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Preparation, Structural Properties, and Charge-Transfer Complexes of Novel Anthracenophanes

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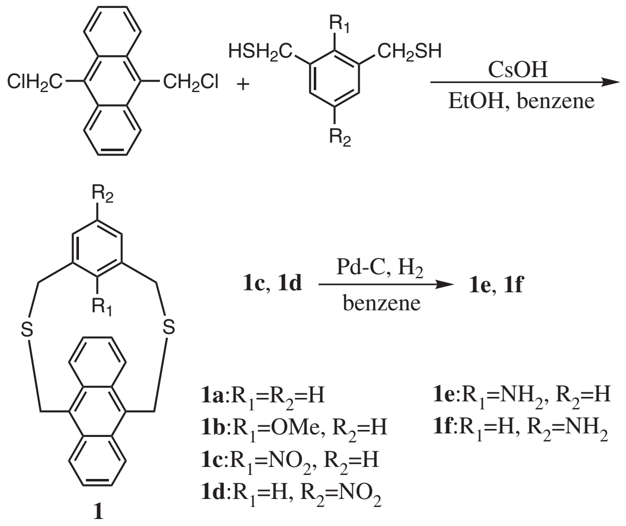
Cyclophanes consisting of the anthracene unit and the aromatic component carrying various substituents at the inner or the outer position (anthracenophanes) have been synthesized. Their structures were characterized by the NMR and the X-ray analyses. NH–π interaction between the anthracene ring and the inner amino group on the opposite ring was observed in this cyclophane system. It has been found out that the $\lambda_{\max}$ values of charge-transfer complexes of anthracenophanes with TCNE are closely related to transannular and NH–π interaction.

Cyclophanes have pervaded the research of transannular interactions between the aromatic components in the molecule[1] since the close proximity of the aromatic units in this system could facilitate intramolecular forces as well as intermolecular ones. This characteristic of cyclophanes can also be employed as a tool for the investigation of weak interactions based on the π-system. We have already discussed the [3.3][2] and [3.3.1] metacyclophane[3] systems in connection with the intramolecular interactions such as hydrogen-bondings or NH–π interaction. Recently it has been reported that benzenophanes[4] and pyrenophanes[5] exhibit unique characteristics based on the specific interactions involving their π-system. These results prompted us to investigate the cyclophanes containing the anthracene unit in order to know more about weak interactions. A number of anthracenophanes have been reported to date mainly in order to study excimer fluorescence or photochemically induced cyclization.[6]

Herein we report the syntheses, structures, and charge-transfer complexes of novel anthracenophanes having the functional groups on the ring of the other side.

Cyclization of 9,10-bis(chloromethyl)anthracene[7] and the mercaptomethyl compounds using CsOH as a base under highly dilute condition afforded the corresponding dithiaanthracenophanes **1a**–**1d** in 25–58% yields. The nitro compounds **1c** and **1d** were reduced with hydrogen gas in the presence of 10% Pd/C to give the corresponding amino compounds **1e** and **1f** in 12 and 15% yields, respectively, accompanied by recovery of the starting materials. These low yields might be due to the steric hindrance of anthracene unit against the nitro group.



Scheme 1.

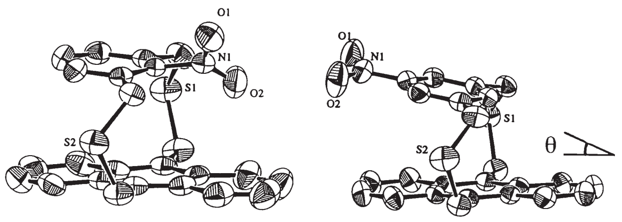
The chemical shifts of the bridge protons and the inner protons (R_1) are summarized in Table 1. **1a** reveals a flexible structure at room temperature as evidenced by two singlets for the bridge protons. The similar NMR patterns are observed for **1d** and **1f**. On the contrary the bridge protons in **1b** as well as **1c** and **1e** exhibit two sets of doublets at room temperature, meaning that they assume the rigid conformation. These results obviously imply that a mobility of the molecule strongly depends on the inner substituent (R_1) on the aromatic ring of the other side. Substitution at the inner position clearly prevents the aromatic components from their flipping. The inner protons in **1a**, **1d**, and **1f** are subject to large upfield shift, indicating that they plunge into the shielding region of the anthracene unit.

Unfortunately the coalescence temperatures for the anthracenophanes described here were not obtained since no obvious

Table 1. Chemical shifts[a] in anthracenophanes

Compd	Bridge proton				R_1 proton
	δ (J/Hz)				δ
1a	3.26(s, 4H)	4.92(s, 4H)			3.29(s, 1H)
1b	3.06(d, $J = 15.5$, 2H)	3.66(d, $J = 15.5$, 2H)	4.39(d, $J = 13.6$, 2H)	5.34(d, $J = 13.6$, 2H)	2.73(s, 3H)
1c	3.33(d, $J = 15.9$, 2H)	3.84(d, $J = 15.9$, 2H)	4.51(d, $J = 14.1$, 2H)	5.26(d, $J = 14.1$, 2H)	—
1d	3.29(s, 4H)	4.90(s, 4H)			4.25(s, 1H)
1e	3.20(d, $J = 15.9$, 2H)	3.49(d, $J = 15.9$, 2H)	4.70(d, $J = 14.1$, 2H)	4.87(d, $J = 14.1$, 2H)	—
1f	3.28(s, 4H)	4.90(s, 4H)			4.03(s, 1H)

[a] In $CDCl_3$ at 27 °C.



