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Synthesis and Properties of Triply-Bridged *syn*-Carbazolophanes

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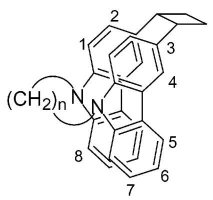
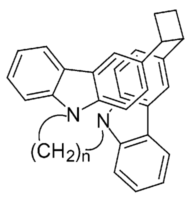
Abstract: The intramolecular [2 + 2] photocycloaddition of α,ω-bis(3,6-divinyl-*N*-carbazolyl)alkanes **3** afforded triply bridged *syn*-[2.2.*n*](3,6,9)carbazolophanes **4a**−**6a** (*n* = 4) and **4b**,**5b** (*n* = 5) composed of isomers derived from the difference in the direction of cyclobutane rings. In major isomers **4a** and **4b**, excimer fluorescence was observed, the maximum position remarkably depending on the tether length.

Carbazole is the constituent of poly(*N*-vinylcarbazole), which is well-known as a photoconductor, and the photophysical properties of its dimer model compounds[1] and polymers[2] have been extensively investigated. Poly(*N*-vinylcarbazole) affords two types of excimer fluorescence, which have been suggested to be derived from sandwich and partial-overlap excimers on the basis of the study on the two diastereomers of 2,4-di(*N*-carbazolyl)pentane,[1c] as a model polymer unit. A cyclophane composed of carbazoles, namely, carbazolophane, in which the relative arrangement of two carbazole chromophores is fixed more rigidly, is a desirable compound for the elucidation of the relationship between the chromophore arrangement and fluorescence properties. Dioxa[3.3](3,6)carbazolophane, first synthesized among carbazolophanes by Tani et al., was found to adopt an *anti*-conformation, leading to small overlap between the carbazole rings and, therefore, the absence of excimer fluorescence.[3]

We have synthesized [2.*n*]cyclophanes possessing various aromatic hydrocarbons by the intramolecular [2 + 2] photocycloadditions of bis(vinylaryl)alkanes.[4] This synthetic method is usually suitable for the preparation of *syn*-isomers; in some cases, *syn*-isomers are exclusively obtained. Recently, by using this method, [2.*n*](3,9)-carbazolophanes **1** and **2** (*n* = 4, 5) were successfully prepared from the corresponding vinyl compounds.[5] In the case of *n* = 4, *syn*-isomer **1a** as well as *anti*-isomer **2a** was obtained and isolated. These isomers displayed quite different fluorescence spectra from each other: **1a** afforded broad emission assigned as sandwich excimer fluorescence, whereas **2a** gave monomer fluorescence with vibrational structures. However, **1b** with *n* = 5 could not be isolated due to the irreversible isomerization into **2b** in solution even at room temperature. Thus, we were stimulated to examine the photoreaction of α,ω-bis(3,6-divinyl-*N*-carbazolyl)alkanes **3**, which are expected to afford triply bridged [2.2.*n*](3,6,9)carbazolophanes (*n* = 4, 5) that adopt the *syn*-conformation exclusively and suffer from no isomerization into the *anti*-conformation. In these carbazolophanes, two carbazole nuclei should be fixed more rigidly by two cyclobutane rings and an oligomethylene linkage. Here, we report the first synthesis of [2.2.*n*](3,6,9)carbazolophanes (*n* = 4, 5) and their properties.



syn-isomer
1a (n=4)
1b (n=5)



anti-isomer
2a (n=4)
2b (n=5)

The intermolecular [2 + 2] photocycloaddition of divinylarenes, such as *o*- or *m*-divinylbenzene,[6] divinylnaphthalenes,[7] and divinylphenanthrenes,[8] is known to afford [2.2]cyclophanes bridged by two cyclobutane rings. Thus, prior to examining the photoreaction of **3**, the intermolecular photocycloaddition of *N*-ethyl-3,6-divinylcarbazole (**9**) was examined for the preparation of [2.2](3,6)-carbazolophane. The photoreaction of **9** was carried out in benzene (ca. 0.1 M) with a 400 W high-pressure mercury lamp through a Pyrex filter. Unfortunately, no desired [2.2]carbazolophane was obtained, although the ^{1}H NMR spectrum of the reaction mixture indicated the formation of a cyclobutane ring. Prolonged irradiation caused only the increase in insoluble polymeric products.

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(1) (a) Johnson, G. E. *J. Chem. Phys.* **1974**, *61*, 3002. (b) Johnson, G. E. *J. Chem. Phys.* **1975**, *63*, 4047. (c) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406. (d) Masuhara, H.; Tamai, N.; Mataga, N.; De Schryver, F. C.; Vandendriessche, J. *J. Am. Chem. Soc.* **1983**, *105*, 7256.

