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Synthesis and Photophysical Properties of *syn*- and *anti*-[2.*n*](3,9)Carbazolophanes

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Abstract: Both *syn*- and *anti*-[2.*n*](3,9)carbazolophanes (n = 4, 5) were obtained by the intramolecular [2 + 2] photocycloaddition of bis(3-vinyl-*N*-carbazolyl)alkanes. In the case of n = 4, the *syn*-isomer afforded sandwich excimer fluorescence, whereas the *anti*-isomer gave monomer fluorescence.

Keyword: cyclophanes; polycyclic heterocyclic compounds; fluorescence; photochemistry

The carbazole chromophore is a 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 studies on the two diastereomers of 2,4-di(*N*-carbazolyl)pentane,[1c] as a model of the 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 one of us, was found to adopt anti-conformation, leading to a 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 intramolecular [2 + 2] photocycloaddition of bis(vinylaryl)alkanes, and in most cases *syn*-isomers have been selectively and sometimes exclusively obtained.[4] Thus, we were stimulated to apply this method to the synthesis of *syn*-[2.*n*]carbazolophanes. Here we describe the first synthesis of [2.*n*](3,9)carbazolophanes and their properties. *syn*-Isomer **2b** was isolated as well as *anti*-isomer **3b**.

Scheme 1 illustrates the synthetic sequence of [2.*n*]carbazolophanes **2** and **3**. α,ω-Di(*N*-carbazolyl)alkanes were formylated by Vilsmeyer reaction using phosphoryl chloride and DMF in 1,2-dichloroethane to give diformyl compounds, which were converted into **1a–c** by Wittig reaction. The intramolecular [2 + 2] photocycloaddition of **1a–c** was carried out in toluene (ca. 1.5 mM) with a 400-W high-pressure mercury lamp through a Pyrex filter in a manner similar to that reported previously.[4] After irradiation for 15 min, the reaction mixture was purified by column chromatography on silica gel and recrystallization.

The photoreaction of **1a** gave a complex mixture along with insoluble polymeric materials, but the desired carbazolophane was hardly detected. Probably, a trimethylene linkage is too short to bring the two vinyl groups close. On the other hand, an isomeric mixture of carbazolophanes **2b** and **3b** was obtained from **1b** in total 39% yield, and **2c** and **3c** from **1c** in 77% yield. The isomer ratio in the two mixtures, however, was in contrast with each other; **2b**:**3b** = ca. 3:1, while **2c**:**3c** = ca. 1:5. Among them, **2b**, **3b**, and **3c** were isolated by repeated recrystallization from hexane–dichloromethane, whereas all attempts to isolate **2c** have been unsuccessful (see below).

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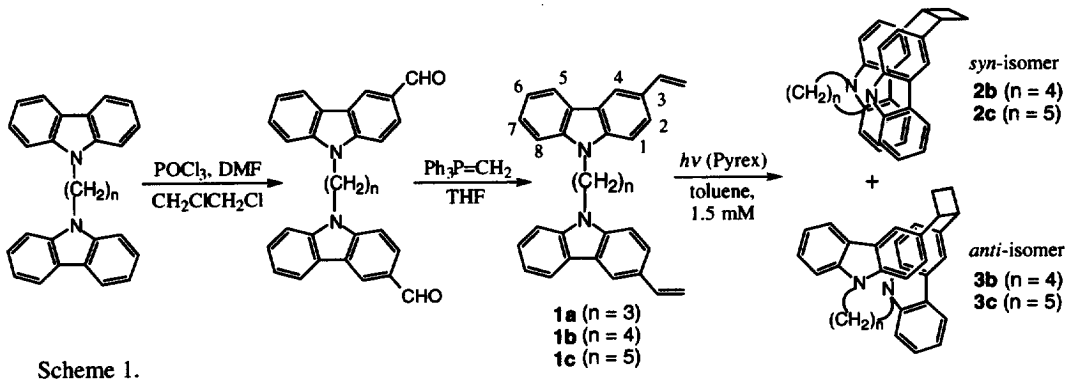

Scheme 1.

