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Twin-Rotor System Created on a [4]Radialene Frame[†]

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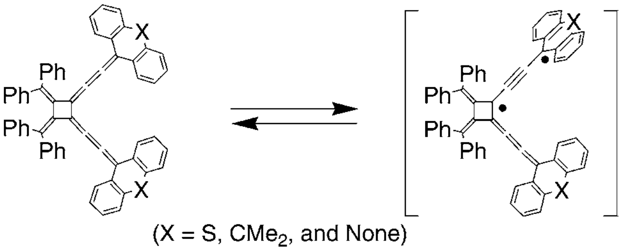
ABSTRACT



Three extended [4]radialenes with two tricyclic rings connected with exocyclic butatriene units have been synthesized. The compounds, possessing thioxanthene and dihydroanthracene moieties as the terminal substituents, show a fast rotation around the butatriene bonds at ambient temperatures ($\Delta G^{\ddagger} = 13.7$ and 14.9 kcal/mol, respectively). In contrast, the fluorene-substituted analogue shows a much higher rotational barrier ($\Delta G^{\ddagger} = 17.8$ kcal/mol) of the butatriene bonds due to the reduced steric repulsion between the two fluorene moieties at the ground state.

There has been considerable recent interest in the restricted rotation of single and double bonds because of their potential use in molecular-scale motors, thermochromic devices, molecular switches, and chemosensors.[1] Thus, the thermal and photochemical rotation of double bonds has been employed for the bottom-up construction of molecular motors.[2,3] In addition, overcrowded homomerous and heteromerous bistricyclic aromatic enes have been synthesized to investigate thermochromism, photochromism, and photo- and thermoswitchable properties.[4] We now report on a twin-rotor system with a very low energy barrier to the rotation of two cumulenic double bonds linked to a crowded [4]radialene skeleton.

Previously, we reported the nickel-catalyzed dimerization of tetraarylhexapentaenes to afford deep blue [4]radialene derivatives extended by cumulative double bonds.[5] We also reported that these [4]radialenes were synthesized by way of a stepwise route.[5] We have now synthesized three new [4]radialenes **1a**−**c** because the proximity of the terminal aromatic moieties may exhibit intriguing features or properties and because high HOMO or low LUMO levels of these [4]radialenes may result in a narrow HOMO−LUMO gap and an unusual light absorption behavior.

The extended [4]radialenes **1a**−**c** were synthesized using the pathway outlined in Scheme 1. The palladium-catalyzed cross-coupling reaction of 1,2-dibromo-3,4-bis(diphenyl-

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[†] This paper is dedicated to Professor Soichi Misumi on the occasion of his 77th birthday.

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(1) For recent examples, see: (a) Geertsema, E. M.; Koumura, N.; ter Wiel, M. K. J.; Meetsma, A.; Feringa, B. L. *Chem. Commun.* **2002**, 2962−2963. (b) Raker, J.; Glass, J. E. *J. Org. Chem.* **2002**, *67*, 6113−6116. (c) Dominguez, Z.; Dang, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 7719−7721. (d) Levy, A.; Biedermann, P. U.; Agranat, I. *Org. Lett.* **2000**, *2*, 1811−1814. (e) Chen, C.-T.; Chou, Y.-C. *J. Am. Chem. Soc.* **2000**, *122*, 7662−7672. (f) Koumura, N.; Geertsema, E. M.; Meetsma A.; Feringa, B. L. *J. Am. Chem. Soc.* **2000**, *122*, 12005−12006.

(2) (a) Feynman, P. P. In *Miniaturization*; Gilbert, H. D., Ed.; Reinhold: New York, 1961. (b) Drexler, K. E. *Nanosystems: Molecular Machinery, Manufacturing and Computation*; Wiley: New York, 1992.

