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Studies on the Complexes of 4′-Substituted Benzo-15-Crown-5 Ligands with Sodium Picrate and Picric Acid

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Abstract. Complexes of nine 4′-substituted benzo-15-crown-5 ligands with sodium picrate were prepared. A good linear relationship of the $\Delta\lambda$ values from the UV spectra and Hammett $\Delta\sigma[\sigma_p - \sigma_m]$ values was observed. Charge transfer complexes of ten 4′-substituted benzo-15-crown-5 ligands with picric acid were isolated in crystalline form. The color of the complexes depended on the nature of the substituents. All of the complexes were identified by elemental analyses, UV and IR spectra.

Key words. Crown ether compounds, substituted benzo crowns, charge transfer complexes, molecular complex, Hammett substituent constant, sodium picrate, picric acid, UV spectra.

1. Introduction

Benzo-15-crown-5 with a cavity size of 1.7–2.2 Å can form complexes with sodium salts [1]. The complexes of a series of 4′-substituted benzo-15-crown-5 ligands with sodium picrate and their spectral properties have been reported [2]. The X-ray crystal structure analysis of the benzo-15-crown-5 complex with sodium picrate has been published [3].

Krishnan and coworkers [4, 5] reported the molecular complexing behavior of some crown ethers with various aromatic neutral molecules such as 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) in solution. In earlier studies, we reported the charge-transfer complexation of 4′-substituted benzo-15-crown-5 ligands with picric acid in chloroform [6], and determined the association constants by an NMR method [7]. It was found that there was a linear relationship between the association constants and the Hammett constants [7]. In order to more fully understand the structural differences between complexes of crown ethers with metal ions and those with neutral molecules, we have prepared nine 4′-substituted benzo-15-crown-5 complexes with sodium picrate and ten 4′-substituted benzo-15-crown-5 charge transfer complexes with picric acid. The latter complexes which have not been reported previously, were isolated in the crystalline form.

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2. Experimental

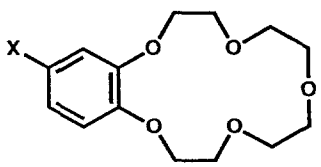
Sodium picrate was prepared as reported [8]. Picric acid was dehydrated by azeotropic distillation with benzene, then was recrystallized from absolute ethanol, m.p. 122°C.

2.1. PREPARATION OF LIGANDS

Benzo-15-crown-5 (**I**, where X = H) was prepared by an improved method [9] as follows. Equal amounts of catechol and the dichloro derivative of tetraethylene glycol were heated together in 1-butanol and sodium hydroxide in a pressure vessel at 135–145°C for 1–3 h under nitrogen. The solvent was removed. The residue was extracted with *n*-heptane and the product separated as white plates, m.p. 81.5–82°C (lit. value: 79–79.5°C [10]), 63–69%.

4′-Iodobenzo-15-crown-5 (**I**, X = I) was prepared as reported [1] as white needles, m.p. 78.5–79°C; *Anal.* Calcd for $C_{14}H_{19}O_5I$: C, 32.33: H, 3.49. Found: C, 32.38; H, 3.43 [11]. 4′,5′-Diiodobenzo-15-crown-5. m.p. 98.5–99.5°C, was also isolated.

4′-Bromo-(**I**, X = Br) [12], 4′-nitro-(**I**, X = NO_2) [12], 4′-formyl-(**I**, X = C(O)H) [1], 4′-acetyl-(**I**, X = $C(O)CH_3$) [13, 14], 4′-propionyl-(**I**, X = $C(O)CH_2CH_3$) [13, 14], and 4′-carboxy-(**I**, X = CO_2H) [15] benzo-15-crown-5 ligands were prepared as reported.



