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The Stability Constants for the 18-Crown-6 Complexes with [2.2]Metacyclophanediazonium Salts

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Synopsis. Transannular interaction between two aromatic rings in [2.2]metacyclophanes was estimated by the determination of the stability constants (K_s) for 18-crown-6 complexes with their diazonium salts. It was found out that the K_s is about 10 times as small as that for the corresponding benzenediazonium salt.

Although a through-space interaction between two aromatic rings in [2.2]metacyclophanes (=MCPs) obviously plays a central role in a lot of unique reactivities of them,[1—4] quantitative estimation for such an interaction, i.e., the degree to which the electronic nature of one aromatic ring could be affected by the other ring seems very limited. As one of the studies directing towards such an evaluation we introduced the azobenzene unit into [2.2]MCP skeletons and examined their spectral properties, by which some useful information could be obtained.[5,6] On the other hand it has been shown that cationic character of the arenediazonium ion can be estimated by its stability constant for the complexation with crown ether.[7—12] This constant is supposed to reflect the electronic nature of the aromatic ring to which the diazonium moiety is attached. So if this estimation is applied to the [2.2]MCPs' system in which a through-space interaction has significant influences on the nature of the aromatic ring, fruitful results concerning this interaction would be obtained. In this note, thus, we report the stability constants (K_s) for 18-crown-6 complexes with [2.2]MCP diazonium salts (**2a** and **2b**) in order to clarify the through-space interaction in detail.

Diazonium salts (**2a** and **2b**) were prepared from the corresponding amino[2.2]MCPs (**1a**[4] and **1b**) (Chart 1) with isopentyl nitrite in EtOH and THF. The structural analysis[13] for [2.2]MCPs indicates that the inner substituent in **2a** or **2b** gives no significant steric hindrance at the coordinate site. The stability constants (K_s) based on Scheme 1 (see Experimental) were determined in 1,2-dichloroethane or methanol according to the reported method.[13] In Table 1 K_s values are summarized together with the spectral properties of the diazonium salts and their complexes. The data of the referential *p*-subsituted benzenediazonium tetrafluoroborates are also shown in Table 1. In any cases blue shifts of λ_{max} can be observed on complexation with 18-crown-6, probably due to the decrease of the ability of the diazonium moiety to withdraw electrons from the ring, resulting in decreasing mesomeric effect in such *p*-disubsituted benzenes. MCP diazonium salts (**2a** and **2b**) show their λ_{max} at longer wavelengths in both free or complexed form compared with **3a** and **3b**, respectively, which is attributable to trans-spacial overlap of the π-orbitals of two aromatic rings. And free MCP diazonium salts (**2a** and **2b**) exhibited blue shifts of their λ_{max} when dissolved in a polar solvent like MeOH. The similar results were obtained for **3a** and **3b**. On the contrary in the complexed form no solvent effect on the λ_{max} was observed. These are explainable since the ground state of the free diazonium salts is more stabilized than that of the complexes in a polar solvent. Interestingly methyl MCP diazonium salt (**2a**) shows its λ_{max} at longer wavelength than methoxy derivative (**2b**) does, which is different from the relation between **3a** and **3b**. This might be attributed to the fact that λ_{max} of 8,16-dimethyl MCP (298 nm) is located at

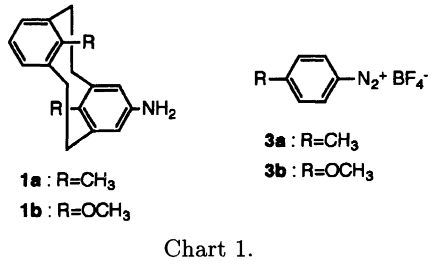
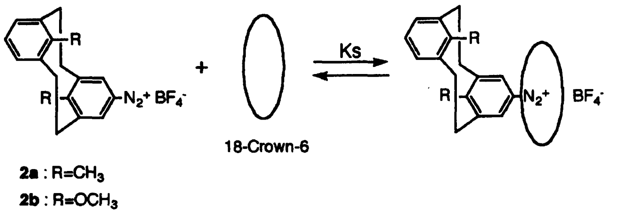


Chart 1.