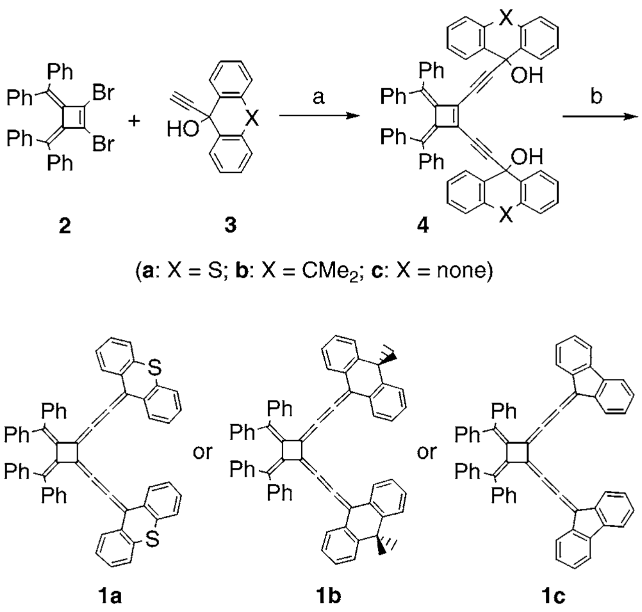
(3) (a) Kelly, T. R.; De Silva, R. A. *Nature* **1999**, *401*, 150−152. (b) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152−155.

(4) For a review, see: Biedermann, P. U.; Stezowski, J. J.; Agranat, I. *Eur. J. Org. Chem.* **2001**, 15−34.

(5) Iyoda, M.; Kuwatani, Y.; Oda, M. *J. Am. Chem. Soc.* **1989**, *111*, 3761−3762.

10.1021/ol030055g CCC: $25.00

Scheme 1. Synthesis of Extended [4]Radialenes **1a**−**c**[a]



(**a**: X = S; **b**: X = CMe_2; **c**: X = none)

[a] Reagents and conditions: (a) $PdCl_2(PPh_3)_2$, CuI, Et_3N, 85 °C, 2 h; (b) $SnCl_2{\cdot}2H_2O$, HCl, ether, −65 °C, 30 min.

methylene)cyclobutene (**2**)[6] with the propargyl alcohols **3a**−**c** proceeded under Sonogashira's conditions to afford the corresponding enediynediols **4a**−**c** in 37, 62, and 68% yields, respectively. The reductive dehydroxylation of **4a**−**c** at low temperatures gave the corresponding [4]radialene derivatives **1a**−**c** in 93, 61, and 49% yields, respectively.[7]

These new extended [4]radialenes **1a**−**c** exhibited a deep color in solution (**1a**, dark brown; **1b**, dark green; **1c**, dark blue). The electronic spectra of **1a** and **1b** showed intense absorption bands tailing up to the near infrared region with maxima of 754 nm (log ϵ 4.47) and 688 nm (log ϵ 4.44), respectively. The corresponding absorption band of **1c** shifted hypso- and hypochromically with the absorption maximum at 583 nm (log ϵ 3.93). Since the octaheptaene possessing two fluorene moieties as the terminal groups showed absorption maxima at 540 and 597 nm,[8] the longest absorption maxima of **1a**−**c** may mainly reflect the maximum conjugation of the π-system, together with the effect of twisted double or cumulenic bonds.

To elucidate the structural features of **1**, X-ray crystallographic analysis of **1a** was carried out.[9] As shown in Figure 1, **1a** has approximate C_2-symmetry with a 2-fold axis passing through the midpoints of the C(1)−C(2) and C(3)−C(4) bonds. The four-membered ring is almost planar, in contrast to the puckered geometries hitherto reported for the substituted [4]radialenes.[10] The four phenyl groups are twisted in the same sense to adopt a half-propeller conformation, and the two diphenylmethylene groups repel each other and buttress the butatriene bonds so that the thioxanthene rings get closer and significantly twist to relieve the repulsion. The butatriene bonds bend out of the four-membered ring plane by 6.5−7.1°, and the two thioxanthene rings are twisted by 14.5 and 25°, the face-to-face distance between the closely located carbons being 3.42−3.46 Å (Figure 1b). Interestingly,

