Synthesis and Properties of Partially Overlapped [3.*n*](3,9)Carbazolophanes

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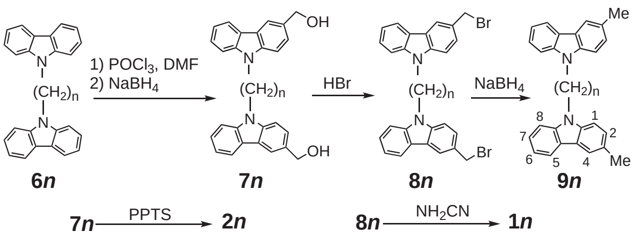
Cyanamide- and oxa-bridged [3.*n*](3,9)carbazolophanes **1*n*** and **2*n*** ($n = 4$ and 5) were synthesized. X-ray analysis of **1**$_4$ and **2**$_5$ revealed that carbazole rings are taken to be partially overlapped geometry. Electronic spectra of **1*n*** and **2*n*** ($n = 4$ and 5) showed the existence of transannular π–π electronic interaction between two carbazole rings, whereas fluorescence of these carbazolophanes indicated monomer-like emission.

Carbazole (Cz) chromophore has attracted much attention because of its interesting photophysical properties such as photoluminescence, photoconductivity and its application to photofunctional devices.[1] It has been accepted that Cz chromophore forms two excimers in the excited state:[2] one is a fully overlapped (sandwich) excimer and the other is a partially overlapped excimer. It is thought that cyclophane framework, in which aromatic rings are rigidly fixed and situated in face-to-face orientation, is an excellent model for examining the structural feature of Cz excimer.[3] We reported that fluorescence spectra of **1**$_3$ and **3**$_3$ were assigned as partially and fully overlapped excimer-like emission, respectively,[3c,3d] while cyclobutane-fused **5*n*** ($n = 4$ and 5) as monomer-like emission.[3b] Herein, we describe the synthesis, structure, and photophysical properties of cyanamide- and oxa-bridged [3.*n*](3,9)carbazolophanes **1*n*** and **2*n*** ($n = 4$ and 5), respectively, to investigate further insight into the properties and formation of excimer in Cz chromophore (Chart 1).

The synthetic route of carbazolophanes is shown in Scheme 1. Vilsmeier reaction of dicarbazolylalkanes **6*n*** ($n = 4$ and 5) gave the dialdehydes,[3b,4] which were reduced with sodium borohydride to give diols **7*n***[5] in good yields. Treatment of diols **7*n*** ($n = 4$ and 5) with concd. hydrobromic acid afforded unstable dibromides **8*n***[6] in high yields. The cyclization reaction between **8*n*** ($n = 4$ and 5) and cyanamide, developed by Shinmyozu,[7] yielded **1**$_4$ (36%) and **1**$_5$ (35%).[8] Oxa-bridged carbazolophanes **2**$_4$ and **2**$_5$ were prepared in 20 and 36% yield, respectively,[8] by the intramolecular dehydration of corresponding diols **7*n*** in the presence of acid catalyst, PPTS.[9] Fully overlapped isomers, neither **3*n*** nor **4*n***, was isolated in these cyclization processes. References, **9*n***[10] were prepared by the reduction of **8*n*** with $NaBH_4$.



Scheme 1.

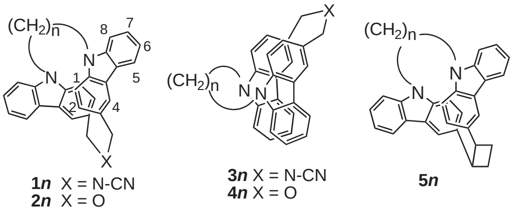


Chart 1.

The suitable crystals of **1**$_4$[11] and **2**$_5$[12] for X-ray analysis were obtained by recrystallization. Figure 1 shows ORTEP drawings[13] of **1**$_4$ and **2**$_5$, respectively. It was clear from X-ray analysis that Cz rings in **1**$_4$ and **2**$_5$ were located in a partially overlapped orientation. Reflecting a difference of the lengths of alkylene chains, the least-squares planes of two Cz rings in **1**$_4$ and **2**$_5$ are inclined 15.0 and 23.4°, respectively, much larger than that in **1**$_3$ (6.2°).[3c]