The structures of the carbazolophanes obtained were characterized mainly by ^{1}H NMR spectroscopy.[5] In **2b**, seven sets of aromatic proton peaks are observed and are generally high-field shifted compared to those of **1b**. The two methine protons of the cyclobutane ring appear as an equivalent peak. These results apparently indicate that **2b** adopts a *syn*-conformation where the two chromophores are well overlapped. The configuration of the cyclobutane ring was revealed as *endo* by the X-ray crystallographic analysis (Figure 1).[6] The isomer with an *exo*-directed cyclobutane ring was not detected at all, although the origin of the selectivity is not clear.[7] The ^{1}H NMR spectra of **3b** and **3c** suggest a lower symmetrical structure; fourteen peaks are observed for the aromatic protons and two peaks for the methine protons. Among the aromatic protons, H1, H2, and H4 are remarkably high-field shifted relative to **1b** or **1c**, while H5–8 are hardly shifted. Therefore, both **3b** and **3c** are concluded to be of *anti*-conformation where the two carbazole rings are partially overlapped. The ^{1}H NMR spectrum of **2c** is similar to that of **2b**, though the isomer-free spectrum has not been obtained. Thus, it is reasonable that **2c** is also assigned as *syn*-isomer (see below).

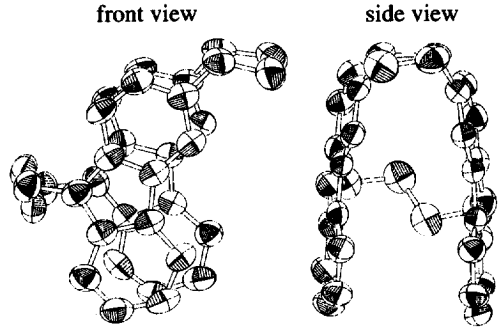

Figure 1. X-ray crystallographic analysis of **2b**.

According to the X-ray crystallographic analysis of **2b**, the two carbazole rings favorably overlap with each other, although they are slightly deviated from parallel arrangement (dihedral angle = 19.4°); the distance between the two nitrogen atoms (4.49 Å) is much longer than that between the C3 atoms (2.86 Å).

Intriguingly, irreversible isomerization from **2c** to **3c** was observed in solution even at room temperature, making the isolation of **2c** quite difficult. For example, when a mixture of **2c**:**3c** = 1:2 was allowed to stand in chloroform at room temperature in the dark for 3 days, the ratio changed to 1:10 without regeneration of **1c** or decomposition, whereas pure **3c** remained unchanged even after several weeks. Since **1c** was not detected, this isomerization process is not accompanied with the cleavage of the cyclobutane ring, but brought about only by the rotation of the carbazole moieties along the linkages. These results apparently indicate that **3c** is thermodynamically more stable than **2c**. In solid states, however, such isomerization was not observed for at least several months. No interconversion took place between **2b** and **3b** even in solution, probably because the rotation of the chromophores was disturbed due to the shorter linkage.

The absorption spectrum of **3b** is rather similar to that of *N*-ethylcarbazole (**4**), though slight broadening and red shift (7 nm for the $S_1 \leftarrow S_0$ band) are observed, suggesting a small transannular π-π interaction in this *anti*-conformation. In **2b**, the shape of absorption bands around 300 and 350 nm is considerably different from that in **3b** and **4**. This feature may result from the relatively large electronic interaction between the carbazole rings overlapped with each other in **2b**.

The fluorescence spectra of **2b** and **3b**, measured in cyclohexane at room temperature, are remarkably different, as shown in Figure 2. Both **3b** and **3c** afforded quite similar spectra in spite of the difference in the bridging tether length.

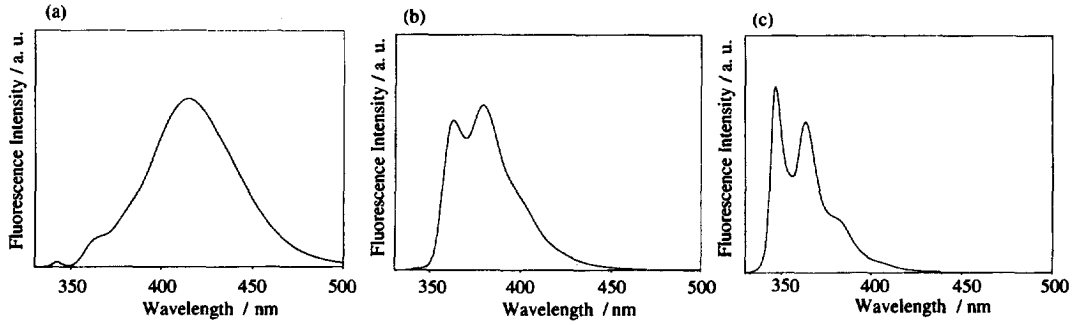

Figure 2. Fluorescence spectra of (a) **2b**, (b) **3b**, and (c) **4** upon 310-nm excitation in cyclohexane at room temperature.

