Synthesis and Properties of [2.2]Paracyclo- and [2.2](1,4)Naphthaleno-(3,6)carbazolophanes

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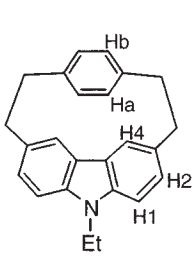
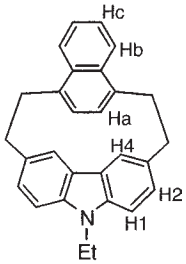
[2.2]Paracyclo(3,6)carbazolophane (**1a**) and [2.2](1,4)-naphthaleno(3,6)carbazolophane (**1b**) were prepared. The structures of **1a** and **1b** were characterized by ^{1}H NMR. X-ray analysis of **1a** revealed that the carbazole ring extremely deviates from the conjugated plane. Electronic spectra of **1a** and **1b** showed the broadening and bathochromic shift compared with the references.

It is well known that the poly(*N*-vinylcarbazole) is a famous photoconductive aromatic polymer and the photophysical properties of carbazole chromophores have attracted much attention.[1] We have recently reported the synthesis and photophysical properties of [m.n]carbazolophane derivatives to elucidate the interchromophoric interaction in carbazole moiety.[2] Cyclophane has been employed as useful model compounds for examining weak transannular interaction in aromatic systems and for studying the novel structure of the strained aromatic rings.[3] However, neither the transannular π–π electronic interaction between carbazole and other aromatic ring nor the properties of the strained carbazole ring have been sufficiently studied so far. Thus, we describe here the synthesis, spectral and structural properties of [2.2]paracyclo(3,6)carbazolophane (**1a**) and [2.2](1,4)naphthaleno(3,6)carbazolophane (**1b**).

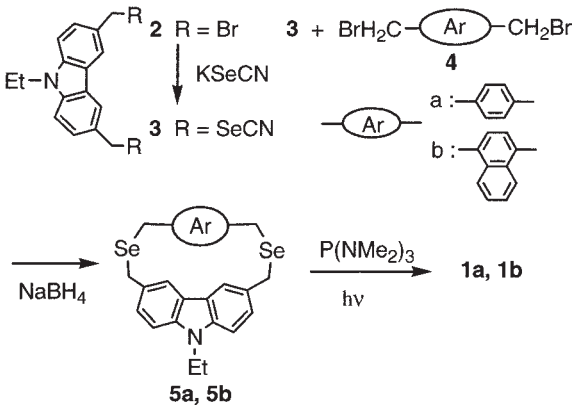


1a



1b

We have synthesized various [2^n]cyclophanes by photodeselenation of selenacyclophanes,[4] and this method was also applied to the synthesis of **1a** and **1b**. Scheme 1 illustrates the synthetic route of the carbazolophanes. Dibromide **2**[2a] was treated with potassium selenocyanate to give 3,6-bis(selenocyanatomethyl)-9-ethylcarbazole (**3**)[5] in 90% yield. 1,4-Bis(bromomethyl)benzene (**4a**) and **3** were coupled with sodium borohydride under high dilution conditions to afford **5a** in 56% yield. Selenocyanate **3** was a stable solid and easily purified by recrystallization in contrast to the unstability of bromide **2**. As selenacyclophanes are generally prepared from bromides and selenocyanates, it is expected that various kinds of selenacarbazolophanes will be prepared from **3** as key intermediates. Photodeselenation of **5a** with hexamethylphosphorous triamide afforded the desired **1a**[6] in 59% yield. Similar reaction sequence was applied for 1,4-bis(bromomethyl)naphthalene **4b** in place of **4a** to give **1b**[7] in 21% overall yield. Both **1a** and **1b** were noted to be the first example of carbazolophanes not only bridged by short [2.2]-phane framework, but also belonging to the mixed-carbazolophanes, where the carbazole and other aromatic chromophores were fixed in a distinct geometry.



Scheme 1.