I, 4′-XB15C5

4′-Ethylbenzo-15-crown-5 (**I**, X = C_2H_5) was synthesized by an improved method [13] as follows. Palladium hydroxide on carbon catalyst (0.1 g) was shaken in 10 mL of glacial acetic acid under 2–3 kg/cm^2 hydrogen gas pressure at room temperature for 1 h. A solution of 3 g of 4′-acetylbenzo-15-crown-5 in 20 mL of glacial acetic acid was added to the catalyst mixture and the resulting mixture was shaken under 3–4 kg/cm^2 hydrogen gas pressure at 50–60°C for 1.5 hours. The mixture was cooled and the catalyst was filtered. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina using hexane as the eluent. The solvent was removed and the residue was recrystallized from *n*-hexane to give 94% of white needles, m.p. 35–35.5°C. The product gave a satisfactory elemental analysis.

4′-Alkoxycarbonylbenzo-15-crown-5 [**I**, X = $CH_3OC(O)$, $C_2H_5OC(O)$, *n*-$C_3H_7OC(O)$, *n*-$C_4H_9OC(O)$ and *n*-$C_5H_{11}OC(O)$] were prepared as reported [16] as follows. Concentrated sulfuric acid (3–8 mL) was slowly dripped into a stirred mixture of 5–10 mmole of 4′-carboxybenzo-15-crown-5 and 20–40 mL of the appropriate alcohol. The mixture was stirred st 65°, 85°, 95°, 95° and 98°C for 4, 5, 6.5, 9 and 9 hours, respectively, for the five reactions. The excess alcohol was removed under reduced pressure and the residue was poured into 30 mL of water. The mixture was extracted with chloroform. The chloroform layer was washed with

5% aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The solvent was then removed and the residue was recrystallized from *n*-heptane to give 92–99% of the product as white needles. The melting points were 80.5–81°C (lit. value 80–82°C [15]), 74–75°C, 69.5–70°C, 70–70.5°C and 43.5–44.5°C for the five products. The elemental analyses for the new products are as follows: X = $C_2H_5OC(O)$, Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11. Found: C, 59.88; H, 7.07; X = $C_3H_7OC(O)$, Calcd for $C_{18}H_{26}O_7$: C, 61.00; H, 7.39. Found: C, 60.44; H, 7.36; X = $C_4H_9OC(O)$, Calcd for $C_{19}H_{28}O_7$: C, 61.94; H, 7.66. Found: C, 61.91; H, 7.64; X = $C_5H_{11}OC(O)$, Calcd for $C_{20}H_{30}O_7$: C, 62.81; H, 7.90. Found: C, 62.99; H, 8.01.

4′-N-*o*-Hydroxybenzylideneaminobenzo-15-crown-5 (**I**, X = *o*-HOC_6H_4CH=N-) [6] was synthesized as follows. 4′-Nitrobenzo-15-crown-5 was first reduced to the amino-crown [17]. *o*-Hydroxybenzaldehyde (1.5 mL) was slowly dripped into 2.5 g of the amino-crown in 25 mL of stirred ethanol at room temperature under an atmosphere of nitrogen. The mixture was stirred for 15 minutes and the yellow precipitate was filtered. The solid was recrystallized from ethanol to give 2.9 g (overall 94%) of yellow needles, m.p. 127–127.5°C; *Anal.* Calcd. for $C_{21}H_{25}NO_6$: C, 65.10; H, 6.51; N, 3.64. Found: C, 65.10; H, 6.51; N, 3.76.

Bis(4′-Benzo-15-crown-5) ketone [**I**, X = —C(O)—] was prepared as reported [18] as follows. 4′-Carboxybenzo-15-crown-5 (1.25 g) was added to a stirred mixture of 30 g of polyphosphoric acid, 8 mL of phosphoric acid and 1.1 g of benzo-15-crown-5 at 70°C. The mixture was stirred an additional 7 hours at 80°C. The red solution was cooled and hydrolyzed with 100 mL of water. The aqueous mixture was extracted with 100 mL of chloroform and the chloroform extract was washed with 5% aqueous sodium hydroxide and dried over anhydrous sodium sulfate. The solvent was then removed under vacuum and the residue was recrystallized from ethanol to give 2.1 g (93%) of white crystals, m.p. 143.5–144.5°C; *Anal.* Calcd for $C_{29}H_{38}O_{11}$: C, 61.91; H, 6.81. Found: C, 61.75; H, 6.79.

