge-to-face contacts. (iii) The left flank of the phenylene group in Figure 7a is covered by the edge of a triptycyl group in molecule A and (iv) by the methyl group of a *m*-xylene. The top views in Figure 7b illustrate the location of the solvent molecules, acting as spacers, and the relative displacement of molecules A, B, and C with respect to the long axis of the reference molecular rotor (R), reproduced in the same position to analyze each pair.

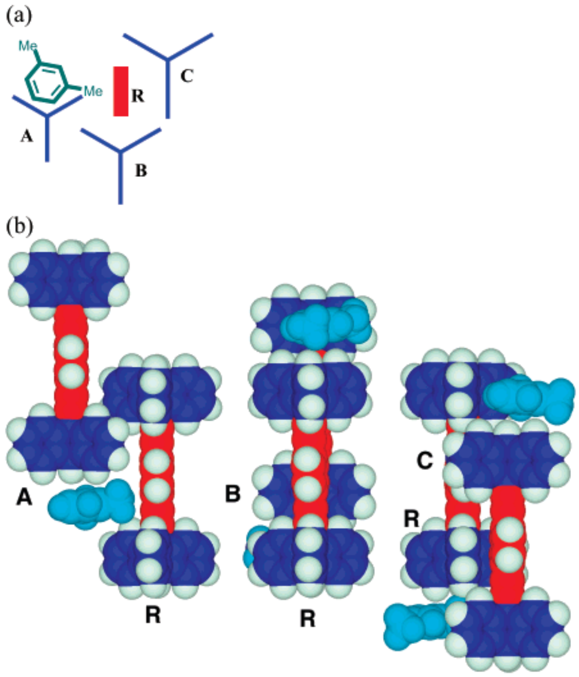
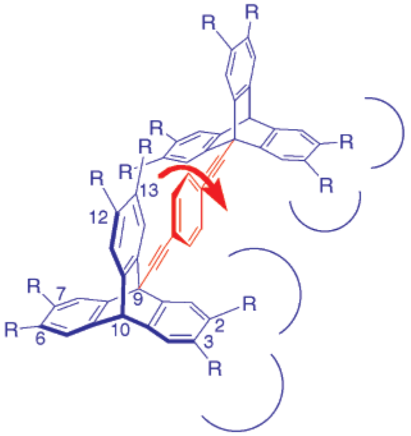


Figure 7. (a) Close packing interactions around the phenylene group of rotor **1** (in red) shown by a projection along the principal molecular axis. A solvent molecule is shown in turquoise and triptycyl groups in blue. (b) Top view of space-filling models showing close packing interactions between the phenylene group in **1** and its close neighboring molecules A, B, and C, as labeled in the top diagram. The reference molecule is labeled R.

Scheme 8



The close packing interactions that most severely hinder the rotation of the phenylene group come from tight interdigitation of adjacent molecules. Interdigitation occurs as the protruding triptycenes fill in the voids left by the smaller phenylene rotors. It is worth noting that this interaction is accompanied by close contacts between hydrogens at C2, C3, C6, C7, C12, and C13 of adjacent triptycenes (Scheme 8). This observation suggests that analogous compounds with bulky substituents at those positions should not interdigitate as efficiently. At the same time, as illustrated in Scheme 8, bulky substituents at those positions should help prevent the inclusion of solvent molecules near the phenylene rotor. The synthesis of these compounds by the convergent procedure described in this paper will require the use of 2,3,6,7-tetrasubstiuted anthracenes and 3,4-disubstituted anthranylic acids.

4. Conclusions

We have developed a simple convergent procedure for the synthesis of molecular rotors consisting of aromatic groups with two axial alkynes linked to two bulky triptycenes. The molecular rotors reported here, with 1,4-phenylene (**1**), 1,4′-1,1′-biphenylene (**2**), 9,10-anthracenylene (**3**), and 2,7-pyrenylene groups (**4**), were fully characterized by conventional spectroscopic methods. Semiempirical calculations with the AM1 method indicate that rotation about tryptycene−alkyne and aryl−alkyne single bonds should be essentially frictionless in the gas phase. Rapid rotation in solution was deduced in all cases from a dynamically averaged ^{1}H and ^{13}C NMR spectra. Although compounds **1**−**4** formed insoluble crystals, only those of compound **1**, grown from *m*-xylene, were suitable for single-crystal X-ray diffraction analysis. Compound **1** crystallized in a near C_{2v} conformation with the plane of the phenyl group eclipsed with one of the three aromatic planes of each of the two flanking triptycenes. As expected from its rigid, rodlike structure, compound **1** packs in a low symmetry space group ($P\bar{1}$) with all molecules aligned in the same direction. Rotation of the phenylene group of **1** in the solid state is prevented by interdigitation of adjacent molecules and by close contacts with the solvent of crystallization. Analysis of the packing structure of **1** suggests that interdigitation may be prevented by substituents at C2, C3, C6, C7, C12, and C13. Work in progress is directed to the synthesis of such compounds and to the characterization of their rotational dynamics in solution and in crystals. A photophysical characterization of compounds **1**−**4**, including their UV−vis dichroism and fluorescence depolarization, is also in progress.

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Supporting Information Available: Stereoscopic data of compounds **1**−**4** and X-ray data tables for rotor **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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