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Synthesis and Conformational Properties of 2-Carboxy-15-crown-5 and Its Cation Complexes

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2-Carboxy-15-crown-5 has been prepared by potassium permanganate oxidation in modest yield. Its native conformation has been assessed by using infrared, NMR, and both MM2′ and MNDO calculations. Neutral cation complexes (of the form crown-COOH.MX) of this macrocycle with NaCl, NaBr, NaI, KCl, and $CaCl_2$ have been prepared and studied. It is concluded that the carbonyl oxygen atom is a donor for the ring bound cation, an observation supported by the calculated lowest energy conformation of the non-complexed macrocycle.

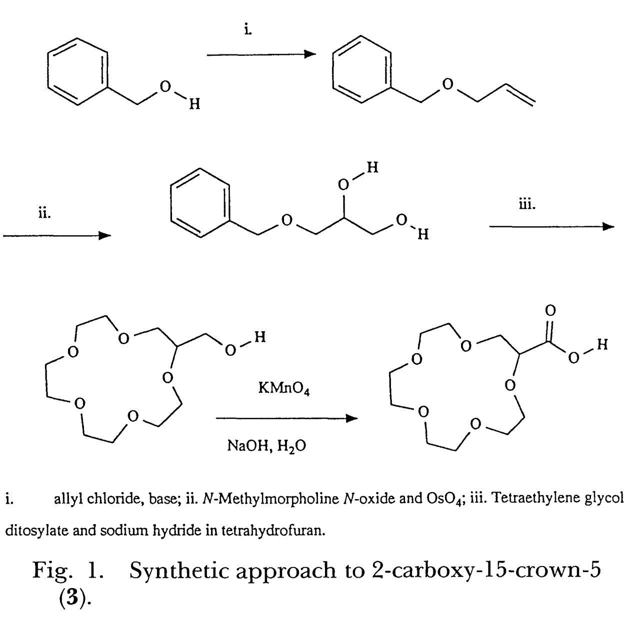
At the inception of the lariat ether research program,[1] we considered several possible subunits which could serve as integral portions of the macroring and as pivot-points (points of attachment) for the sidearms. Ultimately for the carbon-pivot compounds, it was resolved to use the glycerol subunit ($HOCH_2CHOHCH_2OH$, available as glycerol or, with some modification, as epichlorohydrin or allyl chloride) since one of the primary and the secondary hydroxyl groups were equivalent to an ethyleneoxy ($-CH_2CH_2O-$) unit and the remaining primary hydroxyl provided a versatile attachment point. The nitrogen-pivot lariat ethers used diethanolamine as the precursor thus incorporating two ethyleneoxy subunits into the macroring simultaneous with providing a secondary amine to which the sidearm could be bound.[2]

An alternative to the strategy of incorporating the precursor unit is to prepare a functionalized crown to which various sidearms could be attached. Such a system should be readily prepared and amenable to connection of diverse sidearms. A molecule that is intriguing in this context, but one that is relatively unknown, is 2-carboxy-15-crown-5 (**3**). Although it should be a versatile intermediate for the preparation of carbon-pivot lariat ethers,[1] its synthetic inaccessibility has proved problematic. The compound has not previously been reported in the literature even though it is one of the simplest derivatives of 15-crown-5. We report here its synthesis and some of the unusual properties that make it both interesting and difficult to obtain.

Results and Discussion

Synthesis. The obvious precursor to **3** is 2-hydroxymethyl-15-crown-5 (**2**). It and its close relatives have been reported several times in the past.[3] Our own preparation of this compound was accomplished as follows. Benzyl alcohol was treated with allyl chloride in the presence of base. Benzyl allyl ether was then oxidized using *N*-methylmorpholine *N*-oxide and catalytic osmium tetroxide.[4] The resulting diol, $Ph-CH_2-O-CH_2-CHOH-CH_2OH$, was treated with tetraethylene glycol and sodium hydride in tetrahydrofuran (THF). Cyclization was accomplished in 58% yield and 2-benzyloxymethyl-15-crown-5 (**1**) was obtained as a colorless oil after short path (Kugelrohr) distillation. Hydrogenolysis (H_2, Pd-C, ethanol) afforded **2** in 93% yield as an oil.