2.2. PREPARATION OF 4′-XB15C5–SODIUM PICRATE COMPLEXES

Each crown ether (2 mmol) in 2–4 mL of chloroform was added to a stirred solution of 2 mmol of sodium picrate in 20–40 mL of methanol at 50°C. The mixture was stirred at 50°C until a yellow solid formed. The mixture was cooled and the solid was filtered and recrystallized from methanol. Table I lists the complexes formed together with their m.p. and elemental analyses.

2.3. PREPARATION OF 4′-XB15C5–PICRIC ACID COMPLEXES

Each crown ether (2 mmol) in 2–4 mL of chloroform was added to 2 mmol of picric acid in 15–20 mL of hot chloroform. The orange colored solution was evaporated until most of the chloroform was removed and a small amount of acetone was added. The mixture was allowed to stand for 3–5 days and the resulting solid was filtered. Table II lists the physical form and properties for these complexes.

3. Results and Discussion

The series of 4′-substituted-benzo-15-crown-5 ligands was prepared to study the effects of various types of substituents on the complexation behavior of benzo-15-

Table I. Properties of the 1 : 1 4′-XB15C5-sodium picrate complexes.

Complex No.	X	Color and form of crystal	mp °C	Elemental Analysis Calcd. % C	H	N	Found % C	H	N
1	I	Bright yellow transparent	182–184	37.23	3.28	6.51	37.07	3.21	6.42
2	CHO	Bright yellow transparent	174.5–175.5	46.08	4.05	7.68	46.25	4.05	7.50
3	HOC(O)	Yellow	236–237	44.77	3.94	7.46	44.38	3.80	7.21
4	$CH_3OC(O)$	Yellow needle	171.5–172.5	45.76	4.19	7.28	45.48	4.18	7.52
5	$C_2H_5OC(O)$	Yellow needle	143.5–144.5	46.71	4.43	7.10	46.79	4.42	6.96
6	n-$C_3H_7OC(O)$	Yellow needle	165–166	47.61	4.66	6.94	47.18	4.36	6.94
7	n-$C_4H_9OC(O)$	Yellow needle	162–163	48.47	4.88	6.78	48.86	4.84	6.42
8	o-$HOC_6H_4CH{=}N$	Yellow needle	191.5–192.5	50.79	4.26	8.78	50.72	4.26	9.05
9	O=C	Yellow needle	145.5–146.5	46.24	3.98	7.89	46.10	3.84	7.72

Table II. Properties of the 4′-XB15C5-picric acid complexes.

Complex No.	X	Formation	Color and form of crystal	mp °C	Elemental Analysis Calcd. % C	H	N	Found % C	H	N
1	CH_3CH_2	$C_{22}H_{27}O_{12}N_3/H_2O$	Orange red needle	78.5–60	48.64	5.38	7.74	48.34	5.27	7.33
2	H	$C_{20}H_{23}O_{12}N_3/H_2O$	Orange	58–59.5	46.60	4.89	8.15	46.76	4.91	7.85
3	Br	$C_{20}H_{22}O_{12}N_3Br/H_2O$	Orange yellow	56–57	40.42	4.07	7.07	40.23	4.01	7.02
4	I	$C_{20}H_{22}O_{12}N_3I/H_2O$	Orange yellow	63–65	37.46	3.77	6.55	37.15	3.70	6.41
5	CH_3CO	$C_{22}H_{25}O_{13}N_3/H_2O$	Orange yellow needle	75.5–76.5	48.29	4.97	7.68	48.29	5.00	7.61
6	C_2H_5CO	$C_{23}H_{27}O_{13}N_3/H_2O$	Yellow needle	84.5–85.5	48.34	5.11	7.35	48.33	5.14	7.56
7	$CH_3OC(O)$	$C_{22}H_{25}O_{14}N_3/H_2O$	Yellow needle	72–73.5	46.08	4.75	7.33	45.72	4.67	7.28
8	$C_2H_5OC(O)$	$C_{23}H_{27}O_{14}N_3/H_2O$	Yellow needle	66–67	47.02	4.97	7.15	47.02	4.93	6.80
9	n-$C_3H_7OC(O)$	$C_{24}H_{29}O_{14}N_3/H_2O$	Yellow transparent	50–51.5	47.92	5.19	6.98	47.94	5.00	6.80
10	NO_2	$C_{20}H_{22}O_{14}N_4/H_2O$	Pale yellow	53–54	42.86	4.32	10.00	42.99	4.19	10.63