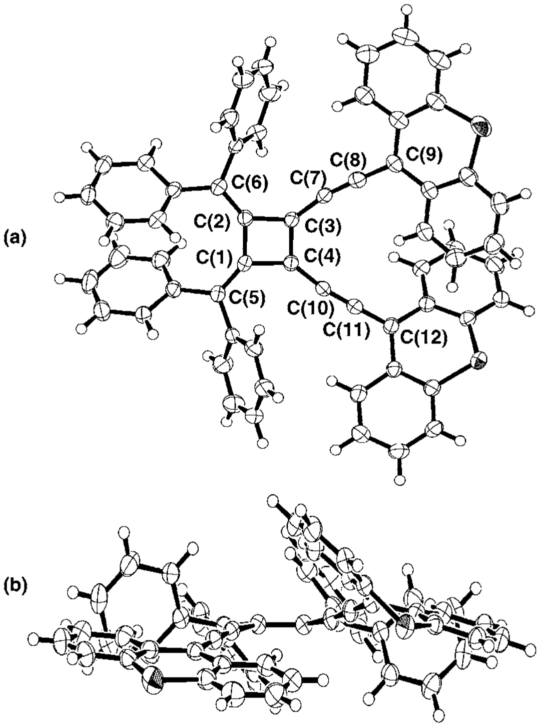


Figure 1. ORTEP drawing of extended [4]radialene **1a**. (a) Top view. (b) Side view of the two thioxanthene moieties. Selected bond lengths (Å): C(1)−C(2), 1.525(3); C(2)−C(3), 1.485(3); C(3)−C(4), 1.459(3); C(4)−C(1), 1.490(3); C(1)−C(5), 1.353(3); C(2)−C(6), 1.353(3); C(3)−C(7), 1.364(3); C(7)−C(8), 1.218(3); C(8)−C(9), 1.375(3); C(4)−C(10), 1.357(3); C(10)−C(11), 1.216(3); C(11)−C(12), 1.361(3). Selected bond angles (deg): C(1)−C(2)−C(3), 88.8(2); C(2)−C(3)−C(4), 91.4(2); C(3)−C(4)−C(1), 91.2(3); C(1)−C(2)−C(6), 140.1(2); C(3)−C(2)−C(6), 130.9(2); C(2)−C(3)−C(7), 139.4(2); C(4)−C(3)−C(7), 128.3(2); C(1)−C(4)−C(10), 138.7(2); C(3)−C(7)−C(8), 169.0(3); C(7)−C(8)−C(9), 177.7(3).

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(6) (a) Toda, F.; Ishihara, H.; Akagi, K. *Tetrahedron Lett.* **1969**, 2531−2534. (b) Toda, F.; Kumada, K.; Ishiguro, N.; Akagi, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3535−3539.

(7) All new compounds were fully characterized by spectroscopic and elemental analyses.

(8) Kuhn, R.; Zahn, H. *Chem. Ber.* **1951**, *84*, 566−570.

(9)) Crystal data for **1a**: $C_{60}H_{36}S_2$, MW = 821.06, monoclinic, space group $P2_1/c$ (No. 14), a = 14.236(4) Å, b = 11.462(5) Å, c = 25.810(6) Å, β = 92.39(3)°, V = 4207(2) Å^3, Z = 4, D_c = 1.296 g/cm^3, $F(000)$ = 1712, μ(Mo Kα) = 1.69 cm^{-1}, R = 0.048, R_w = 0.052, GOF = 1.71. All measurements were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα (λ = 0.71069 Å) radiation at −100 °C. Among a total of 10 555 reflections measured, 9647 were unique, and the observed ($I > 3.00\sigma(I)$) 5592 reflections were used for the refinement. The crystal structure was solved by a direct method and refined by the full matrix least-squares method.

