Synthetic Macrocyclic Di- and Tetraester Compounds

JERALD S. BRADSHAW,* GARREN E. MAAS, REED M. IZATT, and JAMES J. CHRISTENSEN

*Departments of Chemistry and Chemical Engineering and Contribution No. 146 from the Thermochemical Institute,
Brigham Young University, Provo, Utah 84602*

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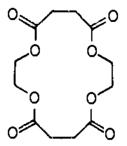
I. Introduction

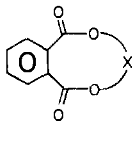
The first macrocyclic compound prepared from a diacid was dimeric ethylene succinate reported by Vorländer in 1894.[1]



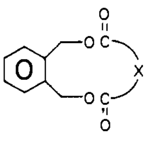
Subsequently, very little work was done with macrocyclic diesters until the 1930's when Carothers and his co-workers commenced a study of polyesters including the macrocyclic monomeric and dimeric carbonates, oxalates, etc.[2-5] The main interest in macrocyclic diester compounds involved their use in the preparation of perfumes.[6] Carothers and his co-workers also studied the theoretical aspects of reactions producing both cyclic and polymeric products.[4]

Following the Carothers work, there was little reported interest in macrocyclic diester compounds until the past decade. Recently, however, many new and interesting cyclic di- (and tetra-) ester compounds have been prepared to study the theoretical aspects of medium- and large-size ring formation; to study the rigidity of the paracyclophane ring system; and to compare metal cation complexation properties of synthetic macrocyclic multidentate compounds with those of naturally occurring macrocyclic antibiotics.

Drewes and his associates commenced a study of the steric factors which control the formation of medium and large rings in 1970.[7] They prepared a number of macrocyclic di- and tetraesters from phthalic[7-9] and maleic acids[10] and from aliphatic diacids but using the *o*-xylylene moiety as a rigid steric factor.[11] Their results are discussed in other sections of this review.

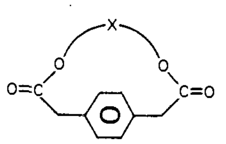


X= various carbon groups
including another
o-phthalate



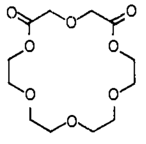
X= various carbon groups
including another
o-xylylene

Sakamoto and Oki have published a series of papers covering the preparation of hetera-*p*-cyclophanes.[12-16] They studied a number of interesting physical properties of those compounds, including internal rotation,[12-14] long-range asymmetry[15] and binding sites.[16]

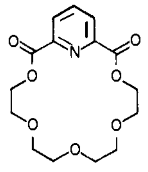


X= various hydrocarbon
and oligoethylene
glycol moieties

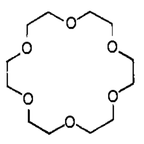
Within the past year, macrocyclic multidentate polyether-diester compounds have been prepared which exhibit metal cation complexation properties similar to those of certain naturally occurring macrocyclic antibiotics.[17-19] Log *K* values for the reaction of **56c** with Na$^+$, K$^+$, and Ba^{2+} in methanol are smaller than corresponding values for the reaction of these cations with 18-crown-6. On the other hand, the stabilities of the corresponding complexes of **75c** with these cations are comparable to those of 18-crown-6. In addition, the stability sequences of several cations pairs (e.g., Na$^+$, Rb$^+$; K$^+$, Ba^{2+}) are altered markedly in going from one ligand to another.[18,19] More details of the interactions of metal cations with these multidentate compounds will be given in section IV.



56c



75c



18-Crown-6

Macrocyclic polyethers, particularly derivatives of 18-crown-6, have received considerable attention in recent years because of the ability of these compounds to complex with metal cations.[20] Some of the properties of the synthetic macrocyclic polyethers are similar to those of certain naturally occurring cyclic antibiotics.[21-24] Some of the more interesting properties include the selective transport of metal cations across liquid and naturally occurring biological membranes[25] and chiral recognition.[26-28]

This review is the first to cover the synthesis and use of macrocyclic di- and tetraester compounds derived from dibasic acids. The macrocyclic lactones (and lactides), which are defined as "a class of inner esters of hydroxy carboxylic acids . . . , characterized by the carbonyl-oxy grouping -OCO- in a ring, and classed according to the position of the hydroxyl group in the parent acid",[29] have not been included; however, separate reviews concerning these compounds have been published.[30-33] Also not included are compounds in which the ester functions are not an integral part of the macro-ring.