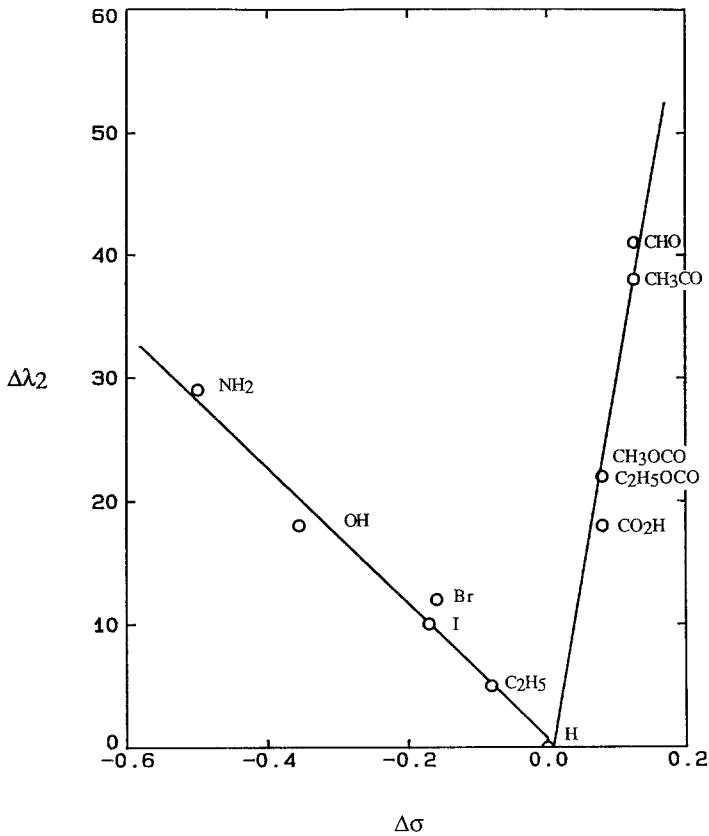


Fig. 1. Plots of $\Delta\lambda_2$ for 4′-XB15C5-sodium picrate complexes versus $\Delta\sigma$ ($\Delta\lambda_2$ = the difference between the λ for the complexes of substituted and unsubstituted ligands).

crown-5 with sodium picrate (see Table I). It has been reported that the color of the complex is related to the electronic effects of the 4′-substituent [2]. The color darkens with electron-donating species and lightens with electron-withdrawing groups. A study of the UV spectra of these complexes showed that there were B-band shifts caused by the 4′-substituent and that the magnitude of the shifts was in a crossed-linear relationship with the differences in Hammett σ values. This latter difference ($\Delta\sigma = \sigma_p - \sigma_m$) is a measure of the conjugative effects of the substituents. The UV data for the B-band for these complexes are given in Table III. The new data in this paper concerns complexes **1**–**9**. A plot of $\Delta\lambda_2$ (the difference between λ for the complexes of the substituted and unsubstituted ligands) versus $\Delta\sigma$ shows straight line relationships (Figure 1). Plots for $\Delta\lambda_1$ and $\Delta\lambda_3$ *versus* $\Delta\sigma$ would be similar except that in the latter case the lines would have smaller slopes. The linear equations are as follows (d = electron-donating species and w = electron-withdrawing species):