Oxidation was attempted under a variety of conditions, most of which proved unsuccessful. Among these were chromium trioxide (1.7—3.6 molar equivalents) in sulfuric acid and acetone, chromium trioxide (2.7 equiv) in aqueous sulfuric acid, neutral potassium permanganate (1.1 equiv) in benzene, and potassium permanganate (2.15 equiv) in aqueous sulfuric acid. Ultimately, basic potassium permanganate in water (see Experimental section) was found to



i. allyl chloride, base; ii. *N*-Methylmorpholine *N*-oxide and OsO_4; iii. Tetraethylene glycol ditosylate and sodium hydride in tetrahydrofuran.

Fig. 1. Synthetic approach to 2-carboxy-15-crown-5 (**3**).

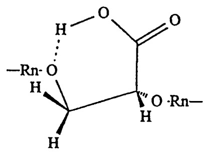


Fig. 2. Presumed "axial" conformation of 2-carboxy-15-crown-5 (**3**). "Rn" in the figure means a ring.

be most effective although the yield of **3** was barely 40% in the best case. Multi-gram samples were obtained by the permanganate oxidation and the product could be purified without distillation to a colorless oil which proved to be analytically pure. Metal salt complexes and esters of this compound were all prepared as described in the Experimental section.

Conformations of 2-Carboxy-15-crown-5. In $CDCl_3$ solution, **3** exhibits a triplet at δ 4.21 [$CH_2C\underline{H}(COOH)$] and a doublet at δ 3.86 [$C\underline{H}_2CH(COOH)$], J=4 Hz. The spectrum is essentially first order with $\Delta\nu/J$=5.3. The coupling constant normally observed for gauche protons is 2—4 Hz and for trans methylene protons, J is usually 9—13 Hz. From the observed coupling constants, it appears that the two macroring carbons adjacent to the carboxyl carbon are in the gauche conformation. This suggests that the carboxyl group occupies an "axial" position in the crown ring as illustrated in Fig. 2.

In contrast, the methyl ester of **3** exhibits second order coupling patterns for the corresponding protons. This implies that the ester group occupies an "equatorial" position of the crown macroring. An examination of Corey-Pauling-Koltun (CPK) space-filling molecular models suggested to us that the carboxyl group proton might be hydrogen bonded to macroring oxygens. This would obviously not be the case for the ester which cannot function as a hydrogen bond donor and, in any case, appears to be in the wrong conformation for such an interaction. Spectral observations relevant to the interaction of the carboxyl group with macroring oxygen(s) in **3** were obtained by ^{1}H NMR and IR spectral analyses.

2-Carboxy-15-crown-5 almost always exhibited a broad, single carboxyl group resonance ($CDCl_3$) at δ 9.5. The proton resonance of carboxylic acids is usually observed between δ 10 and 13 in this solvent. Thus, the carboxyl group proton in **3** is more shielded than expected. The carboxyl proton resonance was occasionally observed in the range δ 7.26 to 9.15, a phenomenon we attribute to the presence of trace water. Indeed, when the NMR spectrum was obtained in D_2O solution, a quartet was observed for the protons of **3** suggesting a conformational change. It seems reasonable to assume that a molecule of water (D_2O in this case) interacts with both the macroring and the carboxyl group. This interaction should be especially influential if an intramolecular hydrogen bond exists in the compound.

Table 1. Infrared Spectra of 2-Carboxy-15-crown-5 Derivatives

Compound	$\nu_{C=O}$ /cm^{-1} [a]
2-Carboxy-15-crown-5	1745 ± 3 [b]
2-Methoxycarbonyl-15-crown-5	1750 ± 3 [c]
2-Ethoxycarbonyl-15-crown-5	1745 [d]

a) Spectrum determined in Nujol. b) Several determinations of carbonyl frequencies for 2-carboxy-15-crown-5 were in the range 1742—1748 cm^{-1} ; we judged 1745 cm^{-1} to be the most representative value. c) Several determinations of carbonyl frequencies were in the range 1747—1753 cm^{-1}; we judged 1750 cm^{-1} to be the most representative value. d) Error estimated to be ±3 cm^{-1}.