The fluorescence spectrum of **3b**, composed of vibrational structures similar to **4**, exhibits a mirror image of the longest absorption band, though some broadening and red-shift (12 nm for the 0-0 transition) are observed compared to **4**. This fluorescence, obviously different from the partial-overlap excimer fluorescence which is reported to show a broad band around 370 nm,[1c] can be virtually interpreted as the monomer fluorescence of the carbazole chromophore. This result is rather in contrast with the expectation that **3b** is seemingly suitable for partial-overlap excimer. Probably, the two carbazole rings are not sufficiently overlapped with each other. This is actually demonstrated by the ^{1}H NMR data of **3b**, although the X-ray crystallographic analysis has not yet been accomplished. The high-field shifts of H1 (1.12 and 1.06 ppm) and H2 (1.45 and 1.07 ppm) of **3b** relative to **1b** are much larger than those of H4 (0.54 and 0.22 ppm), indicating that H1 and H2 are located over the opposite carbazole moiety, whereas H4 is not; the benzene rings on the cyclobutane side are only partially overlapped with each other. The broadening and red-shift in the fluorescence spectrum of **3b** relative to **4** are more remarkable than in the absorption spectrum; the Stokes shift in **3b** is larger than in **4** (780 vs. 250 cm^{-1}). This means that in the excited state the two carbazole moieties more or less approach each other and the interaction between them becomes larger than in the ground state.

On the other hand, **2b** afforded broad and structureless fluorescence with a peak at 415 nm, much red-shifted in comparison with **3b**. This is apparently assigned as sandwich excimer fluorescence which usually appears around 420 nm,[1] in agreement with the well-overlapped arrangement in **2b**. The slight blue shift in **2b** relative to the typical position may be associated with the deviation from parallel arrangement. The contribution of the monomer fluorescence, however, is much smaller than that in *meso*-2,4-di(*N*-carbazolyl)pentane.[1c] This result appears to be realized by the presence of the cyclobutane ring in addition to the oligomethylene linkage between the nitrogen atoms; these bridging units efficiently keep the two carbazole rings in the arrangement favorable for the sandwich excimer formation.

In summary, both *syn*- and *anti*-[2.*n*](3,9)carbazolophanes (*n* = 4, 5) (**2** and **3**) were first obtained by the intramolecular [2 + 2] photocycloaddition of **1**. The fluorescence spectra of *syn*-isomer **2b** and *anti*-isomer **3b** were different, depending upon their conformation; **2b** afforded sandwich excimer fluorescence, whereas **3b** gave monomer fluorescence.

