CHEMISTRY LETTERS, pp. 1189-1192, 1980.

COMPLEX FORMING BEHAVIOR OF BIS(BENZOCROWN ETHER)S LINKED BY POLY(OXYETHYLENE) CHAIN AND 4'-ALKOXYBENZOCROWN ETHERS 1)

Fumio WADA,* Yoshiko WADA, Tokio GOTO, Kiyoshi KIKUKAWA,
and Tsutomu MATSUDA
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

New bis(benzocrown ether)s linked by various length of poly(oxyethylene) chain, $-OCH_2(CH_2OCH_2)_mCH_2O-$; m = 1 - 4, shows much increased extractability and selectivity to larger cations than the hole size of the crown ether ring in the extraction of alkali metal picrates. The spectra of the bis(benzo-18-crown-6) complexes in THF suggested the existence of more complex ionic species than those of bis(benzo-15-crown-5) series.

We previously reported the preparation of new bis(benzocrown ether)s linked by poly(oxyethylene) chain (**4** and **5**) by the reaction of sodium salts of 4'-hydroxybenzocrown ethers with ditosylate of polyethylene glycols.2) The similar reaction with bromoalkane and 1,6-dibromohexane can be used to introduce a lipophilic group to give 4'-alkoxybenzocrown ethers such as **2** or **3** and another bis(benzocrown ether) (**6**), respectively. In analogy with bis(benzocrown ether)s reported previously,3)4)

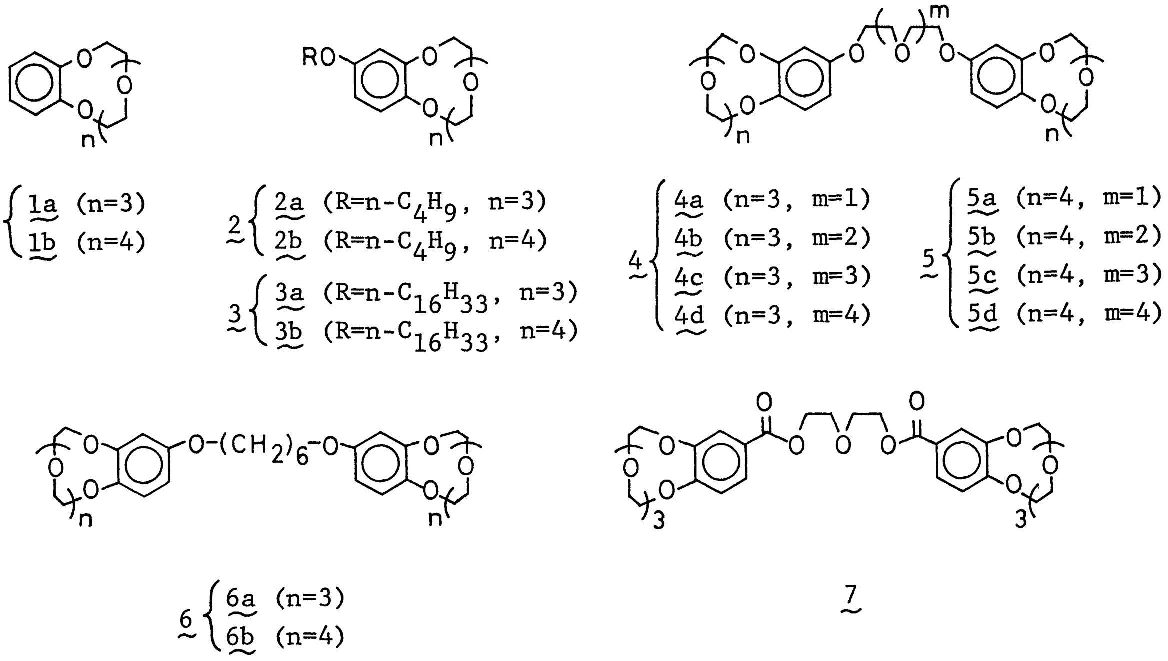

Fig. 1 Schematic representation of crown ethers in this study

4, 5 and 6 are expected to form the complexes of sandwich type and to show enhanced complexation capability with alkali metal cations. Effect of the lipophilic group in 2 or 3 on the complex formation is also intersting in view of the reported efficacy of the [2.2.2] cryptant and/or 18-crown-6 bearing a lipophilic chain as phase transfer catalyst.5)6)

This paper presents the complex forming behavior of these substituted benzocrown ethers (2 to 6) with alkali metal picrates.