The carbonyl vibration in the infrared spectrum of **3** (Nujol mull) occurs at nearly the same frequency as that of the methyl or ethyl esters of **3** (see Table 1). In the case of fatty acid compounds,[5] the carbonyl stretch is usually observed at lower wavenumbers than for the corresponding ester. This is due to intermolecular hydrogen bond formation (dimerization). The carbonyl group of **3** does not, therefore, appear to interact as strongly with hydroxyl groups. On the other hand, the broad -OH band is similar in shape to that observed for fatty acids suggesting that some hydrogen bond formation occurs. These data suggest, and the large number of proximate oxygen atoms reinforce the notion, that an intramolecular hydrogen bond(s) forms between the carboxyl and the macroring oxygen(s).

The infrared spectra of compound **3** were determined in $CHCl_3$ (serial dilution) in order to determine whether or not the hydrogen bonding was intramolecular. The lack of any significant deviation in the spectra from each other or from the spectra obtained in Nujol led us to conclude that the hydrogen bonding was intramolecular.

Acidity Trends for 2-Carboxy-15-crown-5 Complexes. It was thought that complexation of an alkali or alkaline earth metal cation by **3** would affect the acidity by a remote substituent effect. If the carboxyl group is, indeed, axial then either the carbonyl or hydroxyl oxygen would be rotated over the ring-bound-cation. Stabilization of the developing anion by a metal-ion-to-carbonyl group interaction should acidify the hydroxyl. The more charge-dense the bound cation, the greater should be the pK_A reduction (increase in acidity). Determination of the pK_A for **3** (in methanol) in the presence of no cation, K^+, Na^+, and Ca^{2+} afforded the following values: 3.08, 3.05, 3.02, 2.88.[6] These differences admittedly are small and the first three values effectively overlap within experimental error. Nevertheless, the trend is suggestive and certainly in the correct direction. Moreover, the largest effect on pK_A is expected for the divalent calcium complex and such a difference is observed and is well outside of experimental error.

Computer Simulated Conformation of 3. The conformation of **3** was assessed using the MM2′ molecular mechanics program and the MNDO molecular orbital calculation program. Calculations were performed on an IBM 3090 computer. More than 100 model conformers were constructed and these conformers were energy-minimized using MM2′.[7] From these results, twenty low energy conformers were chosen for further energy minimization calculations using MNDO.[8] The structure of the lowest energy conformer thus obtained is shown in Fig. 3 and selected calculation results are shown in Table 2. Note that there is currently no unequivocal evidence that the conformer shown in Fig. 3 represents the global minimum although it is in reasonable agreement with the spectral information reported herein.

In the conformation shown, the carboxyl group occupies an axial position of the macroring and the protons discussed above are gauche. Further, this lowest energy conformer has the highest net charge on the carboxyl group proton. A graph of net charge vs. total energy for the four conformers identified in Table 2 was linear. It thus appears that the carboxyl group is the donor for a trans-annular hydrogen bond, again as suggested by the spectral data.

Intramolecular Hydrogen Bond Formation. The conformers designated A—D (see Table 2) differ slightly from each other but in all cases the carboxyl group is axial. Additional calculations were undertaken using MNDO and also the "Quanta" program. The minimum energy conformation is always the one in which the carboxyl group is axial to the mean plane of the oxygen atoms and the carboxyl hydrogen participates in a transannular hydrogen bond. Quanta shows this orientation but reports "no hydrogen bond" because the H-bond distance parameter is arbitrarily set to 2.5 Å. This is not an unreasonable distance but hydrogen bond interactions are known to be felt over longer distances.[9] The calculations also show that there is little energy difference between transannular hydrogen bonding of the carboxyl group to either O9 or O12. Indeed the hydrogen bond, long as it is, may be bifurcated. It is known that hydrogen bonds to sp^3 oxygen acceptors does not show as high a preference for linearity as observed for sp^2 oxygen or nitrogen.[10] The ball and stick figure is shown in Fig. 4.