(2) (a) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697. (b) Sakai, H.; Itaya, A.; Masuhara, H.; Sasaki, K.; Kawata, S. *Polymer* **1996**, *37*, 31.

(3) (a) Tani, K.; Tohda, Y.; Hisada, K.; Yamamoto, M. *Chem. Lett.* **1996**, 145. (b) For a recent contribution of this group on the synthesis of carbazolophanes, see: Tani, K.; Tohda, Y.; Takemura, H.; Ohkita, H.; Ito, S.; Yamamoto, M. *Chem. Commun.* **2001**, 1914. Ohkita, H.; Ito, S.; Yamamoto, M.; Tohda, Y.; Tani, K. *J. Phys. Chem. A* **2002**, *106*, 2140.

(4) (a) Nishimura, J.; Doi, H.; Ueda, E.; Ohbayashi, A.; Oku, A. *J. Am. Chem. Soc.* **1987**, *109*, 5293. (b) Nishimura, J.; Ohbayashi, A.; Doi, H.; Nishimura, K.; Oku, A. *Chem. Ber.* **1988**, *121*, 2019. (c) Nishimura, J.; Takeuchi, M.; Takahashi, H.; Ueda, E.; Matsuda, Y.; Oku, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3161. (d) Takeuchi, M.; Nishimura, J. *Tetrahedron Lett.* **1992**, *33*, 5563. (e) Nishimura, J.; Okada, Y.; Inokuma, S.; Nakamura, Y.; Gao, S. R. *Synlett* **1994**, 884. (f) Nishimura, J.; Nakamura, Y.; Hayashida, Y.; Kudo, T. *Acc. Chem. Res.* **2000**, *33*, 679.

(5) Nakamura, Y.; Kaneko, M.; Yamanaka, N.; Tani, K.; Nishimura, J. *Tetrahedron Lett.* **1999**, *40*, 4693.

(6) (a) Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. *J. Am. Chem. Soc.* **1991**, *113*, 3485. (b) Nakamura, Y.; Hayashida, Y.; Wada, Y.; Nishimura, J. *Tetrahedron* **1997**, *53*, 4593.

(7) Takeuchi, M.; Tuihiji, T.; Nishimura, J. *J. Org. Chem.* **1993**, *58*, 7388.

(8) Nakamura, Y.; Tsuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Am. Chem. Soc.* **1996**, *118*, 1006.

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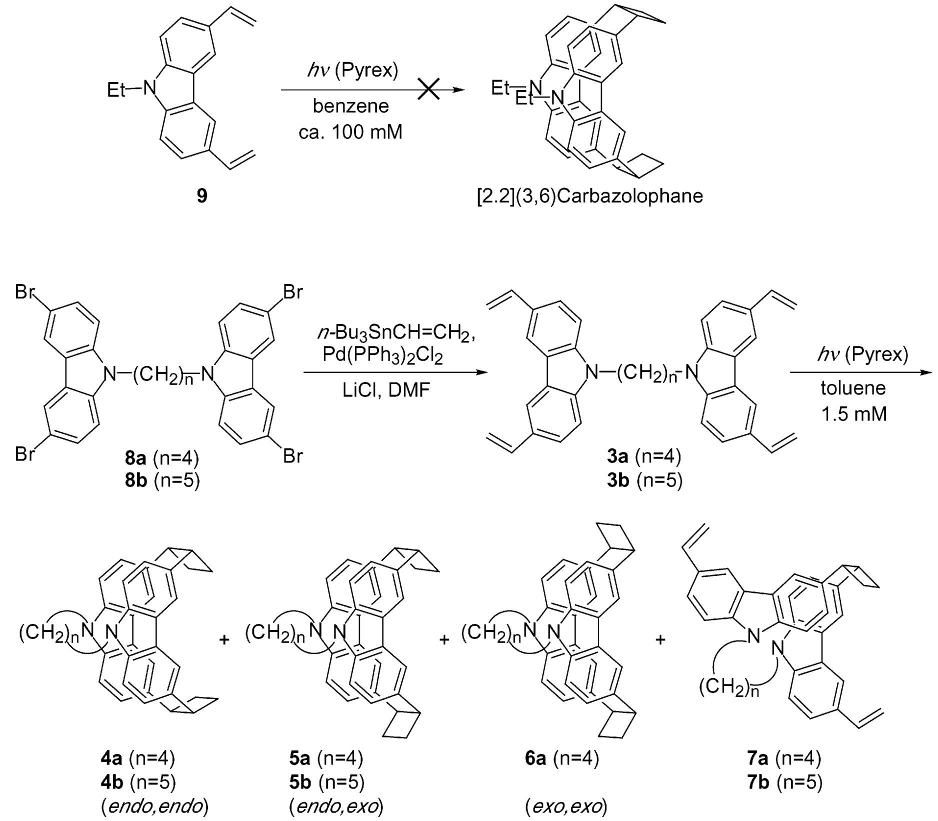
SCHEME 1