Perhydrodibenzo-18-crown-6 (DC18C6), 1 and 7 are obtained by the conventional methods.3)7) Yields and analytical data of 2, 3 and 6 are as follows; (Calcd. values in parenthesis). 2a, 70%, mp 46.3 - 46.5°C, C, 63.29%; H, 8.40% (C, 63.51%; H, 8.29%). 2b, 73%, mp 29.5 - 30.0°C, C, 62.51%; H, 8.53% (C, 62.48%; H, 8.39%). 3a, 69%, mp 67.6 - 68.1°C, C, 69.84%; H, 10.39% (C, 70.83%; H, 10.30%). 3b, 67%, mp 54.9 - 56.3°C, C, 68.78%; H, 10.16% (C, 69.53%; H, 10.21%). 6a, 75%, mp 102.0 - 104.1°C, C, 62.61%; H, 7.77% (C, 62.75%; H, 7.74%). 6b, 72%, mp 74.9 - 77.1°C, C, 61.64%; H, 7.98% (C, 61.77%; H, 7.91%).

Formation of intramolecular sandwich type complex (2:1 complex) with bis(benzo-15-crown-5)s has been recognized by a large red shift in the electronic spectra of the alkali metal picrate complexes.3)4) Table 1 shows the absorption maxima of the picrate complexes of 4 and 5 in THF at 25±0.1°C. The values in parenthesis are the molar ratio of the crown ether being necessary to reach to the maximum shift, and are considered to be a qualitative measure of the facility to form the ionic species. The type (6 and 7 to 4 or 5) and the length (4a - 4d and 5a - 5d) of the bridging chain did not materially affect the absorption maxima. The picrate complexes of 4 with K^+, Rb^+ and Cs^+ in THF produced a pronounced red shift from the corresponding maxima of the picrates to 381 nm, and the appearance of the maxima at the same position are reasonably accounted for by the formation of the species of crown-separated loose ion pair. On the other hand, a small red shift from 352 nm to 356 nm for sodium picrate complex is indicative of its existence as a contact ion pair.

Rather different features were observed in the complexes of 5. The spectral change of the cesium picrate complex in the solvent, obtained by stepwise addition of the crown ether, was very similar to those for the complexes of 4 with the picrates of K^+, Rb^+ and Cs^+, and led to the same absorption maximum. However, the maxima (371 nm) appeared in the intial stage of the addition for the K^+ and Rb^+ complexes did not alter by the further addition of 5, and an isosbestic point which existed in the spectra of complex of 4 was not observed for certain. The behavior of the latter complexes may be explained by assuming that they exist as a mixture of 1:1 and 2:1 complexes. Together with the unexpected large red shift for the sodium picrate complex of 5, the nature of the complexes of 5 in THF, as compared to those of 4, did not allow to evaluate formation constants by the spectrometric method.

A quantitative comparison of the complexation capability of the benzocrown ethers was then carried out by solvent extraction technique according to the Pedersen's procedure.8) The results listed in Table 2 were obtained by extraction aqueous alkali metal picrate solution with equal volume of dichloromethane solution of a crown ether at 25±0.1°C. The extractability of the bis(benzocrown ether)s

(4 and 5) are much larger than the corresponding mono(benzocrown ether)s except for DC18C6 with K$^+$. Increased capability for extraction of larger cations than the hole size of the crown ring is proved to be the common feature4) of bis(benzocrown ether)s. Thus, 4 of 15-crown ring shows large selectivity for K$^+$ and Rb$^+$, and 5 of 18-crown ring does for Cs$^+$. An irregularity of 5 for K$^+$ might be ascribed to the intrinsic large selectivity of benzo-18-crown-6 itself for the cation. It is to be noted that the extractability of 4 for K$^+$ and Rb$^+$ are larger than that of 5.