The following sections will discuss synthetic methods employed and give an extensive table in which we have attempted

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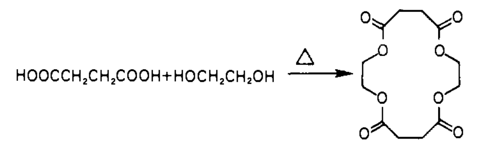
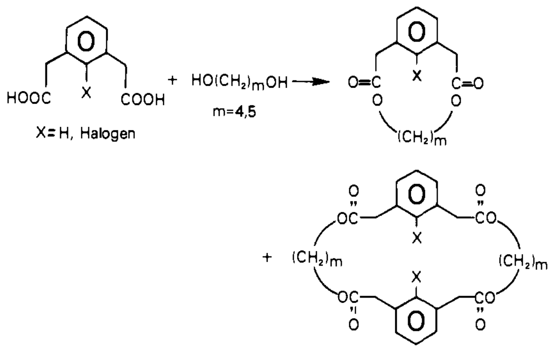
to list all of the compounds which have been reported together with their physical properties, and the applications which have been found for these compounds. The numbers used for individual compounds correspond to the number in Table I. The compounds in Table I are listed in order of the complexity of the corresponding dibasic acid, i.e., carbonates, oxalates, malonates, succinates, glutarates, adipates, higher aliphatic dicarboxylates, maleates, diglycolates, phthalates, pyridinedicarboxylates, and many miscellaneous dicarboxylates.

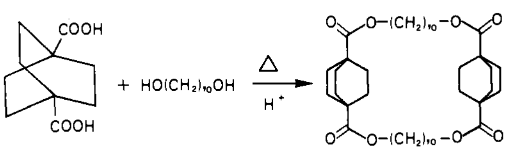
II. Synthetic Methods

A. From Dibasic Acids or Diesters and Glycols

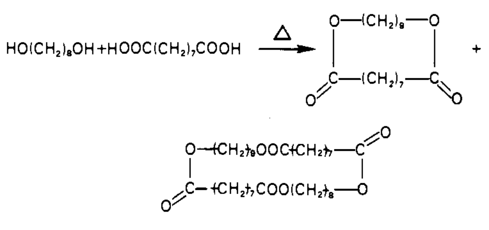
The earliest reported macrocyclic compound prepared from a dibasic acid was dimeric ethylene succinate which was described by Vorländer in 1894.[1] The same compound has been prepared by others in the intervening years.[2,34,35] Since that time a variety of macrocyclic diesters have been made from the dibasic acids or open-chain diesters. Vögtle and Neumann have prepared some macrocyclic di- and tetraesters from *m*-phenylenediacetic acid and various glycols.[36] Hahn and co-workers have prepared two unusual macrocyclic "Paddlanes" with four ester units from the reaction of either 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane and sebacoyl chloride or 1,4-dicarboxylbicyclo[2.2.2]octane and 1,10-decanediol.[37]

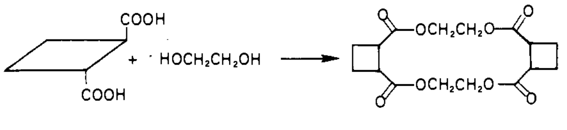






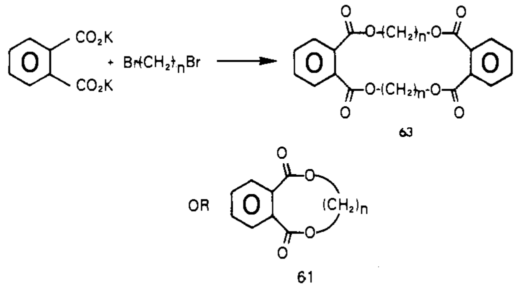
By reacting various glycols with aliphatic dibasic acids, Stoll and Rouvé obtained both cyclic one-to-one (monomeric) and two-to-two (dimeric) adducts.[38] Stueben isolated a macrocyclic tetraester containing the cyclobutane unit when he polymerized *trans*-1,2-cyclobutanedicarboxylic acid and ethylene glycol.[39]



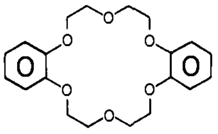


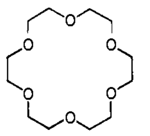
B. From Salts of Dibasic Acids and Alkyl Dihalides