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5. Selected spectroscopic data of **2b**, **3b**, and **3c**. **2b**: Colorless prisms (hexane–dichloromethane); m.p. 205.0–205.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ = 7.64 (d, *J* = 7.6 Hz, 2H; H(5)), 7.56 (s, 2H; H(4)), 6.96 (dd, *J* = 8.1, 7.0 Hz, 2H; H(7)), 6.85 (d, *J* = 8.1 Hz, 2H; H(8)), 6.81 (dd, *J* = 7.6, 7.0 Hz, 2H; H(6)), 6.73 (d, *J* = 8.3 Hz, 2H; H(1)), 6.62 (d, *J* = 8.3 Hz, 2H; H(2)), 4.32 (m, 2H), 4.00 (m, 4H), 2.80 (m, 2H), 2.69 (m, 2H), 1.77 (m, 2H), 1.36 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ = 140.65, 138.69, 132.08, 128.23, 124.49, 123.07, 122.98, 119.55, 118.53, 118.47, 108.72, 108.34, 46.26, 42.66, 28.97, 21.19; HRMS (FAB) *m/z* found 440.2253; calcd for $C_{32}H_{28}N_2$ (M^+) 440.2252. **3b**: Colorless needles (hexane–dichloromethane); m.p. 226.0–226.5 °C; ^{1}H NMR ($CDCl_3$) δ = 8.15 (d, *J* = 7.6 Hz, 1H; H(5)), 8.04 (d, *J* = 7.6 Hz, 1H; H(5)), 7.90 (s, 1H; H(4)), 7.56 (s, 1H; H(4)), 7.43 (dd, *J* = 8.1, 7.0 Hz, 1H; H(7)), 7.41 (dd, *J* = 8.1, 7.0 Hz, 1H; H(7)), 7.32 (d, *J* = 8.1 Hz, 1H; H(8)), 7.29 (d, *J* = 8.1 Hz, 1H; H(8)), 7.24 (dd, *J* = 7.6, 7.0 Hz, 1H; H(6)), 7.20 (dd, *J* = 7.6, 7.0 Hz, 1H; H(6)), 6.46 (d, *J* = 8.3 Hz, 1H; H(2)), 6.14 (d, *J* = 8.3 Hz, 1H; H(1)), 6.08 (s, 2H; H(1), H(2)), 4.40 (m, 1H), 4.17 (m, 3H), 4.01 (m, 2H), 2.72 (m, 2H), 2.54 (m, 1H), 1.24 (m, 2H), 1.00 (m, 1H), 0.88 (m, 2H); ^{13}C NMR δ = 142.16, 141.90, 137.63, 137.23, 132.51, 131.82, 128.64, 124.96, 124.81, 124.69, 122.69, 122.80, 122.69, 122.57, 120.59, 120.20, 120.14, 118.35, 118.31, 117.14, 109.24, 108.66, 108.55, 108.52, 46.86, 46.11, 46.02, 41.17, 22.91, 22.84, 22.08, 20.36; HRMS (FAB) *m/z* found 440.2249; calcd for $C_{33}H_{30}N_2$ (M^+) 440.2252. **3c**: Colorless needles (hexane–dichloromethane); m.p. 241.0–241.5 °C; ^{1}H NMR δ = 8.18 (d, *J* = 7.6 Hz, 1H; H(5)), 8.08 (d, *J* = 7.6 Hz, 1H; H(5)), 7.95 (s, 1H; H(4)), 7.65 (s, 1H; H(4)), 7.43 (dd, *J* = 8.1, 7.0 Hz, 1H; H(7)), 7.34 (dd, *J* = 8.1, 7.0 Hz, 1H; H(7)), 7.33 (d, *J* = 8.1 Hz, 1H; H(8)), 7.31 (d, *J* = 8.1 Hz, 1H; H(8)), 7.26 (dd, *J* = 7.6, 7.0 Hz, 1H; H(6)), 7.22 (dd, *J* = 7.6, 7.0 Hz, 1H; H(6)), 6.55 (d, *J* = 8.4 Hz, 1H; H(2)), 6.37 (d, *J* = 8.4 Hz, 1H; H(1)), 6.33 (d, *J* = 8.4 Hz, 1H; H(1)), 6.16 (d, *J* = 8.4 Hz, 1H; H(2)), 4.35 (m, 1H), 4.27 (m, 1H), 4.22 (m, 1H), 4.19 (m, 1H), 3.90 (m, 2H), 2.73 (m, 3H), 2.58 (m, 1H), 1.97 (m, 2H), 1.33 (m, 2H), 0.14 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 139.96, 139.46, 139.39, 139.26, 132.45, 131.63, 128.32, 124.74, 124.64, 124.58, 123.49, 123.38, 121.13, 121.01, 120.25, 120.20, 120.09, 118.35, 116.66, 108.79, 108.75, 108.28, 107.85, 45.99, 45.66, 41.60 (2C), 28.95 (2C), 24.08, 23.27, 20.79; HRMS (FAB) *m/z* found 454.2407; calcd for $C_{33}H_{30}N_2$ (M^+) 454.2409.
6. Crystal data for **2b**: orthorhombic, $P2_12_12_1$, *a* = 11.610(9), *b* = 21.779(4), *c* = 9.424(2) Å, *V* = 2382 Å^3, ρ_{calcd} = 1.228 g cm^{-3}, $2\theta_{max}$ = 55°, MoKα radiation (λ = 0.71010 Å), *T* = 288 K, 2716 reflections were measured. The data were corrected for Lorentz and polarization effects. No absorption correction was applied (μ = 0.7 cm^{-1}). The structure was solved by direct methods (SAPI91) and hydrogen atoms were refined isotropically. Refinement by the full-matrix least-squares method gave a *R* value of 0.048 (*wR* = 0.043) for 2016 reflections with $I > 3\sigma(I)$ and 420 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-104997.
7. PM3 or AM1 calculation suggested no significant difference in the stability between the two possible isomers of **2b**.