Scheme 1.

Table 1. Stability Constants (K_s) for the 18-Crown-6 Complexes at 15 °C

Diazonium salt	Solvent	λ^F_{max} nm[a)]	λ^C_{max} nm[b)]	$\log K_s$[c)]
2a	$ClCH_2CH_2Cl$	391	347	4.12
2b	$ClCH_2CH_2Cl$	355	327	3.73
3a[d)]	$ClCH_2CH_2Cl$	282	264	5.10
3b[d)]	$ClCH_2CH_2Cl$	321	298	4.67
2a	Methanol	369	343	2.36
2b	Methanol	344	327	2.19

a) Maximum wavelength of the free diazonium salt.
b) Maximum wavelength of the complex. c) K_s: M^{-1}.
d) Ref. 12.

longer wavelength than that of 8,16-dimethoxy MCP-(293 nm).[14] It is known[10,11] that the cations with the more effective positive charge on the nitrogen atoms of the diazonium ion form the stronger complexes and vice versa. The stability constants for **2a** and **2b** in 1,2-dichloroethane are about 10 times as small as those for **3a** and **3b**, respectively, which is chiefly derived from the decrease of electron density on MCP diazonium cations. In more detail the aromatic ring possibly increase π-electron density of the aromatic ring of the other side and consequently reducing cationic character of the diazonium ion. This decrease in stability is nearly consistent with the decrease observed when the *p*-substituent of a benzenediazonium salt is changed from hydrogen to dimethylamino group in the similar titration (from 2.4 to 1.56 in log K_s[12]). Although it may be rough assumption, the electron-releasing effect of one aromatic ring toward the other aromatic ring in [2.2]MCP skeleton corresponds to that of dimethylamino group. These results also indicate there has to exist a through-space interaction between two aromatic rings. The difference in the stability constant between **2a** and **3a** is almost same as that between **2b** and **3b**. This fact implies that the nature of the inner substituent on the aromatic ring is not so effective on electronic nature of the other ring. On the other hand the stability constants in MeOH are smaller than those in 1,2-dichloroethane, that is because the free diazonium ions are more stabilized in a polar solvent such as MeOH. So slight difference in stability constants in MeOH between **2a** and **3a** (K_s=2.39[12]) or **2b** and **3b** (K_s=2.09[12]) could be attributed to this aspect. In conclusion it is demonstrated for first time that in [2.2]MCPs a cationic character of the benzenediazonium ion is reduced about 10 times in the term of K_s by the aromatic ring of the other side, from which the electron-releasing effect of the aromatic ring in [2.2]MCPs is comparable to that of the dimethylamino group.

Experimental

^{1}H NMR spectra were recorded on a Nippon Denshi FX-60 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were measured on a Hitachi 260-30 spectrometer. Absorption spectra were recorded on a Shimadzu UV-180 spectrophotometer.

Methyl[2.2]MCP Diazonium Salt (2a). To a stirred solution of 5-amino-8, 16-dimethyl[2.2]MCP (**1a**)[4] (150 mg, 0.6 mmol) in 20 ml of tetrahydrofuran and methanol (1 : 1) was added 0.5 ml of 30% hydrochloric acid at room temperature, and the mixture was stirred for 10 min. After the addition of isopentyl nitrite (0.1 ml, 1 mmol) at 0 °C, the reaction mixture was stirred for 30 min to which 42% tetrafluoroboric acid (1 ml) was added. After stirring for 10 min, 60 ml of absolute ether was added to the reaction mixture. The resulting precipitates were collected by filtration and washed with ethanol and ether to give 180 mg (0.52 mmol, 87% yield) of **2a** as pale green powder, mp decomp, over 100 °C. IR (KBr) 2951, 2260, 1562, 1145, 1060, and 739 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ=0.70 (3H, s), 0.82 (3H, s), 2.60—3.15 (8H, m), 6.65—7.15 (3H, m), and 8.36 (2H, s). Found: C, 61.02; H, 5.53; N, 7.60%. Calcd for $C_{18}H_{19}N_2BF_4 \cdot 0.25H_2O$: C, 60.96; H, 5.54; N, 7.90%.