Drewes and co-workers have prepared a number of macrocyclic di- and tetraesters by reacting the salts of dibasic acids with various dihalides.[7-11] When dipotassium phthalate was used, they obtained dimer **63** where $n = 2, 3, 7, 9, 11$ and monomer **61** where $n = 4, 5, 6, 8, 10, 12$.[8] The rings contained even numbers in all cases except where $n = 5$. Drewes suggested that for intermediate rings (ring size 8 to about 18), odd-numbered rings are more difficult to prepare than the even-numbered owing to greater interferences during ring closure.[8] Spanagel and Carothers also observed this general phenomenon in their synthesis of macrocyclic diesters.[5]

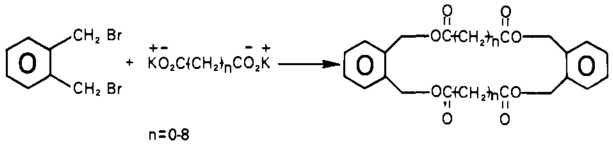


One steric factor which seems to control ring formation is the incorporation of a rigid structure comprising four atoms in a plane with angles of 120°.[40] The macrocyclic phthalates that Drewes and co-workers prepared[7,8] are good examples of this requirement. Baker, McOmie, and Ollis suggested that ortho-disubstituted benzene derivatives should easily form 8-, 12-, 16-, and higher membered ring systems.[40] That the rigid structure is an important factor in ring formation was shown by the work of Pedersen where he obtained dibenzo-18-crown-6 in 45 or 80% yields depending on reactants employed while 18-crown-6 (no rigid groups) was obtained in only a 2% yield.[20] The unsubstituted 18-crown-6 compound has since been obtained in high yields and ring closure reactions to form the crown compounds seem to be controlled more by a complexation or template effect than by other factors.[41]

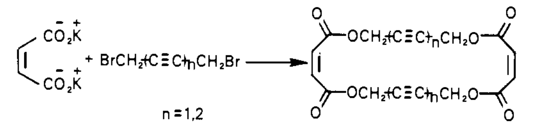

Dibenzo-18-Crown-6


18-Crown-6

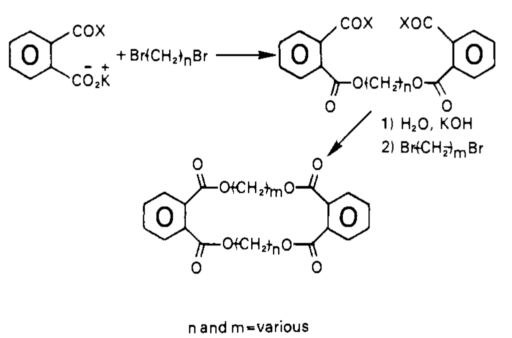
The rigid structure effect for ring formation is also shown by the synthesis of macrocyclic compounds from α,α'-dibromo-*o*-xylene and the salts of various aliphatic dibasic acids.[11] The work of Drewes and Riphagen showed that ring sizes of 16, 20, 28, and 32 were most easily prepared as suggested by Baker and co-workers.[40] The other even-numbered ring systems (sizes 18–30) were also isolated, but in much diminished yields, i.e., 0.6% for the 18-membered ring compound vs. 35.3% and 16% for the 16- and 20-membered ring compounds, respectively.[11]



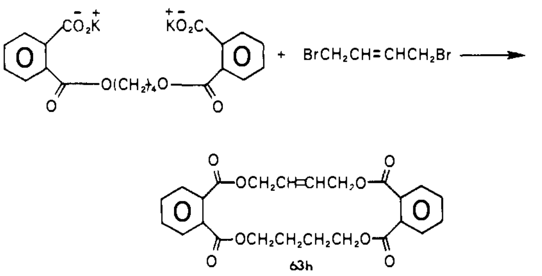
Drewes and Riphagen also prepared macrocyclic tetraester compounds from dipotassium maleate, citraconate, and phthalate with diacetylenic dibromides.[10] These compounds were all either 20- or 24-membered rings.