Metal Cation Complexes of 2-Carboxy-15-crown-5. Since the carboxyl group appears to be perpendicular to the mean oxygen plane of the macroring, the interaction between it and a ring-bound cation is expected to occur with the carbonyl group. The location of the counter anion is less clear but may either be on the

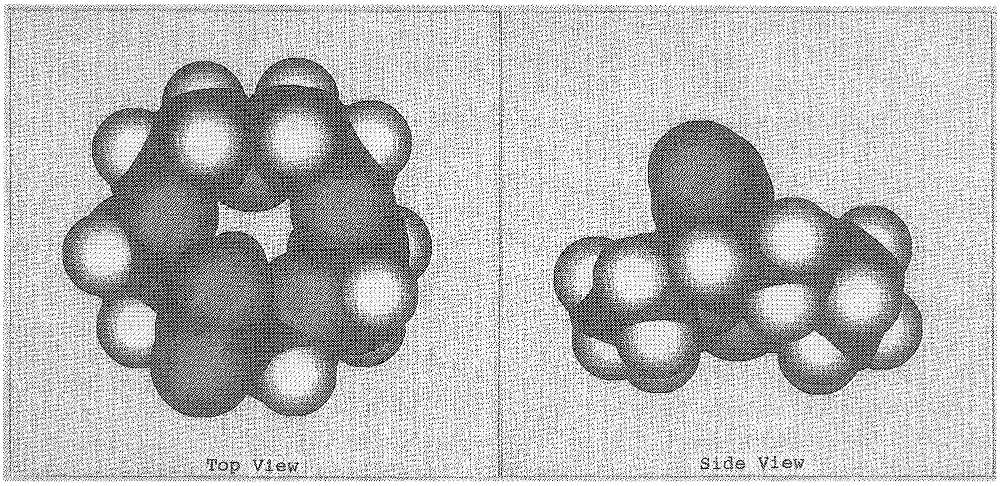


Fig. 3. Two views of the calculated energy surface for the lowest energy conformer of 2-carboxy-15-crown-5 (**3**) (Conformer C).

Table 2. Four Lowest Energy Conformers of 2-Carboxy-15-crown-5

Conformers having heats of formation less than −270 kcal	Total energy eV	Heat of formation kcal mol^{-1}	Proton positions[a]	Net charge of the -COOH proton
Conformer A	−3945.45774	−275.97684	G G	0.22083
Conformer B	−3945.40443	−272.74747	G G	0.21668
Conformer C[b]	−3945.84170	−284.83130	G G	0.23115
Conformer D	−3945.81514	−284.21874	G G	0.22923

a) For the protons on two adjacent macroring carbons, one of which bears the carboxyl group; G=gauche. b) Lowest energy conformer.

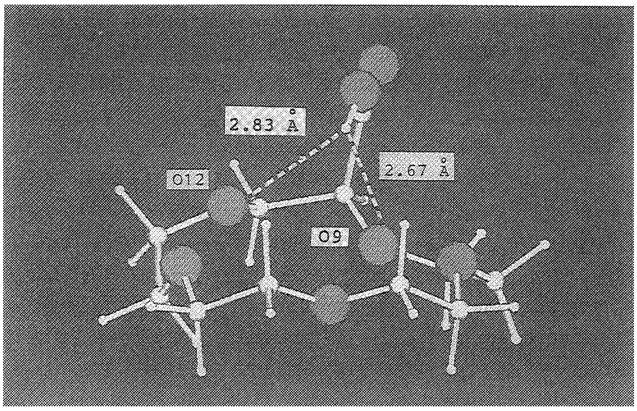


Fig. 4. Ball-and-stick representation of 2-carboxy-15-crown-5 (**3**), which shows hydrogen bond directionality.

opposite side of the ring or involved in a hydrogen bond to the hydroxyl group. The latter arrangement has the advantage that the carbonyl group becomes more charged and single-bond-like. This analysis is in accord with both the observed infrared spectra and the calculated, lowest energy conformation of the non-complexed system.