It seemed that the first cyclization proceeds to give a cyclobutane ring, whereas the second one is hindered for some reasons. Then, the synthesis of [2.2.*n*](3,6,9)-carbazolophanes was undertaken by the intramolecular photoreaction of **3**, in which two carbazole rings are connected with an oligomethylene linkage at the *N*-position (9-position).

As shown in Scheme 1, **3a**,**b**, precursors of [2.2.*n*]-(3,6,9)carbazolophanes ($n = 4, 5$), were prepared by the Stille reaction using tetrabromides **8a**,**b**[9] and tributylvinyltin. The intramolecular [2 + 2] photocycloaddition of **3a**,**b** was carried out in toluene (1.5×10^{-3} M) with a 400 W high-pressure mercury lamp through a Pyrex filter in a manner similar to that reported previously.[4] After irradiation for 35 min, the reaction mixture was purified by column chromatography on silica gel (eluent; hexane/toluene (1:1)).

The irradiation of both **3a** and **3b** provided *syn*-carbazolophanes, composed of two or three isomers derived from the difference in the direction of cyclobutane rings. Such isomers had been also obtained in the case of [2.2](3,6)phenanthrenophanes.[8] All three isomers **4a**, **5a**, and **6a** were obtained from **3a** in total 25% yield (9:3:1), and **4b** and **5b** from **3b** in 12% yield (7:1). No *exo,exo*-isomer was detected in the photoreaction of **3b**. The much lower yields than those in the case of **1** and **2** (39−77%)[5] are partly ascribable to the formation of **7a** and **7b**, which possess only one cyclobutane ring and never afford the desired carbazolophanes due to their *anti*-conformation. Major isomers **4a** and **4b** were successfully isolated by repeated recrystallization from benzene, whereas minor isomers **5a**, **6a**, and **5b** could not been isolated because of their low yields. The oligomethylene linkage connecting the nitrogen atoms apparently plays a critical role in the photoreactions of **3a** and **3b**, since the intermolecular photoreaction of **9** failed to give [2.2]carbazolophanes.

The structures of the carbazolophanes obtained were characterized mainly by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **4a** and **4b** gave a quite simple pattern, as demonstrated by the three aromatic and one methine proton peak. In the isomeric mixture, **6a** also showed a pattern quite similar to **4a** and **4b**, but the aromatic H4 (or H5) and H2 (or H7) protons were high-field ($\Delta\delta = -0.46$ ppm) and low-field ($\Delta\delta = 0.38$ ppm) shifted, respectively, compared with **4a**. Judged from the symmetry, **4a**, **4b**, and **6a** obviously adopt *endo,endo*- or *exo,exo*-configuration. Since the *endo*- and *exo*-directed cyclobutane rings induce the low-field shift of the H4 (or H5) and H2 (or H7) protons, respectively, due to the steric compression effects, the configuration of the two cyclobutane rings in **4a** and **4b** was assigned as *endo*, while those in **6a** as *exo*. Actually, the X-ray crystallographic analysis of **4a** proved the *endo,endo*-configuration (Figure 1). The ^{1}H NMR spectra of **5a** and **5b** showed six aromatic and two methine proton peaks, apparently indicating *endo,exo*-configuration. According to the X-ray crystallographic analysis of **4a**, the two carbazole rings are favorably overlapped and fixed closely by the two cyclobutane rings. The distance between the two nitrogen atoms (4.43 Å) and that between C3 atoms (2.87 Å) are comparable to those in **1a** (4.49 and 2.86 Å, respectively), while the distance between C6 atoms (2.86 Å) is much

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[9] Braun, D.; Langendorf, R. *J. Prakt. Chem.* **1999**, *341*, 128.