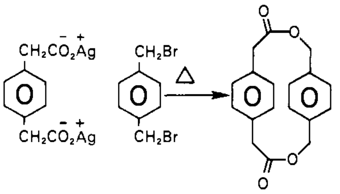
The steric effect of rigid structures did not operate in a two-step synthesis of macrocyclic diphthalates.[9] The yields of all



rings both even and odd numbered were 10% or below except 19-, 20-, and 22-membered rings where the yields were slightly higher. One notable exception to these low yields was found in the preparation of compound **63h**, a 20-membered ring, where the yield was 31.7%. This compound has a new rigid group in the form of a double bond.[9]

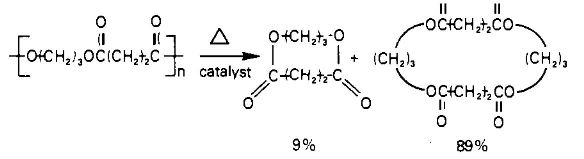


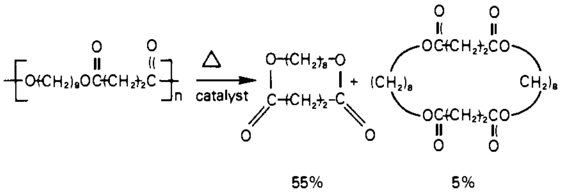
Kaplan and Truesdale prepared *p*-xylylene-1,4-benzenediacetate by heating the disilver salt with α,α'-dibromo-*p*-xylene.[42] The resulting macrocyclic diester was irradiated with ultraviolet light to yield the [2.2]paracyclophane.



C. By Depolymerization of Linear Polyesters

Probably the most interesting early development in the synthesis of macrocyclic diester compounds was the discovery by Carothers and co-workers that linear polyesters could be depolymerized using certain metal catalysts to yield the cyclic monomeric and dimeric adducts.[4,5] The latter adducts prevailed when the unit lengths were 8–11 and the monomeric cyclic adducts for unit lengths of 13 or greater. For example, when polymeric trimethylene succinate (unit length 9 atoms) was depolymerized, a 46% yield of a crude distillate was isolated which contained 9% of the cyclic monomer and 89% of the cyclic dimer whereas with octamethylene succinate (unit length 14 atoms), the crude distillate contained 55% monomer and only 5% dimer.[5] The best depolymerization catalysts were the divalent salts of tin, manganese, iron, magnesium, and cobalt.[5]





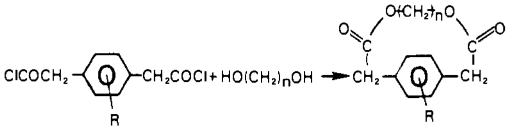
Spanagel and Carothers also observed that the odd-membered rings were relatively more difficult to prepare.[5] This alternating effect of yields was also observed by Hill and Carothers in the preparation of macrocyclic anhydrides[43] and by Ziegler and Aurnhammer in the synthesis of large cyclic ketones.[44]

A typical procedure to prepare the cyclic di- or tetraester is to first synthesize the polyester by heating an equivalent amount of the dibasic acid (or diester) and glycol until the water (or alcohol) is completely removed. The polyester is then mixed with 1 to 2% of the catalyst ($SnCl_2{\cdot}2H_2O$ or $MgCl_2{\cdot}6H_2O$, for example) and heated to 270 °C at ~1 mm pressure. The cyclic monomer or dimer slowly distills from this mixture. The distillate is then purified usually by recrystallization from alcohol.[5,45]

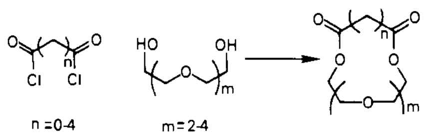
Many different macrocyclic di- and tetraesters have been prepared using this method, either from the polyester or from reaction mixtures containing various oligomers and polymers. The glycols used in these reactions were mostly the oligo(methylene glycols). The dibasic acid units include carbonic,[4] oxalic,[3,4,46] malonic,[4] succinic,[2,4,5] glutaric,[5,47] adipic,[5,47] and the higher alkanedicarboxylic acids[4,5,47] as well as phthalic,[48] and resorcinol and hydroquinone diacetic acids.[45]

D. From Diacid Chlorides and Glycols

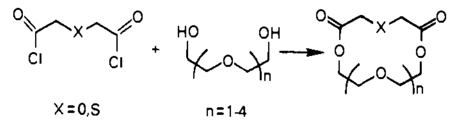
Although esters are often easier to prepare from acid chlorides, only recently has this technique been generally used to synthesize macrocyclic diester compounds. Zahn and coworkers in 1970 reported the preparation of macrocyclic terephthalates and bis(terephthalates) from terephthaloyl chloride.[49,50] Sakamoto and Oki described the synthesis of a series of hetera-*p*-cyclophanes from substituted 1,4-phenylenediacetyl chloride and various glycols.[12-16] They studied the interesting correlations among the NMR spectra, size, and rigidity of the paracyclophane rings.