Table 1. Absorption Maxima of New Bis(crown ether)s - Alkali Metal Picrate Complexes in THFa)

	λ max (nm)			
Bis(crown ether)	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
none	352	358	361	362
4 (4a - 4d)	356	381	381	381
	(50 - 70)	(2)	(6)	(50 - 70)
5 (5a - 5d)	381	371	371	381
	(20 - 48)	(2)	(10)	(5)

a) Initial concentration of picrates = 3 x 10^{-5} mol/dm^{-3}. The values in parenthesis are the molar ratio of the crown ether being necessary to reach to the maximum shift.

Table 2. Extraction of Alkali Metal Picrates with Various Crown Ether Derivatives

	picrate salt extracted (%)a)					picrate salt extrated (%)a)			
crown	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	crown	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
1a	2.6	14.2	11.2	7.7	1b	3.3	54.1	27.2	15.8
2a	2.2	9.1	4.6	1.7	2b	3.8	56.7	30.0	17.6
3a	2.2	8.4	3.8	1.3	3b	3.8	56.5	29.8	17.3
4a	9.1	86.5	61.5	18.2	5a	6.5	62.7	54.7	85.1
4b	10.2	86.7	60.2	18.2	5b	6.0	62.5	54.6	82.5
4c	9.4	84.5	58.6	19.0	5c	5.9	60.8	51.2	78.9
4d	8.0	80.5	52.7	15.5	5d	6.1	60.6	51.4	77.8
6a	7.5	79.2	46.9	11.6	6b	5.4	61.0	45.7	71.9
7	9.5	89.4	59.9	15.9	DC18C6b)	9.5	84.7	55.2	21.3

a) This values were based on picric acid. Solvent extraction conditions are as follows, CH_2Cl_2 = H_2O = 10 ml, picric acid = 7 x 10^{-5} M (M = mol/dm^{-3}), metal hydroxide = 0.01 M, and crown unit = 3.5 x 10^{-4} M at 25 ± 0.1°C.

b) Perhydrodibenzo-18-crown-6 (cis-anti-cis).

Effect of the length of bridging chain and the type of the chain is rather small. Variation of the conformational energies of the bis(crown ether)s in the sandwich form would be the principal reason for the change of extractability. Introduction of a lipophilic group to benzo-15-crown-5 depressed the extractability, especially that for larger cations. The lipophilic group might either exert steric restraint to form 2:1 complex or destabilize the hydration of the cation in the 1:1 complex.

The similar study on the bis(benzocrown ether)s linked at 3'-positions is in progress.

References

1) Part VI in the series, " New Application of Crown Ethers "; Part V in this series, F. Wada, Y. Wada, K. Kikukawa, and T. Matsuda, to be published in Bull. Chem. Soc. Jpn.

2) F. Wada, R. Arata, T. Goto, K. Kikukawa, and T. Matsuda, Bull. Chem. Soc. Jpn., 53, 2061 (1980)

3) M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid, J. Am. Chem. Soc., 97, 3462 (1975).

4) a) K. Kimura, H. Tamura, T. Tsuchida, and T. Shono, Chem. Lett., 1979, 611.
b) K. Kimura, T. Maeda, and T. Shono, Talanta, 26, 945 (1979).

5) D. Landini, F. Montanari, and F. M. Pirisi, J. Chem. Soc., Chem. Comm.,1974, 879.

6) M. Cinquini and F. Montanari, J. Chem. Soc., Chem. Soc., 1975, 393.

7) C. J. Pedersen, J. Am. Chem. Soc., 89, 7017 (1967).

8) C. J. Pedersen, Fed. Pro., Fed. Am. Soc. Exp. Biol., 27, 1305 (1968).

(Received July 31, 1980)