5-Amino-8,16-dimethoxy[2.2]MCP (1b). After hydrogen gas was introduced into a suspension of 5-nitro-8,16-dimethoxy[2.2]MCP (100 mg, 0.32 mmol)[3] and 10% Pd/C in 10ml of benzene with stirring for 1 h at room temperature, the Pd/C was filtered off. The filtrate was evaporated in vacuo to leave the residue, which was recrystallized from benzene to give 90 mg (0.32 mmol, quant.) of **1b** as colorless prisms, mp 210—213 °C. IR (KBr) 3351, 2935, 1622, 1600, 1480, 1215, and 1018 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.50—2.20 (2H, brs (=broad singlet), exchanged by D$_2$O), 2.40—2.80 (8H, m), 2.84 (3H, s), 3.00 (3H, s), 6.40 (2H, s), and 6.60—7.05 (3H, m). Found: C, 76.54; H, 7.48; N, 4.82%; M$^+$, 283. Calcd for $C_{18}H_{21}O_2N$: C, 76.30; H, 7.47; N, 4.94%; M, 283.

Methoxy[2.2]MCP Diazonium Salt (2b) was obtained from 5-amino-8,16-dimethoxy[2.2]MCP (**1b**) in a similar method. Pale yellow crystal, mp decomp over 116 °C. IR (KBr) 2950, 2226, 1564, 1471, 1409, 1280, and 1091 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ=2.60—3.00 (8H, m), 3.05 (3H, s), 3.32 (3H, s), 6.90—7.10 (3H, m), and 8.12 (2H, s). Found: C, 56.33; H, 5.21; N, 7.45%. Calcd for $C_{18}H_{19}O_2N_2BF_4$: C, 56.57; H, 5.01; N, 7.33%.

pK_s Measurement. pK_s values were determined according to the literature.[12] A solution of MCP diazonium salts (**2a**, **2b**) (ca. 1×10^{-6} M, 1 M=1 mol dm^{-3}) in 1,2-dichloroethane or methanol was prepared. When a portion (5 ml) of this solution was added to a solution containing specified amounts of 18-crown-6 at 15 °C, an absorption spectrum was recorded. The stability constants (K_s) based on Eq. 1 was obtained by using [MCP-N$_2^+$, Crown, BF$_4^-$]/[MCP-N$_2^+$BF$_4^-$] ratio which can be determined spectrally according to Eq. 2;

$$\text{MCP-N}_2^+\text{BF}_4^- + \text{Crown} \overset{K_s}{\rightleftharpoons} \text{MCP-N}_2^+,\text{Crown},\text{BF}_4^-$$

$$K_s = [\text{MCP-N}_2^+,\ \text{Crown},\ \text{BF}_4^-]/[\text{MCP-N}_2^+\text{BF}_4^-][\text{Crown}] \tag{1}$$

$$\begin{aligned}[\text{MCP-N}_2^+\text{BF}_4^-]_0 &= [\text{MCP-N}_2^+\text{BF}_4^-] \\ &\quad + [\text{MCP-N}_2^+,\text{Crown},\text{BF}_4^-] \\ [\text{Crown}]_0 &= [\text{Crown}] + [\text{MCP-N}_2^+,\ \text{Crown},\text{BF}_4^-]\end{aligned} \tag{2}$$

where [MCP-N$_2^+$BF$_4^-$]$_0$ and [Crown]$_0$ denote the initial concentrations of diazonium salt and the crown ether, respectively.

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14) λ_{max} was measured in $CHCl_3$ at 25 °C.