Bradshaw and co-workers have described a large variety of compounds prepared from diacid chlorides. Their work has concerned the synthesis of macrocyclic multidentate polyether–diester compounds from various diacid chlorides and oligo(ethylene glycols), some of which contained sulfur atoms. Their first compounds were prepared from aliphatic diacid chlorides and oligo(ethylene glycols). These include examples of oxalates,[46] malonates,[17,51,52,54] succinates,[35,52,54] glutarates,[52,54] and adipates.[54] More than 25 of these compounds have been prepared.

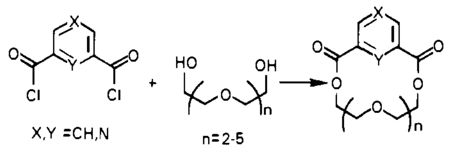


Another series of compounds have been prepared from the diglycolyl and thiodiglycolyl chlorides and various oligo(ethylene glycols), some of which contain sulfur atoms.[17,18,53] Some 15-

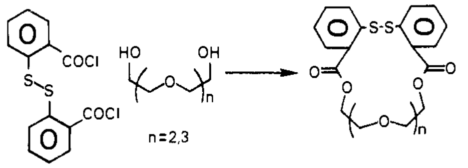


and 18-membered rings in this series which contain two or four methyl substituents have also been prepared.[57]

A third series of macrocyclic diesters comprising more than 25 compounds have been prepared from aromatic diacid chlorides. Compounds have been prepared from the following aromatic diacids: 2,6-pyridinedicarboxylic,[18,56,57] 3,5-pyridinedicarboxylic,[56] phthalic,[54,55] isophthalic,[55] and terephthalic acids.[55] Vögtle and co-workers have also prepared some of these compounds.[19] Complexation of the macrocyclic multidentate polyether–diesters with various cations[17,18] will be discussed in section IV.

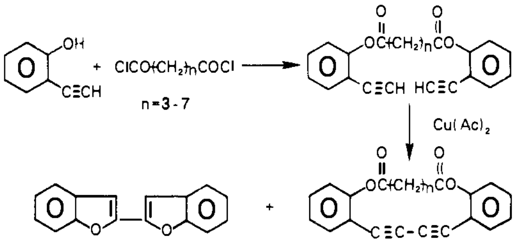


Similar macrocyclic multidentate compounds have been prepared by Drewes and Riphagen from 2,2′-dithiodibenzoyl chloride.[58]

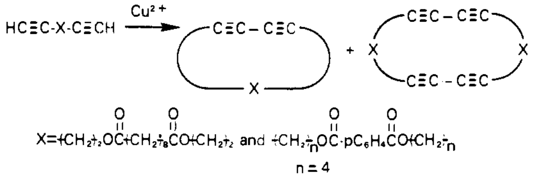


E. By Oxidative Coupling of Diacetylenes Containing a Diester Unit

Oxidative coupling of diacetylenic compounds containing a diester unit has been used by Nakagawa and Toda,[59,60] Eglinton and Galbraith,[61,62] and Bohlmann and co-workers[63] to prepare macrocyclic diester–diacetylenic compounds. Nakagawa and Toda[59,60] found 2,2′-dibenzofuranyl as a by-product in their preparation of cyclic derivatives of *o,o*′-dihydroxydiacetylene. It is interesting to note that even though this system is highly strained, the 16-membered ring (*n* = 4) was isolated in a relatively high yield (40% vs. 21% or less for the other rings).

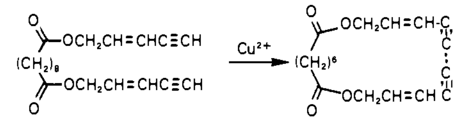


Eglinton and Galbraith prepared 20-membered cyclic monomers and 40-membered cyclic dimers when they coupled α,ω-diacetylenic compounds containing diester groups.[61,62]



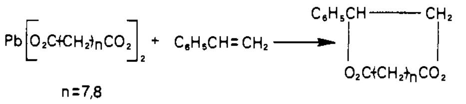
Again it is instructive to note that Eglinton and Galbraith could not isolate products where *n* = 1 or 2. This may only be fortuitous, however; the products that were formed (*n* = 4) had 20- or 40-ring members.