(10) (a) Iyoda, M.; Tanaka, S.; Otani, H.; Nose, M.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8494−8500. (b) van Remoortere, F. D.; Boer, F. P. *J. Am. Chem. Soc.* **1970**, *92*, 3355−3360. (c) Hart, H.; Ward, L.; Tanaka, K.; Toda, F. *Tetrahedron Lett.* **1982**, 2125−2128. (d) Sugimoto, T.; Awaji, H.; Misaki, Y.; Yoshida, Z.; Kai, Y.; Nakagawa, H.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 5792−5793. (e) Nader, F. W.; Waker, C.-D. *Ang. Chem., Int. Ed. Engl.* **1985**, *24*, 852−853. (f) Matsuo, T.; Sekiguchi, A.; Ichinohe, M.; Ebata, K.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1705−1711.

the butatriene units show clear bond alternations with shorter C(sp)−C(sp) bonds (averaged 1.217 Å) and longer C(sp)−C(sp^2) bonds (averaged 1.364 Å) as compared with the corresponding bond lengths (1.260 and 1.348 Å, respectively) of tetraphenylbutatriene,[11] presumably due to the bending and twisting of the butatriene bonds in **1a**.

Since we could not carry out the X-ray crystallographic analysis for **1b** and **1c**, density functional calculations [B3LYP/6-31G(d)] were performed for these compounds as well as with **1a** (Figure 2). All of the compounds **1a**−**c** are C_2-symmetric. The calculated structure of **1a** agrees well with that obtained by the X-ray analysis. The structure of **1b** is calculated to be similarly deformed as **1a**, and the two dihydroanthracene rings are twisted and mutually overlapped. The distance between the closest carbons is 3.61 Å. In contrast, the molecular deformation in **1c** is less noticeable, the twist angles of the fluorene rings with the four-membered ring plane being ca. 11° and the distance between the two closest hydrogens being 2.3 Å.

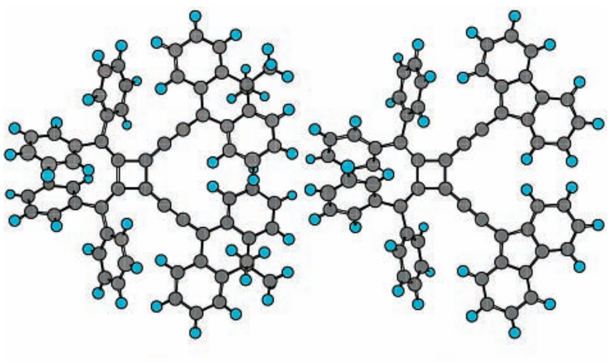

Figure 2. Optimized molecular structures of **1b** and **1c** (B3LYP/6-31G(d)).

The ^{1}H NMR spectrum of **1a** was dependent on the temperature, as shown in Figure 3. The signals of the phenyl groups were sharp throughout the temperature range examined, indicating that the rotation of the phenyl groups is fast on the NMR time scale, and their chemical shifts are similar to those in **2**. The signals of the thioxanthene moieties were quite broad at ambient temperatures, split into eight separate signals upon lowering the temperature, and coalesced into four signals at high temperatures. This behavior was reasonably ascribed to the internal rotation about the cumulene bonds. Decoupling and qualitative saturation transfer experiments at low temperatures enabled the signal assignments given in Figure 3. Coalescence of the H^4 and H^5 signals ($\Delta\nu = 52$ Hz) took place at 15 °C, which gave a rate constant of $k_c = 116$ s^{-1}. Quantitative saturation transfer experiments (H^2 was irradiated, and H^7 was observed) at -20 ± 1 °C gave a rate constant of 3.6 ± 0.4 s^{-1}.[12] A similar temperature dependence of the ^{1}H NMR spectrum was also observed in **1b** at a higher temperature range than in **1a**. The exchange rate was estimated as $k = 3.5 \pm 0.4$ s^{-1} at 0 °C by the saturation transfer method. The free energies of activation for the cumulenic bond rotation were deduced to be $\Delta G^\ddagger = 13.7$ and 14.9 kcal/mol for **1a** (in $CDCl_3$ at −20 °C) and **1b** (in $CDCl_3$ at 0 °C), respectively.