The structures of the carbazolophanes were primarily characterized by ^{1}H NMR spectroscopy. The chemical shifts of aromatic rings of **1a**, **1b**, and the references, 9-ethyl-3,6-dimethylcarbazole **6**, *p*-xylene **7**, and 1,4-dimethylnaphthalene **8** are summarized in Table 1. The carbazole protons in **1a** and **1b** appeared at distinguishable ABX system. These signals shifted generally at higher field compared with those of **6** owing to the anisotropic effect of a faced aromatic ring. Marked high-field shifts were observed for H4 and Ha, both of which are located nearly above the opposed aromatic ring. On the other hand, a slight low-field shift was observed for Hb of **1a** and **1b**, Hc of **1b** compared with the corresponding references. These protons are situated apart from the center of the carbazole ring and hence, it is assumed that they are in the deshielding field of the carbazole benzene rings.

Table 1. Chemical shifts of aromatic rings (400 MHz, $CDCl_3$, δ)

	H1	H2	H4	Ha	Hb	Hc
1a	7.14	7.00	6.74	4.75	7.16	
$\Delta\delta$	−0.12	−0.26	−1.12	−2.31	+0.10	
1b	7.15	7.04	6.22	5.20	8.20	7.65
$\Delta\delta$	−0.11	−0.22	−1.64	−2.01	+0.19	+0.12
6	7.23–7.28		7.86			
7				7.06	7.06	
8				7.21	8.01	7.53

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The structure of **1a** was confirmed by the X-ray crystal analysis as shown in Figure 1.[8] The intramolecular distances between bridged aromatic carbons, C4–C15 and C10–C18, are 2.99 Å and 2.97 Å, respectively. The angle between right (C1–C6) and left (C7–C12) side benzene in carbazole ring is as much as 40 ° as shown in Figure 1, while the upper benzene ring kept the planarity. To our knowledge, this angle is the largest of all the carbazole derivatives ever reported. Reflecting strong deformation from the conjugated plane, the distance of C16–C3 (3.22 Å) is shorter than that of C16–C2 (3.48 Å). X-ray analysis of **1a** corresponded to the behavior of the chemical shifts of aromatic protons in solution. Therefore, **1a** remained the rigid structure even in solution. From the comparison of the chemical shift differences ($\Delta\delta$) of **1a** and **1b** from the corresponding references as shown in Table 1, **1b** will be also rigid and the geometry of the carbazole and the naphthalene is taken to be of *anti*-conformation.

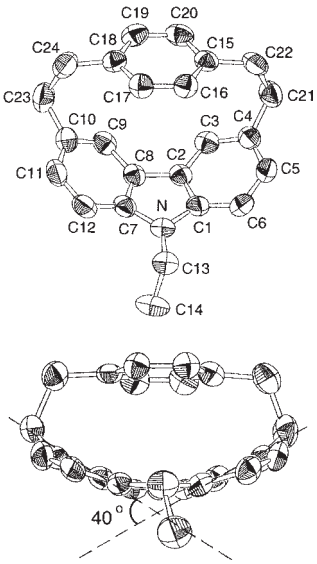

Figure 1. X-ray analysis of **1a**.

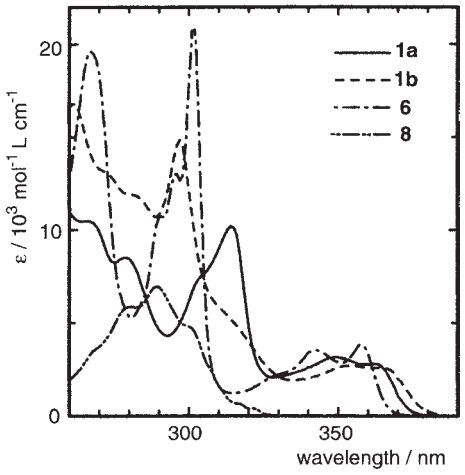

Figure 2. Electronic absorption spectra in THF.