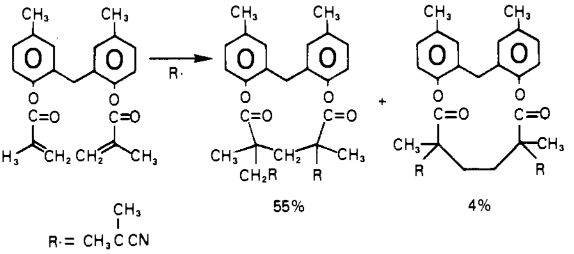
Bohlmann and co-workers also isolated a highly unsaturated macrocyclic diester compound by the diacetylene coupling process.[63]

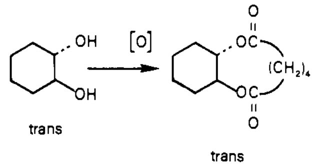


F. Miscellaneous Methods

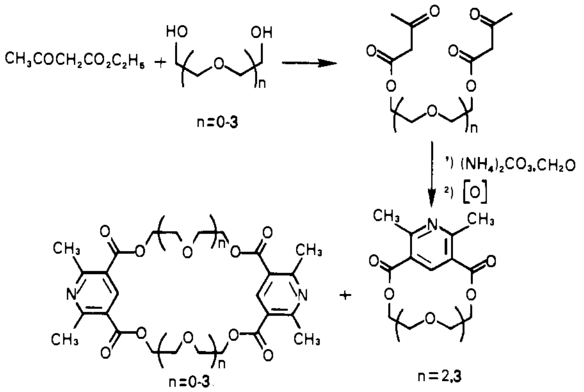
A few macrocyclic diesters have been prepared by oxidative reactions of alkenes, dienes, and glycols. Yukawa and Sakai reported that styrene reacts with lead bis(dicarboxylate) to form a cyclic diester.[64] Kammerer and Pachta have shown that 2,2′-azobisisobutyronitrile reacts with a diene which contains two ester groups to form two macrocyclic diesters.[65,66] Another oxidative process to form cyclic diesters was reported by Suga and Matsuura.[67] They isolated a cyclic diester when *trans*-1,2-cyclohexanediol was oxidized with *tert*-butyl chromate.

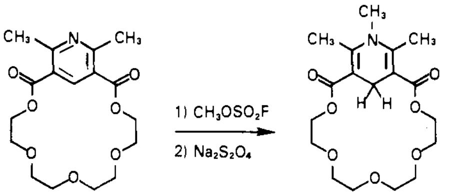






van Bergen and Kellogg were able to prepare macrocyclic polyether–diester compounds containing one or two pyridine moieties by reacting the bis(acetoacetic) ester of various oligo(ethylene glycols) with ammonium carbonate and formaldehyde.[68] Their compounds were then converted into *N*-methyl-1,4-dihydropyridine moiety by treatment with a methylating agent and reduction. This latter compound displays NAD(P)H-like character by donating hydride to sulfonium salts.[69]





III. Listing of Compounds Together with Physical Properties

Table I is an effort to list all the macrocyclic di- and tetraester compounds that have appeared in the chemical literature. The authors have conducted a search of the literature through *Chemical Abstracts* and *Current Abstracts of Chemistry*. The esters of every conceivable diacid were reviewed to see if macrocyclic diesters were listed. The table is organized by acid complexity with the aliphatic esters first (carbonate, oxalate, etc.) followed by the aromatic esters (phthalates, etc.). Physical properties and other data as well as references are listed in the table.