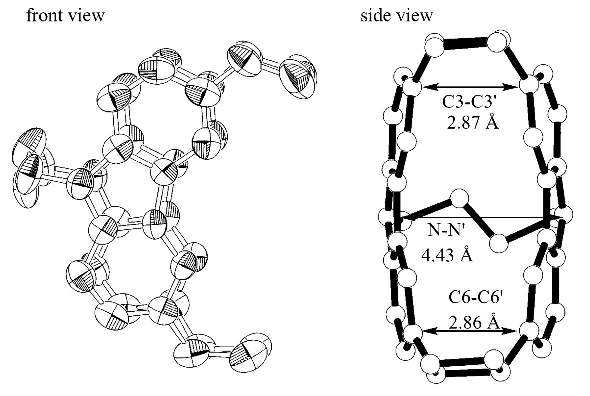

FIGURE 1. X-ray crystallographic analysis of **4a**.

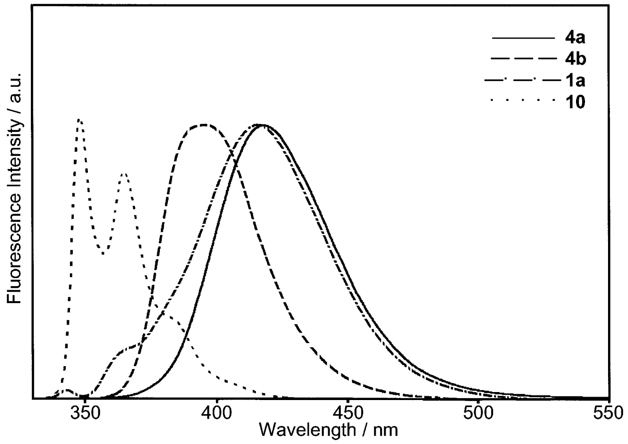

FIGURE 2. Fluorescence spectra of **4a**, **4b**, **1a**, and **10** upon 310 nm excitation in cyclohexane at room temperature.

shorter than that in **1a** (4.40 Å) due to the presence of the second cyclobutane ring.

The absorption spectra of **4a** and **4b** were quite different from that of *N*-ethylcarbazole (**10**), but similar to that of **1a**. The vibrational structures of the $S_1 \leftarrow S_0$ band were hardly detected in **4a** and **4b**. This feature results from relatively large electronic interaction between the carbazole rings overlapped with each other in the *syn*-conformation. The slight red-shift in **4a** relative to **1a** reflects the further proximity of the two carbazole rings, as demonstrated in the X-ray crystallographic analysis.

Figure 2 shows the fluorescence spectra of **4a** and **4b** measured in cyclohexane at room temperature along with those of **1a** and **10** for the comparison.[10] Both **4a** and **4b** exhibit a broad emission similar to **1a**, indicative of excimer fluorescence. In **4a**, the peak maximum is further shifted to the longer wavelength (417 nm) in comparison with **1a** (415 nm). This shift, corresponding to the absorption spectrum, can be explained by the fact that two carbazole rings are fixed closer by the second cyclobutane ring as the third bridge, though more strain is loaded on the carbazole rings. In **4b** with a pentamethylene linkage, however, the peak maximum is considerably blue-shifted (396 nm). This observation apparently results from the enhanced distance between two carbazole rings linked by a pentamethylene chain at the *N*-positions. In the optimized structure of **4b** calculated by the MM2 method, the distance between the two nitrogen atoms is 4.77 Å, which is longer than that in **4a**. Such arrangement in **4b** is obviously less suitable for the excimer formation.

In summary, triply bridged *syn*-[2.2.*n*](3,6,9)-carbazolophanes ($n = 4, 5$) (**4**−**6**) were first obtained by the intramolecular [2 + 2] photocycloaddition of **3**. In both **4a** and **4b**, excimer fluorescence was observed similar to **1a**, the maximum position depending on the tether length. The fluorescence spectra of carbazolophanes are sensitively influenced by the distance between the carbazole rings.

Experimental Section

General Methods. X-ray crystallographic analysis was made on an imaging plate diffractometer with graphite-monochromated Mo Kα radiation.

General Procedure for the Preparation of Vinyl Compounds 3a,b. To a solution of tetrabromide **8a**[9] (3.00 g, 4.26 mmol) in DMF (50 mL) were added tributylvinyltin (8.10 g, 25.6 mmol), bis(triphenylphosphine)palladium(II) (1.20 g, 1.70 mmol), lithium chloride (3.58 g, 85.2 mmol), and a few crystals of 4-*tert*-butylcatechol as a polymerization inhibitor. The resulting suspension was heated at 80 °C for 2 h and cooled to room temperature. The solution was treated with a large excess of 20% aqueous potassium fluoride solution and stirred vigorously for 2 h and filtrated. The aqueous phase was extracted with toluene three times, and the combined extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 (2:1)) to afford **3a** as a colorless solid (826 mg, 39%).