Table 1 shows chemical shifts of aromatic protons in **1*n*** ($n = 3$–5), **2*n*** ($n = 4$ and 5), and **9*n*** ($n = 3$–5) along with the chemical shift differences ($\Delta\delta$) between cyclophanes and corresponding references **9*n***. Chemical shifts of aromatic protons, H1 and H2, in **1*n*** ($n = 3$–5) and **2*n*** ($n = 4$ and 5) shifted up-field (large negative values of $\Delta\delta$) compared with corresponding references **9*n***. It can be assigned from these shifts that **1*n*** and **2*n*** listed in Table 1 take partially overlapped geometry. It is very interesting that comparing cyanamide-bridged **1*n*** with oxa-bridged **2*n*** with the same *n* number, chemical shifts of all corresponding aromatic protons agree well each other within the deviation of only 0.03 ppm. This fact indicates that the geometry of [3.*n*](3,9)carbazolophanes ($n = 4$ and 5) is little affected by the difference of cyanamide- and oxa-bridge. The degree of up-field shifts is in the order of **1**$_3$ > **1**$_4$ > **1**$_5$ and

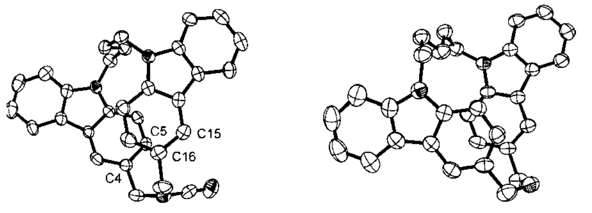


Figure 1. Molecular structure of **1**$_4$ (left) and **2**$_5$ (right).

Table 1. Chemical shifts of aromatic ring protons (400 MHz, $CDCl_3$, δ/ppm)

	H1	H2	H4	H5	H6	H7	H8
1$_3$[3c]	5.44	6.41	7.81	8.15	7.33	7.53	7.56
$\Delta\delta$	−1.65	−0.79	−0.09	0.09	0.13	0.16	0.39
1$_4$	6.12	6.56	7.94	8.11	7.26	7.47	7.32
$\Delta\delta$	−1.05	−0.66	0.05	0.06	0.06	0.06	0.08
1$_5$	6.34	6.62	7.98	8.14	7.28	7.47	7.35
$\Delta\delta$	−0.86	−0.64	0.08	0.07	0.08	0.05	0.06
2$_4$	6.10	6.59	7.91	8.09	7.24	7.44	7.31
$\Delta\delta$	−1.07	−0.63	0.02	0.04	0.04	0.03	0.07
2$_5$	6.32	6.65	7.95	8.12	7.25	7.45	7.34
$\Delta\delta$	−0.88	−0.61	0.05	0.05	0.05	0.03	0.05
9$_3$	7.09	7.20	7.90	8.06	7.20	7.37	7.17
9$_4$	7.17	7.22	7.89	8.05	7.20	7.41	7.24
9$_5$	7.20	7.26	7.90	8.07	7.20	7.42	7.29

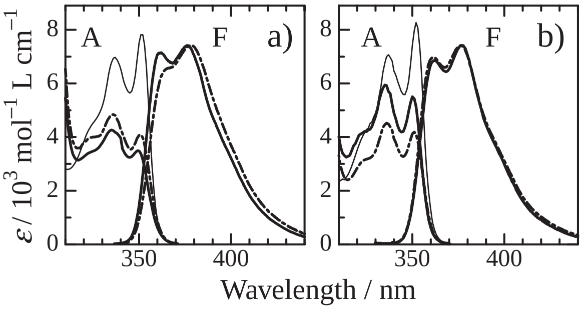


Figure 2. Absorption (A) and emission (F) spectra of **1*n*** and **2*n*** in THF at room temperature: a) thick solid lines **1**$_4$, thick dashed–dotted lines **2**$_4$, thin solid line **9**$_4$, b) thick solid lines **1**$_5$, thick dashed–dotted lines **2**$_5$, thin solid line **9**$_5$.

2$_4$ > **2**$_5$, which reflects the inclined angle of two Cz rings revealed by X-ray analyses. Therefore, the structure of carbazolophanes in solid state would be essentially maintained even in solution.