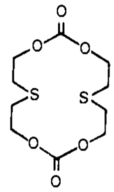
IV. Applications

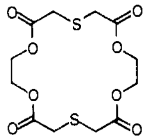
The most important early use of the macrocyclic diester compounds was in the production of perfumes. Carothers, Spanagel, and co-workers prepared nearly 100 diesters, many of which were directly used in perfume preparations.[6] In one paper dealing with macrocyclic ester formation by the degradation of polyesters, they remarked that rings of 18–20 members were practically odorless, but all 17-atom rings had a musk-like odor.[5] It is interesting that when extracts from pine-needle wax were depolymerized, ethylene glycol cyclic brassylate, also a 17-atom ring with a musk-like odor, was isolated.[86] The stated reason to prepare cyclic diynes containing two ester groups was to provide a flexible preparation of potential synthetic musks.[81]

Carothers and co-workers found that at least one of the macrocyclic diesters was unstable and readily transformed to a high polymer.[3] Indeed others also found that cyclic diesters of high purity could be used in the preparation of high polymers and as plasticizers.[2,4,74,88]

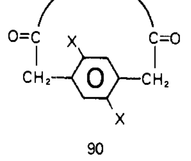
Workers at Kodak in 1961 reported the synthesis of various sulfur-containing macrocyclic di- and tetraesters such as **3a** and **59b.** These compounds increased the sensitivity of silver halide emulsions already sensitized with gold compounds.[71]

An interest in studying macrocyclic compounds containing strained ring systems prompted Drewes and co-workers to prepare these compounds from phthalic acid and other rigid moieties.[7-11] Their results are discussed at some length in section II.B. Toda and Nakagawa were also interested in strained systems in their preparation of macrocyclic diacetylenic diesters.[60]

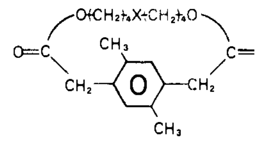

3a


59b

The study of the proton magnetic resonance as a method to determine rotational barrriers in hetera-*p*-cyclophanes caused Sakamoto and Oki to prepare a number of macrocyclic diesters.[12-16] They found that ΔG for rotation of the aromatic ring in compound **90** was 11.0 kcal/mol where X = CH_3 (**90ℓ**) and 21.7 kcal/mol where X = OCH_3 (**90m).** These were the first specific data indicating that the methoxy group is bulkier than a methyl group.[12] Sakamoto and Oki also found that the barrier to rotation greatly increased as the size of the paracyclophane ring was reduced.[14] The effects of oxygen and sulfur-atoms in the paracyclophane ring system was also studied. In compound **92** for example, the barrier to rotation increased for X = sulfide < sulfoxide < sulfone.[13]

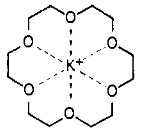


90

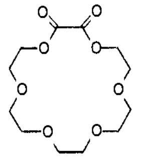


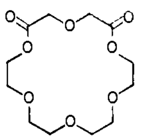
92

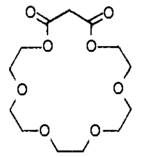
The most recent use of the macrocyclic diesters involves the multidentate properties of those compounds prepared from the oligo(ethylene glycols).[17-19] These compounds resemble the macrocyclic polyethers or so-called "crown" compounds which exhibit unique metal cation complexing properties. Excellent reviews of the crown compounds and their complexing ability have been published.[21-26] The crown–metal cation complexes have been shown to be of the inclusion type with the cation situated in the center of the crown cavity.[93,94] This type of complexing ability has been compared to that for valinomycin, a natural antibiotic.[17]



The metal cation complexing properties of some of the macrocyclic multidentate polyether–diester compounds have been studied.[17-19] Compounds **9c** and **56c** exhibited complexing properties similar to that for 18-crown-6 (i.e., they formed strong complexes with Ba^{2+} and K^+ in methanol with log K for Ba^{2+} > log K for K^+).[17,95] Compound **16e**, on the other hand, formed a stronger complex with K^+ (log K = 2.55) than with Ba^{2+} (log K = 1.41).[17] This compound was one of the first examples reported in which the K^+ complex was more stable than the corresponding Ba^{2+} complex. The cations have nearly identical crystal radii.

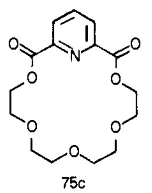

9c

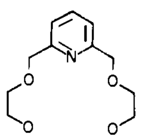

56c


16e

A potassium thiocyanate salt of compound **56c** has been isolated.[53] The infrared spectra for compound **56c** and its complex are instructive. Compound **56c** exhibited two carbonyl bands at 1715 and 1730 cm^{-1}. The metal complex exhibited only one band at 1740 cm^{-1}. These observations show that (i) since the carbonyl stretch of the complex has been shifted to a higher resonance frequency, the complex probably does not involve the carbonyl oxygen atoms, and (ii) the molecule is organized in a planar arrangement around the central K^+ ion.[53] Preliminary X-ray crystallographic results of compound **56c** and its complex are consistent with the IR analysis in that one of the carbonyl oxygen atoms of compound **56c** is about 90° out of plane while the other is nearly coplanar with the ether oxygen atoms.[96]