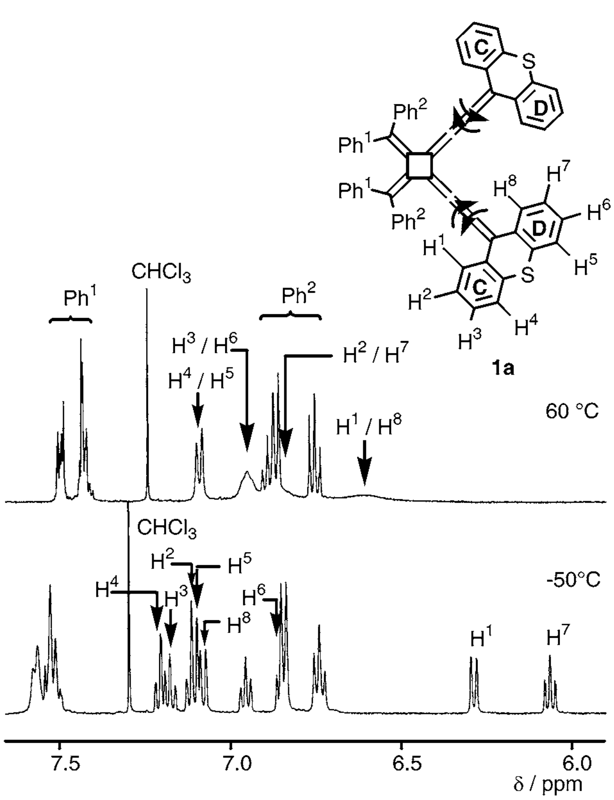

Figure 3. ^{1}H NMR spectra of **1a** in $CDCl_3$ at 60 and −50 °C.

In contrast with the cases of **1a** and **1b**, the ^{1}H NMR spectrum of **1c** at room temperature showed sharp and well-resolved signals, suggesting that the energy barrier to bond rotation in **1c** is fairly high. In fact, the free energy of activation for the rotation was found to be $\Delta G^\ddagger = 17.8$ kcal/mol in $C_2D_2Cl_4$ at 27 °C by saturation transfer studies.

To discuss the observed energy barriers, the stability of both the ground states and the transition states for rotation should be considered. As shown in Figures 1 and 2, the inner wings of the thioxanthene and dihydroanthracene rings in **1a** and **1b** significantly twist and overlap each other, the shortest C···C distance being the sum of the van der Waals radii (3.4 Å). In the case of **1c**, however, the fluorene rings do not overlap, although they are twisted to some extent because of the H···H repulsion. In accordance with these structural features, the H^7 proton shows a large upfield shift in **1a** (*δ* 6.06 at −50 °C) and **1b** (*δ* 6.03 at −30 °C) in the

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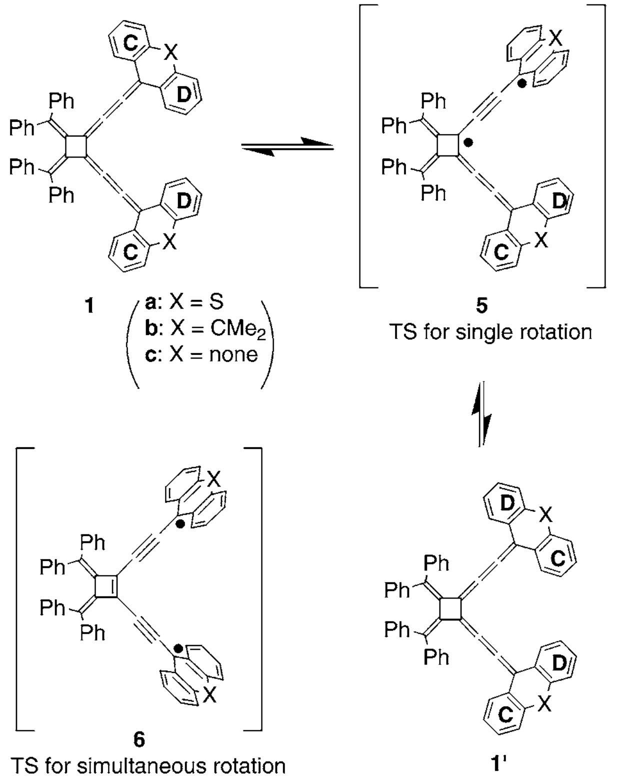
(11) Berkovitch-Yellin, Z.; Leiserowitz, L. *Acta Crystallogr. B* **1977**, *33*, 3657−3669.