$$\Delta\lambda_1^{d} = 1.13 - 34.2\Delta\sigma \qquad (\gamma = 0.969)$$

$$\Delta\lambda_1^{w} = -3.47 + 250\Delta\sigma \qquad (\gamma = 0.956)$$

$$\Delta\lambda_2^{d} = 0.79 - 54.8\Delta\sigma \qquad (\gamma = 0.988)$$

$$\Delta\lambda_2^{w} = -2.76 + 324\Delta\sigma \quad (\gamma = 0.979)$$

$$\Delta\lambda_3^{d} = -4.33 - 20.6\Delta\sigma \quad (\gamma = 0.998)$$

$$\Delta\lambda_3^{w} = -3.11 + 74.5\Delta\sigma \quad (\gamma = 0.959)$$

All the substituents (except H) can conjugate with the benzene ring ($p-\pi$ or $\pi-\pi$) and will cause a bathochromic shift of the B-band in the UV spectrum. The magnitude of the shift represents the extent of conjugative interaction. As one would expect, the plot of $\Delta\lambda$ versus $\Delta\sigma$ (Figure 1) shows straight line relationships. The slopes of the lines after complexing [324 (donating species) and -54.8 (withdrawing species)] are larger than the slopes before complexing [250 (donating) and -34.2 (withdrawing)]. These results indicate that conjugation increases after complexation thereby increasing the bathochromic shift.

A study of the UV molar absorptivities (ε) for the 4′-substituted-benzo-15-crown-5 ligands and their sodium picrate complexes was also done. As shown in Table IV, the ε values of the B- and K-bands greatly increased for the complexed over the non-complexed ligands. These results indicate that formation of the complexes results in hypochromic effects.

The picric acid complexes of the 4′-substituted-benzo-15-crown-5 ligands shown in Table II were prepared to compare the physical properties of the picric acid and sodium picrate complexes. The complexes listed in Table II are quite labile and they needed to be dried in air rather than in a vacuum. The complex of picric acid and 4′-N-*o*-hydroxybenzolideneaminobenzo-15-crown-5 was obtained in the form of

Table III. UV data of 4′-XB15C5 and their sodium picrate complexes.

Complex		λ max (B, nm)		$\Delta\lambda_1^a$	$\Delta\lambda_2^b$	$\Delta\lambda_3^c$	$\Delta\sigma$
No.	X	crown	complex	(nm)	(nm)	(nm)	$\sigma p - \sigma m$
	H	276	272	0	0	−4	0
	H_2N [2]	295	301	19	29	+6	−0.499
	HO [2]	287	290	11	18	+3	−0.355
	C_2H_5 [2]	280	277	4	5	−3	−0.081
	Br [2]	285	284	9	12	−1	−0.159
	CH_3CO [2]	307	312	31	38	+5	+0.126
1	I	283	282	7	10	−1	−0.17
2	CHO	307	313	31	41	+6	+0.126[d]
3	HOC(O)	288	290	12	18	+3	+0.08
4	$CH_3OC(O)$	290	294	14	22	+4	+0.08
5	$C_2H_5OC(O)$	290	294	14	22	+4	+0.08
6	n-$C_3H_7OC(O)$	290	294	14	22	+4	e
7	n-$C_4H_9OC(O)$	290	294	14	22	+4	e
8	o-$HOC_6H_4CH{=}N$	350	350	74	78	0	e
9	O=C	316	343	40	71	+27	e

[a]$\Delta\lambda_1$ = difference between the λ for the substituted and unsubstituted benzo-15-crown-5; [b]$\Delta\lambda_2$ = difference between the λ for the complexes of substituted and unsubstituted benzo-15-crown-5; [c]$\Delta\lambda_3$ = difference between the λ for the complexed and uncomplexed species for the same crown; [d]$\Delta\sigma$ of $CH_3C(O)$ is used; [e]No data are available.

Table IV. ε_{max} data of B- and K-bands of 4′-XB15C5 and their complexes.