In the case of carboxylic ester-metal cation complexes, $\nu_{C=O}$ shifted to lower wavenumber and $\nu_{C\text{-}O}$ shifted to higher wavenumber compared with those of the free ester, because of carbonyl group coordination to the metal cation.[11)] Cation complexes of **3** exhibit similar shift tendencies for the $\nu_{C=O}$ and $\nu_{C\text{-}O}$ bands in these complexes. This implies that the carbonyl group of **3** coordinates to the ring-bound metal cation. An examination of CPK models also suggested that sodium ion can be solvated by the macroring donors as well as the carboxyl carbonyl group.

The data shown in Table 3, below, suggest several interesting facts. First, the order of the $\nu_{C=O}$ and $\nu_{C\text{-}O}$ band shifts in complexes having Cl^- counter ions is $Ca^{2+}>Na^+>K^+$ and this implies that the bandshift increases with increasing charge density of the metal cation. The weakness of the K^+ interaction might also be accounted for in part by its larger size which prohibits inclusion in the 15-membered macroring. Second, in the Na^+ complexes, the shift in the C–O and C=O stretching bands varies with the anion. The shift order is $Cl^->Br^->I^-$, suggesting that the anion affects the coordination strength of the carbonyl group to metal.

Table 3. IR Spectra of 2-Carboxy-15-crown-5 Complexes[a)]

Complexed salt	Vibrational frequency/cm^{-1}			
	$\nu_{C=O}$	Difference[b)]	$\nu_{C\text{-}O}$	Difference[b)]
None	1745	—	1200	—
NaCl	1715	30	1233	33
NaBr	1733	12	1220	20
NaI	1738	7	1210	10
KCl	1740	5	1205	5
$CaCl_2$	1640,1705	105,40	1945	45

a) Infrared spectra determined as Nujol mulls. b) Difference between free acid and complex.

The infrared spectra of the complexes exhibit other evidence of interaction between the anion and the carboxyl group. The hydroxyl group stretching band position shows the same tendency as that of $\nu_{C=O}$ and $\nu_{C\text{-}O}$. This implies that the carboxyl group -OH hydrogen bonds to the anion and thus enhances the coordination ability of the carbonyl group.

Summary

2-Carboxy-15-crown-5 has been prepared by oxidation of the corresponding alcohol. Infrared, NMR, and computational studies all confirm that the compound exists primarily in a conformation in which the 2-carboxyl group is "axial" to the macrocyclic ring. This permits a carbonyl group interaction with the ring-bound cation and this is detected in pK_A measurements and complex formation.

Experimental

^{1}H NMR were recorded on a Varian EM 360A NMR Spectrometer or on a Hitachi Perkin-Elmer R-600 High Resolution NMR Spectrometer in $CDCl_3$ solvents and are reported in ppm (delta) downfield from internal Me_4Si. ^{13}C NMR were recorded on a JEOL FX90Q or Varian XL-400 NMR Spectrometer or as noted above. IR spectra (reported in cm^{-1}) were recorded on a Perkin-Elmer 298 or a Perkin-Elmer 599 Infrared Spectrophotometer in $CHCl_3$ (unless otherwise specified) and were calibrated against the 1601 cm^{-1} band of polystyrene. Melting points were determined on a Thomas Hoover apparatus in open capillaries and are uncorrected. Thin-layer chromatographic (TLC) analyses were performed on aluminum oxide 60 F-254 neutral (Type E) with a 0.2 mm layer thickness or on silica gel 60 F-254 with a 0.2 mm layer thickness. Preparative chromatography columns were packed with activated aluminum oxide (MCB 80—325 mesh, chromatographic grade, AX 611) or with Kieselgel 60 (70—230 mesh). Chromatotron chromatography was performed on a Harrison Research Model 7924 Chromatotron with 2 mm circular plates prepared from Kieselgel 60 PF-254. Gas chromatographic analyses were conducted on a Varian Associates Model 1420 analytical gas chromatograph equipped with a thermal conductivity detector and a 5 ft. ×0.25 in. column packed with 1.5% OV-101 on 100/120 mesh Chromosorb G. Helium was used as the carrier gas, and the flow rate was ca. 60 mL min.$^{-1}$.

All reactions were conducted under dry N_2 unless otherwise noted. All reagents were the best grade commercially available and were distilled, recrystallized, or used without further purification, as appropriate or as specified. Molecular distillation temperatures refer to the oven temperature of a Kugelrohr apparatus.

