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NEW BIS(CROWN ETHER)S DERIVED FROM STEREOISOMERS OF DICARBOXYLIC ACID

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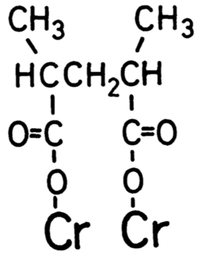
Stereoisomers of bis(crown ether)s were synthesized from *meso*- or *dl*-α,α'-dimethylglutaric acid and maleic or fumaric acid. Preliminary solvent extraction data suggested that the maleate derivative(*cis* form) differs considerably in the cation-complexing ability from the fumarate derivative(*trans* form), while two isomers of α,α'-dimethylglutarate derivatives are almost the same.

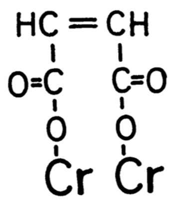
Macrobicyclic polyethers, bis(crown ether)s containing crown ether moieties at the end of a short aliphatic chain generally show attractive cation-complexing abilities.[1-3] However, no report has appeared which is focused on the effect of stereochemical structure of bis(crown ether)s upon their cation-complexing ability and cation-selectivity. We prepared stereoisomers of bis(crown ether)s from *meso*- or *dl*-α,α'-dimethylglutaric acid and maleic or fumaric acid, and screened them for the cation-complexing ability of alkali metal cations.

Bis(crown ether)s, *meso*- or *dl*-I and *cis*- or *trans*-II, were synthesized by esterification reaction of the respective potassium salt of dicarboxylic acid with chloromethylbenzo-15-crown-5 which also acts itself as a phase transfer catalyst. Chloromethylbenzo-15-crown-5 was obtained by the reaction of the hydroxymethyl derivative[4] with dry hydrogen chloride in chloroform. To 2 mmol of chloromethylbenzo-15-crown-5 in 20 ml of acetonitrile was added 1 mmol of an appropriate potassium salt of dicarboxylic acid, and the mixture was refluxed for 20 h with stirring. The crude product was purified by GPC or recrystallization from acetone.

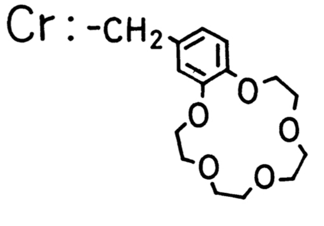
meso-I(67%). colorless oil; ^{1}H-NMR(δ, $CDCl_3$): 1.16(CH_3, 6H, doublet), 1.48 and 2.14($CHC\bar{H}_2CH$, 2H, quintet), 2.54(CH, 2H, sextet); M^+: 720; Anal.: Calcd. for $C_{37}H_{52}O_{14}$ C 61.65 H 7.27, Found C 61.04 H 7.28



meso- or *dl*-I



cis- or *trans*-II



dl-I(76%). colorless oil; ^{1}H-NMR(δ, $CDCl_3$): 1.13(CH_3, 6H, doublet), 1.17 ($CHC\bar{H}_2CH$, 2H, triplet), 2.52(CH, 2H, sextet); M^+: 720; Anal.: Calcd. for $C_{37}H_{52}O_{14}$ C 61.65 H 7.27, Found C 61.66 H 7.40

cis-II(71%). colorless fine crystal; mp : 72-73°C; ^{1}H-NMR(δ, $CDCl_3$): 5.01 (CH_2Ar, 4H, singlet), 6.22(CH, 2H, singlet); M^+: 676; Anal.: Calcd. for $C_{34}H_{44}O_{14}$ C 60.35 H 6.55, Found C 59.95 H 6.63

trans-II(65%). colorless needle; mp: 149-150°C; ^{1}H-NMR(δ, $CDCl_3$): 5.09 (CH_2Ar, 4H, singlet), 6.86(CH, 2H, singlet); M^+: 676; Anal.: Calcd. for $C_{34}H_{44}O_{14}$ C 60.35 H 6.55, Found C 59.94 H 6.57

Solvent extraction was carried out from alkali metal picrate aqueous solution with bis(crown ether) chloroform solution according to Pedersen's method,5) and the results are shown in Table 1. The extractability of *meso*- and *dl*-I suggests that they are almost the same in the cation-complexing ability for metal cations employed. However, it should be noted that *cis*-II is much larger in the extractability for K^+ and Rb^+ than *trans*-II, indicating a marked difference of cation-complexing ability between two isomers of II. Visible spectra offered some information about the stoichiometry of the bis(crown ether)-cation complexes. Addition of a small quantity of *cis*-II to a potassium picrate THF solution causes a pronounced red shift of spectrum of picrate anion1) from 357 to 381 nm, which is indicative of the formation of intramolecular 2:1(crown ether unit/cation) complexes. On the other hand, addition of *trans*-II leads to the formation of 1:1(crown ether unit/cation) complexes which was supported by a slight red shift to 360 nm. Both *meso*- and *dl*-I systems showed a similar spectral change to the *cis*-II system. Thus, the extractability of the bis(crown ether)s for metal cations seems to be related closely to the ease of formation of the lipophilic 2:1 complex. Further study is currently under way.

Table 1. Extraction of alkali metal picrates with bis(crown ether)s I and II

Bis(crown ether)	Picrate salt extracted (%)			
	Na^+	K^+	Rb^+	Cs^+
meso-I	2.2 (1.3)	18.5 (11.5)	4.2 (2.9)	0.4 (0.3)
dl-I	1.9 (1.5)	17.1 (10.4)	3.8 (3.0)	0.5 (0.5)
cis-II	1.9 (1.9)	20.2 (13.1)	4.8 (3.6)	0.8 (0.7)
trans-II	1.9 (2.0)	1.4 (1.3)	1.1 (0.7)	1.1 (0.4)

[metal hydroxide]: 1×10^{-2}M, [picric acid]: 7×10^{-5}M in H_2O;
[crown ether unit]: 7×10^{-4}M or 3.5×10^{-4}M(in parentheses) in $CHCl_3$

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