No.	X	B-band			K-Band		
		Crown	Complex	Δε[a]	Crown	Complex	Δε[a]
	H	2478	4595	2117	7414	24486	17072
1	I	3068	4816	1748	13562	26146	12584
2	CHO	9045	14406	5361	17873	30999	13126
3	HOC(O)	5350	6472	1122	10784	19879	9095
4	$CH_3OC(O)$	5764	8242	2478	12113	18898	6785
5	$C_2H_5OC(O)$	6069	8595	2526	12830	19694	6864
6	n-$C_3H_7OC(O)$	6237	8376	2172	13045	19069	6024
7	n-$C_4H_9OC(O)$	6706	8333	1661	13979	19000	5021
8	o-$HOC_6H_4CH{=}N$	9584	23168	13584	12501	24398	11897
9	O=C	17397	37025	19628	25253	50808	25556

[a]Δε = difference between ε of the complex and crown.

orange-yellow needles with a decomposition temperature of 205–230°C. The complexes with 4′-amino- and 4′-hydroxybenzo-15-crown-5 were red but pure products could not be obtained because they were easily oxidized in air. Picric acid complexes could not be obtained for the 4′-substituted-benzo-15-crown-5 ligands where X = the following groups: n-$C_4H_9OC(O)$—, n,-$C_5H_{11}OC(O)$, $CH_2{=}CHCH_2NHC(S)NH$—, n-C_3H_7—, n-C_4H_9—, n-C_5H_{11}—, n-$C_3H_7C(O)$, n-$C_4H_9C(O)$—, n-$C_5H_{11}C(O)$—, n-$C_{11}H_{23}C(O)$—, n-$C_{13}H_{27}C(O)$—, n-$C_{15}H_{31}C(O)$—, and n-$C_{17}H_{35}C(O)$— [13, 16].

In general, as shown in Table V, the colors of the complexes of 4′-XB15C5 with picric acid are darker than are those of the corresponding complexes with sodium picrate. Jayathirtha and Krishnan reported that the appearance of a red color in solution is evidence of a molecular complex [4d]. From Tables IV and V, it is evident that the nature of the electronic effects of the 4′-substituent has an influence on the properties of the complexes. Electron-donating substituents increase the

Table V. Colors of 4′-XB15C5 complexes with sodium picrate and picric acid.

X	Complex with NaPic	Complex with HPic
O-$HOC_6H_4CH{=}N$	Yellow	Orange red
CH_3CH_2	Yellow [2]	Orange
H	Yellow	Orange
Br	Yellow [2]	Orange yellow
I	Bright yellow	Orange yellow
CH_3CO	Yellow [2]	Orange yellow
C_2H_5CO	Yellow [2]	Yellow
$CH_3OC(O)$	Yellow	Yellow
$C_2H_5OC(O)$	Yellow	Yellow
n-$C_3H_7OC(O)$	Yellow	Yellow
O_2N	Pale yellow	Pale yellow

electron densities on the benzene ring causing a stronger charge-transfer in the complex and the complex becomes a darker color. Electron-withdrawing substituents have the opposite effect, i.e., the electron density is decreased causing a weaker charge-transfer and a lighter color.

The IR spectra of the 4′-XB15C5 complexes with picric acid are also instructive [11]. The IR band of the crown ether at 980 cm^{-1} disappears in the complex with picric acid. The aromatic bands in the IR spectra for 4′-XB15C5 with electron-donating substituents shift to higher frequencies upon complexation. For example, where $X = C_2H_5$, IR bands at 1265 and 1230 cm^{-1} shift to 1270 and 1250 cm^{-1} for the complex and where $X = o\text{-}HOC_6H_4CH{=}N{-}$, IR bands at 1265 and 1240 cm^{-1} shift to 1284 and 1265 cm^{-1} in the complex. In contrast, the aromatic bands for 4′-XB15C5 with electron-withdrawing substituents shift to lower frequencies. For example, where $X = CH_3C(O)$, IR bands at 1290 and 1230 cm^{-1} shift to 1265 and 1215 cm^{-1} in the complex.

The results given in this paper show clearly that the nature of the substituent on the aromatic ring has a significant influence on the complexation of 4′-XB15C5 with sodium picrate and picric acid.

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