1c ($\theta = 3.26°$) **1d** ($\theta = 11.4°$)

Figure 1. X-ray structures of **1c** and **1d**.

changes in their NMR signals were observed in the range of the conventional temperatures.

The inner substituent seems to have a considerable effect on the conformations of the anthracenophanes. Thus, the X-ray structural analyses of **1c**[8] and **1d**[9] were carried out as shown in Figure 1. The angles between two components are indicated in Figure 1. **1c** exhibits a unique feature in which the inner nitro group tilts against the plane of the aromatic ring. This tilted structure of the nitro group possibly results from the steric hindrance toward the methylene bridge. This hindrance is also supposed to contribute the parallel structure indicated by the small angle (3.26°). On the contrary there is no tilt for the outer nitro group in **1d**. Furthermore, **1d** shows a larger angle (11.4°), due to no substituent at the inner position. Although the X-ray analyses of **1e** and **1f** have not been done yet, they can be expected to assume the similar structures of **1c** and **1d**.

The wavenumbers of the amino group in **1e** were observed at 3439 and 3298 $\mathrm{cm^{-1}}$, which are much lower than the corresponding wavenumbers of 3484 and 3400 $\mathrm{cm^{-1}}$ in 2,6-dimethylaniline. Such a large shift probably stems from formation of hydrogen bondings based on NH–π interaction, which arises from the amino group directed toward the π–cloud of the anthracene unit. On the other hand the outer amino group in **1f** shows the wavenumbers at 3470 and 3360 $\mathrm{cm^{-1}}$, indicating smaller shifts compared to those in **1e**.

Charge-transfer complexes of cyclophane compounds with tetracyanoethylene (TCNE) could give information of the π basicity related to the transannular interaction between aromatic rings.[10] **1a** formed the charge-transfer complex with TCNE to show its $\lambda_{\max}$ at 768 nm, which was identified as the 1:1 complex from the Job plot. Table 2 summarizes the spectral data of the complexes. As deduced from the $\lambda_{\max}$ values, TCNE binds the anthracene unit. The $\lambda_{\max}$ of the complex of **1b** shifts to longer wavelength, meaning that the charge-transfer transition occurs at lower energy. It may well be that the anisole unit increases the π-base strength of the anthracene unit through transannular interaction. In agreement of this explanation, substitution of the ring with a nitro group leads the $\lambda_{\max}$ to shorter wavelength. **1c** and **1d** show the same $\lambda_{\max}$.

Table 2. Absorption maxima[a] of CT complexes of anthracenophanes with TCNE

Compound	TCNE complex
	$\lambda_{\max}$/nm
1a	768
1b	782
1c	738
1d	738
1e	713
1f	787

[a] In $\mathrm{CHCl_3}$.

On the other hand interesting results were obtained for **1e** and **1f**. Considering the electron-donating effect of the amino group a bathochromic shift for the complex would have been expected, however, the $\lambda_{\max}$ of **1e** underwent a hypsochromic shift showing at 713 nm in comparison with expected 787 nm of **1f**. In chloroform there could be a small amount of HCl. The fact that the shift of the $\lambda_{\max}$ to 657 nm was observed by addition of a small amount of HCl excludes possibility of an effect of the protonated amino group. Such a hypsochromic shift of **1e** may be related to the NH–π interaction since the less π-basic anthracene ring could be induced by the NH–π interaction.

It should be noted that a quite different TCNE complex was observed between the anthracenophane having the amino group at its inner position and the analog having the amino group at its outer position.

References and Notes

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8 Crystal data for **1c**: $\mathrm{C_{29}H_{19}NO_2S_2}$, M = 417.54, monoclinic, space group $P2_1/n$ (#14), $a = 16.241(1)$, $b = 7.426(9)$, $c = 32.778(3)$ Å, $\alpha = 90°$, $\beta = 102.05(1)°$, $\gamma = 90°$, $V = 3842(3)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 1.400\,\mathrm{g/cm^3}$, $\mu(\mathrm{Mo\,K\alpha}) = 26.76\,\mathrm{cm^{-1}}$, Rigaku AFC7R diffractometer, $R_1 = 0.046$ (for 5329 reflections with $I > 3.0\sigma(I)$, $wR2 = 0.125$ (for all data (7844 reflections)).
9 Crystal data for **1d**: $\mathrm{C_{29}H_{19}NO_2S_2}$, $M_r = 417.54$, triclinic, space group $P\bar{1}$ (#2), $a = 8.914(2)$, $b = 9.726(2)$, $c = 11.528(3)$ Å, $\alpha = 102.07(2)°$, $\beta = 100.03(2)°$, $\gamma = 90.78(1)°$, $V = 964.0(3)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.438\,\mathrm{g/cm^3}$, $\mu(\mathrm{Mo\,K\alpha}) = 26.74\,\mathrm{cm^{-1}}$, Rigaku AFC7R diffractometer, $R_1 = 0.059$ (for 3466 reflections with $I > 3.0\sigma(I)$, $wR2 = 0.113$ (for all data (3673 reflections)).
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