3a: colorless solid; mp 193.0−193.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 8.10 (d, $J = 2.0$ Hz, 4H), 7.52 (dd, $J = 8.6, 2.0$ Hz, 4H), 7.16 (d, $J = 8.6$ Hz, 4H), 6.90 (dd, $J = 17, 11$ Hz, 4H), 5.78 (d, $J = 17$ Hz, 4H), 5.21 (d, $J = 11$ Hz, 4H), 4.17 (m, 4H), 1.92 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 140.43, 137.34, 129.18, 124.21, 123.09, 118.51, 111.27, 108.68, 42.82, 26.65; HRMS (FAB) *m*/*z* found 492.2562; calcd for $C_{36}H_{32}N_2$ (M^+) 492.2565.

3b: yield 48%; colorless solid; mp 77.0−77.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 8.11 (d, $J = 1.5$ Hz, 4H), 7.52 (dd, $J = 8.7, 1.5$ Hz, 4H), 7.22 (d, $J = 8.7$ Hz, 4H), 6.91 (dd, $J = 18, 12$ Hz, 4H), 5.78 (d, $J = 18$ Hz, 4H), 5.22 (d, $J = 12$ Hz, 4H), 4.20 (m, 4H), 1.86 (m, 4H), 1.26 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 140.54, 137.39, 129.08, 124.19, 123.034, 118.44, 111.20, 108.72, 42.95, 28.88, 25.20; HRMS (FAB) *m*/*z* found 506.2722; calcd for $C_{37}H_{34}N_2$ (M^+) 506.2722.

General Procedure for the Photoreactions of 3a,b. Photoirradiation of **3a** (167 mg, 0.34 mmol) was carried out with a 400 W high-pressure mercury lamp through a Pyrex filter in toluene (226 mL) under a nitrogen atmosphere for 35 min. Insoluble substance was filtered off, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, hexane/toluene (1:1)) to give an isomeric mixture of **4a**, **5a**, and **6a** (42 mg, 25%) as a white solid. A small amount of **4a** was isolated by recrystallization from benzene.

4a: colorless prisms (hexane/benzene); mp >300.0 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, $J = 1.7$ Hz, 4H), 6.68 (d, $J = 8.5$ Hz, 4H), 6.49 (dd, $J = 8.5, 1.7$ Hz, 4H), 4.33 (m, 4H), 3.94 (m, 4H), 2.89 (m, 4H), 2.75 (m, 4H), 1.35 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 140.11, 132.41, 127.99, 123.52, 119.37, 109.22, 46.20, 43.40, 28.57, 21.47; HRMS (FAB) *m*/*z* found 492.2569; calcd for $C_{36}H_{32}N_2$ (M^+) 492.2565.

4b: colorless needles (hexane/benzene); mp >300 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 4H), 6.68 (d, $J = 8.2$ Hz, 4H), 6.54 (d, $J = 8.2$ Hz, 4H), 4.31 (m, 4H), 3.98 (m, 4H), 2.89 (m, 4H), 2.77 (m, 4H), 1.50 (m, 4H), −1.05 (m, 2H); ^{13}C NMR (67.8 MHz,

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[10] The fluorescence excitation spectra were in good agreement with the corresponding absorption spectra in all cases.

$CDCl_3$) δ 139.43, 131.79, 126.85, 122.37, 119.62, 108.46, 46.11, 41.48, 27.04, 22.30, 19.23; HRMS (FAB) m/z found 506.2719; calcd for $C_{37}H_{34}N_2$ (M^+) 506.2722.

Crystal data for 4a: triclinic, $P\bar{1}$, $a = 10.6257(4)$ Å, $b = 14.603(1)$ Å, $c = 9.8203(3)$ Å, $\alpha = 99.628(4)°$, $\beta = 107.179(3)°$, $\gamma = 79.737(3)°$, $V = 1421$ Å^3, $\rho_{calcd} = 1.235$ g cm^{-3}, $2\theta_{max} = 55°$, Mo Kα radiation ($\lambda = 0.71010$ Å), $T = 301$ K, 6217 reflections were measured. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient was applied, which resulted in transmission factors ranging from 0.61 to 0.98 ($\mu = 0.7$ cm^{-1}). A correction for secondary extinction was applied (coefficient = 2.36868e^{-06}). The structure was solved by direct methods (SIR92), and hydrogen atoms were included but not refined. Refinement by the full-matrix least-squares method gave an R value of 0.056 ($R_w = 0.088$) for 2180 reflections with $I > 3\sigma(I)$ and 389 variable parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137668. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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