(12) 2) (a) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; Chapter 4. (b) Yamamoto, G. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1967−1975.

Scheme 2. Bond Rotation of Extended [4]Radialenes **1**



^1H NMR spectra ($CDCl_3$) due to the shielding effect of the confronting aromatic ring, while the upfield shift is moderate in **1c** (δ 7.10 at 22 °C in $C_2D_2Cl_4$). These molecular deformations naturally cause the destabilization of the ground state, which will be more severe in **1a** and **1b** than in **1c**. Thus, the molecular deformations in **1a**−**c** at the ground-state allow us to estimate the order of the destabilization as **1a** ≥ **1b** > **1c**.

A unique feature of the overcrowding in **1a**−**c** is the unsymmetrical steric interactions of the aromatic rings on both terminals of the bis-cumulenic linkage, although the known barriers for the thermal bond rotation of double bonds have been mainly investigated in terms of the motion of fundamentally symmetrical olefinic and cumulenic bonds. A plausible bond rotation process is depicted in Scheme 2. The butatriene bonds will rotate one at a time by way of the transition state **5**, rather than simultaneously by way of **6**, because **6** is considered to be far less stable than **5**. This diradicaloid transition state **5** will be stabilized by conjugation of these radicals with both the tricyclic aromatic system and the extended [4]radialene frame. The contribution of the latter conjugation will be similar in **1a**−**c**, while the conjugation in the terminal moieties will significantly depend on X. In **1a**, the sulfur atom will participate in the conjugation, and the transition state for **1a** will be stabilized more effectively than those for **1b** and **1c**.

These considerations satisfactorily explain not only the fact that the rotational barriers for **1a**−**c** are much lower than those for 1,4-dialkyl-1,4-diaryl- and tetraarylbutatrienes and a bis-butatriene derivative (20−30 kcal/mol)[13,14] but also the order of the barrier, **1a** < **1b** < **1c**.

To our knowledge, the $\Delta G^{\ddagger}$ value of 13.7 kcal/mol for **1a** is the lowest so far reported for the energy barriers to rotation around an olefinic or cumulenic bond by way of a diradicaloid transition state.[4,15]

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Supporting Information Available: Experimental details for the preparation and spectroscopic data of **1**, X-ray crystallographic data of **1a**, and DFT-optimized structures of **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] (a) Kuhn, R.; Scholler, K. L. *Chem. Ber.* **1954**, *87*, 598−611. (b) Bertsch, K.; Karich, G.; Jochims, J. C. *Chem. Ber.* **1977**, *110*, 3304−3313.

[14] Rotational barrier (28.9 kcal/mol) of *p*-nitrophenyl-substituted tetraethynylethene dianion was calculated and discussed on the basis of the formation of the bis-butatriene structure: Hilger, A.; Gisselbrecht, J.-P.; Tykwinski, R. R.; Boudon, C.; Schreiber, M.; Martin, R. E.; Lüthi, H. P.; Gross, M.; Diederich, F. *J. Am. Chem. Soc.* **1997**, *119*, 2069−2078.

[15] Diphenoquinone with an azulene substituent was reported to exhibit a very low rotational barrier (14.6 kcal/mol): Bindl, J.; Burgemeister, T.; Daub, J. *Chem. Ber.* **1985**, *118*, 4934−4945.