Electronic absorption spectra of **1*n*** and **2*n*** ($n = 4$ and 5) were measured in THF as shown in Figure 2. The absorption shape of **1*n*** and **2*n*** exhibited slight broadening and hypochromic effect compared with the corresponding references **9*n***, which indicated that transannular π–π electronic interaction exists. This feature can be interpreted by exciton splitting theory, as we have already reported for the absorption spectra of **1**$_3$.[3d]

Fluorescence spectra of **1*n*** and **2*n*** are also shown in Figure 2. Although the geometry of Cz rings in **1*n*** and **2*n*** for $n = 4$ and 5 seemingly adopts in partially overlapped shapes, the emission behavior was monomer-like emission rather than excimer-like one: fluorescence spectra of these carbazolophanes are not broad and rather in the mirror image of absorption spectra. From the X-ray analysis, the intramolecular distances between nonbonding-aromatic rings, C4···C16 and C5···C15, in **1**$_4$ were 3.257(5), 3.534(5) Å (see Figure 1), respectively. It is noted that such a short contact and partial overlap of Cz rings caused transannular π–π electronic interaction in absorption spectra, whereas distinguishable excimeric interaction was not observed. We have already reported that partially overlapped [2.*n*](3,9)carbazolophane **5*n*** ($n = 4$ and 5) emitted monomeric fluorescence.[3b] Among all the partially overlapped carbazolophanes [**1*n*** ($n = 3$–5) and **2*n***, **5*n*** for $n = 4$ and 5] so far synthesized, [3.3](3,9)bis-bridged **1**$_3$ alone exhibited excimeric emission. The N···N distances between partially overlapped Cz rings in **1**$_3$, **1**$_4$, and **2**$_5$ were 3.413(3), 4.702(3), and 5.448(5) Å, respectively. As described in the above, two Cz rings in carbazolophanes were inclined in the order of **1**$_3$ < **1**$_4$ < **2**$_5$, and the geometries of cyanamide- and oxa-bridged carbazolophanes were similar in solution. It can be said that emissive properties of carbazolophanes are governed by the distances and angles between Cz rings.

In conclusion, the structure of an apparent "partially overlapped" geometry taken for **1*n*** and **2*n*** for $n = 4$ and 5 is not enough for excimer formation, which may require an appropriate geometry of Cz rings situated in **1**$_3$ such as the close N···N contact (ca. 3.4 Å) and/or parallel orientation (<7°) of Cz rings.

This work was supported by Grant-in-Aid (Grant No. 16550037) from Ministry of Education, Culture, Sports, Science, and Technology, Japan.

This paper is dedicated to Emeritus Professor Philip Eaton on the occasion of his 70th birthday.

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4 Purification of bis(3-formyl-9-carbazolyl)alkanes was not carried out, as the solubility of these compounds was low.

5 **7**$_4$: mp 197.0–198.0 °C, **7**$_5$: mp 113.0–114.0 °C.

6 As dibromides **8*n*** were unstable and easily polymerized, they were employed to the next cyclization reaction immediately.

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8 **1**$_4$: mp 256.5–257.5 °C, **1**$_5$: mp 264.0–265.5 °C, **2**$_4$: mp 235 °C, **2**$_5$: mp 138.0–140.0 °C. ^{1}H NMR data of carbazolophanes were summarized in Supporting Information, http://www.csj.jp/journals/chem-lett/index.html.

9 Detailed reaction conditions of intramolecular dehydration reaction by PPTS (pyridinium *p*-toluenesulfonate) will be reported elsewhere.

10 **9**$_3$: 155.0–156.5 °C. **9**$_4$: 222.0–224.0 °C, **9**$_5$: 123.0–125.0 °C.

11 Crystal data for **1**$_4$: colorless plate (benzene–hexane), $M_w = 454.6$, orthorhombic, space group $P2_12_12_1$, $a = 12.132(7)$ Å, $b = 17.890(6)$ Å, $c = 11.001(6)$ Å, $V = 2388(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.264$ g cm^{-3}, μ(Mo Kα) = 0.76 cm^{-1}, Rigaku AFC7R diffractometer, 1812 reflections with $I > 2.0\sigma(I)$, $R = 0.041$, $Rw = 0.126$, CCDC 634984.

12 Crystal data for **2**$_5$: $2C_{31}H_{28}N_2O + 4C_6H_6$, colorless plate (benzene–cyclohexane), $M_w = 600.8$, monoclinic, space group $P2_1/c$, $a = 22.820(2)$ Å, $b = 14.615(4)$ Å, $c = 21.729(3)$ Å, $\beta = 111.419(9)°$, $V = 6746(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.183$ g cm^{-3}, μ(Mo Kα) = 0.70 cm^{-1}, Rigaku AFC7R diffractometer, 4556 reflections with $I > 2.0\sigma(I)$, $R = 0.053$, $Rw = 0.149$, CCDC 634985. Two independent molecular structures were contained in unit lattice, and their geometry with respect to carbazole rings was similar with each other. Figure 1 illustrates the full structure of one of them.

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Published on the web (Advance View) February 24, 2007; doi:10.1246/cl.2007.460