2-Hydroxymethyl-15-crown-5 (2), was prepared by hydrogenolysis of 2-benzyloxymethyl-15-crown-5 (**1**), as previously described, in 54% overall yield. The alcohol was obtained as a colorless oil having the spectral properties reported.[2c)]

2-Carboxy-15-crown-5 (3). A 125-mL Erlenmeyer flask was charged with 2-hydroxymethyl-15-crown-5 (1.0 g, 4 mmol), NaOH (0.12 g, 3 mmol), and water (2.4 mL). The mixture was stirred at ambient temperature until the NaOH had dissolved. $KMnO_4$ (1.36 g, 8.6 mmol) in water (20 mL), was added while stirring and the reaction mixture was stirred at room temperature for 6 h. An additional 100 mg of $KMnO_4$ was then added and stirring continued overnight. The reaction mixture was filtered, a small amount of Na_2SO_3 was added to destroy excess $KMnO_4$, and the mixture was filtered again. The filtrate was basified (0.04 g NaOH), washed with $CHCl_3$ (3×30 mL), and then acidified (pH 2) with concd HCl. The product was extracted with CH_2Cl_2, dried (Na_2SO_4), and reduced to minimum volume in vacuo. The product was a colorless oil (0.4 g, 37.9%); ^{1}H NMR: δ=3.68, 3.73, 3.86 (d), 4.21 (t) (ring protons, 19H), and 9.51 (bs, 1H). IR (neat): 1745 ($\nu_{C=O}$), 1200 (ν_{C-O}). Calcd for $C_{11}H_{20}O_7$: C, 49.99; H, 7.63%. Found: C, 50.20; H, 7.90%.

2-Carboxy-15-crown-5·NaCl Complex. A 25-mL, round-bottomed-flask with drying tube atop was charged with **3** (0.5 g, 1.9 mmol), NaCl (0.22g, 3.8 mmol), and CH_3CN (20 mL). The reaction mixture was stirred overnight at room temperature, filtered, and then reduced to minimum volume in vacuo. A small amount of CH_2Cl_2 was slowly and carefully added until a white solid was obtained. The complex (0.10 g, 16%) was filtered and washed with CH_2Cl_2, dried in vacuo, and had the following properties: mp 126—127 °C. IR: 1715 ($\nu_{C=O}$), 1233 (ν_{C-O}). Calcd for $C_{11}H_{20}O_7NaCl$: C, 40.94; H, 6.25%. Found: C, 41.26; H, 6.58%.

2-Carboxy-15-crown-5·NaBr Complex. This complex was prepared from **3** (0.5 g, 1.9 mmol), NaBr (0.39 g, 3.8 mmol) in CH_3CN (20 mL) essentially as described above. The white solid product (0.20 g, 29%) had mp 162—163 °C. IR: 1733 ($\nu_{C=O}$), 1220 (ν_{C-O}). Calcd for $C_{11}H_{20}O_7NaBr$: C, 35.98; H, 5.49%. Found: C, 36.23; H, 5.72%.

2-Carboxy-15-crown-5·NaI Complex. This complex was prepared from **3** (0.4 g, 1.5 mmol), NaI (0.45 g, 3 mmol) and CH_3CN (20 mL). The reaction mixture was stirred for 3 h at room temperature, then reduced to minimum volume. Dichloromethane (5.0 mL) was added to the residue and then filtered. The filtrate was reduced to minimum volume, the brown, pasty residue was diluted with diethyl ether (50 mL) and then allowed to stand for 2 days. The brown paste gradually solidified. The solid obtained by filtration was washed with benzene (3 times) and the white solid product (0.30 g, 48%) was dried at ambient temperature under high vacuum. IR: 1738 ($\nu_{C=O}$), 1210 (ν_{C-O}). Calcd for $C_{11}H_{20}O_7NaI$: C, 31.90; H, 4.87%. Found: C, 31.10; H, 4.83%. Although the other halides were well-behaved, the carbon analysis for this iodide complex was in error by 0.8% on carbon. Although this value is outside of normally acceptable limits, the conclusions drawn here should not be affected.