Electronic absorption spectra of carbazolophanes and the references were measured in THF. The absorption spectra of **1a** around 300 to 380 nm exhibited broadening and bathochromic shift compared with **6** suggesting the existence of transannular π–π electronic interaction. Similar trend was observed for **1b**, though the extent of broadening and bathochromic shift were slightly larger than those for **1a**. These results can be interpreted by means of the exciton coupling interaction[9] and the strain of the carbazole chromophore which was revealed by the X-ray analysis.

In summary, both [2.2]paracyclo(3,6)carbazolophane **1a** and [2.2](1,4)naphthaleno(3,6)carbazolophane **1b** were first prepared by the photodeselenation of **5a** and **5b**, respectively. Their chemical and physical properties were invetigated.[10] It was also found that the carbazole ring in **1a** is able to endure the strong deformation in the rigid [2.2]cyclophane framework.

References and Notes

1 J. M. Pearson and M. Stolka, "Poly(*N*-vinylcarbazole)," Gordon and Breach Sci. Pub., New York (1981).

2 a) K. Tani, Y. Tohda, K. Hisada, and M. Yamamoto, *Chem. Lett.*, **1996**, 145. b) Y. Nakamura, M. Kaneko, N. Yamanaka, K. Tani, and J. Nishimura, *Tetrahedron Lett.*, **40**, 4693 (1999). c) K. Tani, Y. Tohda, H. Takemura, H. Ohkita, S. Ito, and M. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **2001**, 1914. d) H. Ohkita, S. Ito, M. Yamamoto, Y. Tohda, and K. Tani, *J. Phys. Chem. A*, **106**, 2140 (2002).

3 For example: P. M. Keehn and S. M. Rosenfeld, "Cyclophanes," Academic Press, New York (1983); F. Vögtle, "Cyclophane Chemistry," Wiley, Chichester (1989); F. Diederich, "Cyclophanes," The Royal Society of Chemistry, Cambridge (1991).

4 a) K. Tani, H. Seo, M. Maeda, K. Imagawa, N. Nishiwaki, M. Ariga, Y. Tohda, H. Higuchi, and K. Kuma, *Tetrahedron Lett.*, **36**, 1883 (1995). b) H. Higuchi, K. Tani, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **60**, 4027 (1987).

5 **3**: dec. 139–141 °C, ^{1}H NMR ($CDCl_3$, δ): 1.44 (t, J = 7.2 Hz, 3H), 4.36 (q, J = 7.2 Hz, 2H), 4.59 (s, 4H), 7.40 (d, J = 8.4 Hz, 2H, H1), 7.49 (dd, J = 8.4 Hz, 1.6 Hz, 2H, H2), 8.08 (d, J = 1.6 Hz, 2H, H4). Anal. Calcd for $C_{18}H_{15}N_3Se_2$: C, 50.13; H, 3.51; N, 9.74%. Found: C, 49.85; H, 3.43; N, 9.49%.

6 **1a**: mp 164–165 °C: Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30%. Found : C, 88.29; H, 7.07; N, 4.29%.

7 **1b**: mp 197–199 °C: Anal. Calcd for $C_{28}H_{25}N$: C, 89.56; H, 6.71; N, 3.73%. Found : C, 89.40; H, 6.69; N, 3.58%.

8 Crystal Data for **1a**: colorless prism (benzene-hexane), M_r = 325.45, monoclinic, space group $P2_1/c$, a = 5.722(2) Å, b = 17.471(2) Å, c = 18.109(2) Å, β = 94.92(2)°, V = 1803.7(8) Å^3, Z = 4, D_{calc} = 1.198 g/cm^3, μ(Mo Kα) = 0.69 cm^{-1}, Rigaku AFC7R diffractometer, 1866 reflections with I > 3.0σ(I), R = 0.046, R_w = 0.032.

9 M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, *Pure Appl. Chem.*, **11**, 371(1965).

10 The emission properties of **1a** and **1b** are of particular interest and will be reported in a separated paper.