2-Carboxy-15-crown-5·$CaCl_2$ complex was prepared from **3** (0.30 g, 1.1 mmol), $CaCl_2$ (0.24 g, 2.2 mmol) in CH_3CN (1.0 mL) as follows. The reaction mixture was stirred for 2 days at room temperature, then filtered and the filtrate was reduced to minimum volume. To the residue, benzene was added and filtered. The white solid complex [0.20 g, 47%, mp>200 °C (decomp)] was obtained after washing with benzene and drying in vacuo. IR: 1705, 1640 ($\nu_{C=O}$), 1245 cm^{-1} (ν_{C-O}). Calcd for $C_{11}H_{20}O_7CaCl_2$: C, 35.21; H, 5.37%. Found: C, 35.13; H, 5.44%.

2-Carboxy-15-crown-5·KCl Complex. This compound was prepared from **3** (0.30 g, 1.1 mmol) and KCl (0.16 g, 2.2 mmol) in CH_3CN (10 mL). The reaction mixture was stirred at room temperature for 3 h. After treatment similar to that described above, the white solid product (0.16 g, 38%, mp 145—148 °C) was obtained. IR: 1740 ($\nu_{C=O}$), 1205 (ν_{C-O}).

2-Methoxycarbonyl-15-crown-5 (4). A 50-mL round-bottomed-flask with reflux condenser and drying tube atop was charged with the sodium salt of **3** (1.3 g, 4.5 mmol), CH_3I (1.5 g, 10 mmol), and CH_2Cl_2 (20 mL). The reaction mixture was stirred at reflux temperature for 4 h. CH_3I (0.5 g) was added, reflux was continued for 8 h, 3.0 g of CH_3I was added, reflux was continued for an additional 13 h, and finally, 3.0 g of CH_3I was added and the mixture was allowed to stand for 4 d at room temperature. The reaction mixture was dried (Na_2SO_4), filtered, and reduced to minimum volume. The crude product (0.4 g) was purified by Kugelrohr distillation [bp 140 °C (0.15 Torr; 1 Torr≈133.322 Pa)] to afford a colorless oil. ^{1}H NMR: δ=3.68, 3.72, 3.86 (ring protons including $C\underline{H}_2CHCOO$ and ester), 4.16 (1H, m). IR: 1750 ($\nu_{C=O}$). No OH resonance was observed in the NMR and no -OH vibration was detected in the IR.

2-Ethoxycarbonyl-15-crown-5 (5). A 100-mL, round-bottomed flask was charged with **3** (2.1 g, 8 mmol), anhydrous ethanol (50 mL), and H_2SO_4 (5 drops). The reaction mixture was heated at reflux for 4 h and then allowed to stand at room temperature overnight. The mixture was then neutralized (solid Na_2CO_3), dried (Na_2SO_4) and filtered. The filtrate was reduced to minimum volume and distilled using a Kugelrohr apparatus (bp 130—135 °C/0.06 Torr). The product was obtained (1.0 g) as a colorless oil in 41% yield. ^{1}H NMR: δ=1.28 (t), 3.68 (s), 3.82 (s), 4.21 (q); IR $\nu_{C=O}$ 1745 cm^{-1}. Calcd for $C_{13}H_{24}O_7$: C, 53.41; H, 8.28%. Found: C, 53.84; H, 8.60%.

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References

1) a) G. W. Gokel, D. M. Dishong, and C. J. Diamond, *J. Chem. Soc., Chem. Commun.*, **1980**, 1053; b) D. M. Dishong, C. J. Diamond, and G. W. Gokel, *Tetrahedron Lett.*, **22**, 1633 (1981); c) D. M. Dishong, C. J. Diamond, M. I. Cinoman, and G. W. Gokel, *J. Am. Chem. Soc.*, **105**, 586 (1983); d) K. A. Arnold, L. Echegoyen, and G. W. Gokel, *J. Am. Chem. Soc.*, **109**, 3713 (1987).

2) a) G. W. Gokel, D. M. Dishong, and C. J. Diamond, *J. Chem. Soc., Chem. Commun.*, **1980**, 1053; b) R. A. Schultz, D. M. Dishong, and G. W. Gokel, *Tetrahedron Lett.*, **22**, 2623 (1981); c) R. A. Schultz, D. M. Dishong, and G. W. Gokel, *J. Am. Chem. Soc.*, **104**, 625 (1982); d) R. A. Schultz, E. Schlegel, D. M. Dishong, and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, **1982**, 242; e) A. Kaifer, H. D. Durst, L. Echegoyen, D. M. Dishong, R. A. Schultz, and G. W. Gokel, *J. Org. Chem.*, **47**, 3195 (1982); f) H. D. Durst, L. Echegoyen, G. W. Gokel, and A. Kaifer, *Tetrahedron Lett.*, **23**, 4449 (1982); g) A. Kaifer, L. Echegoyen, H. Durst, R. A. Schultz, D. M. Dishong, D. M. Goli, and G. W. Gokel, *J. Am. Chem. Soc.*, **106**, 5100 (1984); h) V. J. Gatto and G. W. Gokel, *ibid.*, **106**, 8240 (1984); i) R. D. Gandour, F. R. Fronczek, V. J.

Gatto, C. Minganti, R. A. Schultz, B. D. White, K. A. Arnold, D. Mazzocchi, S. R. Miller, and G. W. Gokel, *ibid.*, **108**, 4078 (1986); j) V. J. Gatto, K. A. Arnold, A. M. Viscariello, S. R. Miller, and G. W. Gokel, *J. Org. Chem.*, **51**, 5373 (1986); k) R. A. Schultz, B. D. White, D. M. Dishong, K. A. Arnold, and G. W. Gokel, *J. Am. Chem. Soc.*, **107**, 6659 (1985); l) B. D. White, K. A. Arnold, and G. W. Gokel, *Tetrahedron Lett.*, **28**, 1749 (1987); m) S. R. Miller, T. P. Cleary, J. E. Trafton, C. Smeraglia, F. R. Fronczek, and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, **1989**, 806; n) B. D. White, J. Mallen, K. A. Arrnold, F. R. Fronczek, R. D. Gandour, L. M. B. Gehrig, and G. W. Gokel, *J. Org. Chem.*, **54**, 937 (1989); o) K. A. Arnold, J. Mallen, J. E. Trafton, B. D. White, F. R. Fronczek, L. M. Gehrig, R. D. Gandour, and G. W. Gokel, *J. Org. Chem.*, **53**, 5652 (1988).

3) a) F. Montanari and P. Tundo, *Tetrahedron Lett.*, **1979**, 5550; b) B. Czech, *ibid.*, **21**, 4197 (1980).

4) See G. W. Gokel, J. C. Hernandez, A. M. Viscariello, K. A. Arnold, C. F. Campana, L. Echegoyen, F. R. Fronczek, R. D. Gandour, C. R. Morgan, J. E. Trafton, S. R. Miller, C. Minganti, D. Eiband, R. A. Schultz, and M. Tamminen, *J. Org. Chem.*, **52**, 2964 (1987).

5) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds," (4th ed), John Wiley and Sons, Inc., New York (1981), pp. 120—122.

6) We thank Dr. D. M. Goli for obtaining these values.

7) a) C. Jamis and E. Osawa, *Tetrahedron*, **39**, 2769 (1983); b) T. Clark, "A Handbook of Computational Chemistry," Wiley-Interscience, New York (1985), pp. 141—232.

8) a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977); b) M. J. S. Dewar and W. Thiel, *ibid.*, **99**, 4907 (1977); c) M. J. S. Dewar and H. S. Rzepa, *ibid.*, **100**, 4899 (1978); d) M. J. S. Dewar and G. P. Ford, *ibid.*, **101**, 5558 (1979).

9) M. D. Joesten and L. J. Schaad, "Hydrogen Bonding," Marcel Dekker, Inc., New York (1974).

10) R. Taylor, O. Kennard, and W. Versichel, *J. Am. Chem. Soc.*, **105**, 5761 (1983).

11) a) M. F. Lappert, *J. Chem. Soc.*, **1962**, 542; b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York (1970).