Compound **75c** formed strong complexes with Na^+, K^+, Ba^{2+},


75c


Pyridino 18-Crown-6

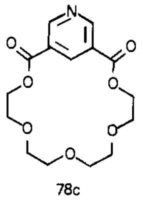

78c

TABLE I

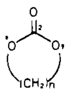
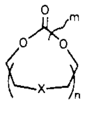
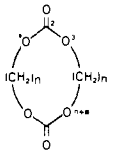
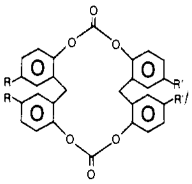
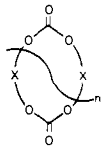
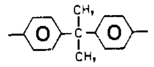
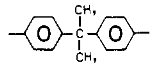
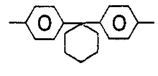
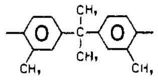
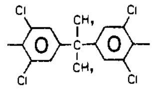
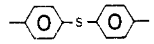
compound	*n*	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other[a]		
Carbonates							
 1	6	H	1a			attempted synthesis, only dimer isolated	4
	6	5,8-di-α-naphthyl	**1b**	108–110			70
	7	H	**1c**			attempted synthesis, only dimer isolated	4
	8	H	**1d**	21.5–23 (74–76/0.5)	E		4
	9	H	**1e**	34–35 (63–64/0.1)	E		4
	10	H	**1f**	10–11 (92–93/1)	E		4
	11	H	**1g**	40–41 (104.5/7)	E		4
	12	H	**1h**	11–12 (118–119/3)	E		4
	13	H	**1i**	23–24.5 (149–150/4.5)	E		4
	14	H	**1j**	21–22 (144–146/2)	E		4
	16	H	**1k**	31 (135/0.5)			86
	18	H	**1l**	36–37 (165–169/1)	E		4
 2,3	2, *m* = 1	X = O	**2a**	liquid	E	mixture with dimer	4
	3, *m* = 1	X = O	**2b**	42–44 (128–130/1)	E		4
	1, *m* = 2	X = S	**3a**			photosensitizer	71
	2, *m* = 2	X = O	**3b**	liquid	E	mixture with monomer	4
 4	2	H	**4a**			attempted synthesis, only monomer isolated	4
	3	H	**4b**			attempted synthesis, only monomer isolated	4
	4	H	**4c**	175–176			4
	4	5,6:12,13-dicyclobutano	**4d**	209–210	B,E	polymerized on heating	39
	5	H	**4e**	117–118	E		4
	6	H	**4f**	128–129	E		4
	7	H	**4g**	97–98	E		4
	8	H	**4h**	116–117	E		4
	9	H	**4i**	95–95.5	E		4
	10	H	**4j**	105–106	E		4
	11	H	**4k**	97–97.5	E		4
	12	H	**4l**	93–95			4
 5		R = R′ = Me	**5a**	274.5–275			72–74
		R = R′ = Cl	**5b**	365–368			72
		R = Me, R′ = Cl	**5c**	330–333			72
 6, 7	2	X = 	**6**	335–340		polymerizes at the melting point	73, 74
	3	X = 	**7a**	375			75
	3	X = 	**7b**			polymerizes spontaneously at 330 °C	75
	3	X = 	**7c**	301–303			75
	3	X = 	**7d**	420			75
	3	X = 	**7e**	320–322			75
Oxalates							
 8	10	H	**8a**	(125–126/0.2)	E		4
	11	H	**8b**	23–24.5 (120–123/0.5)	E		4
	11	8,12-dithia	**8c**	101–102	A,B,E		57

TABLE I (*Continued*)

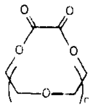
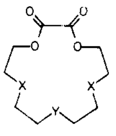
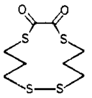
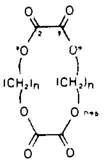
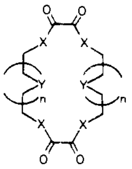
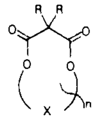
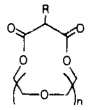
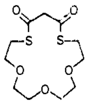
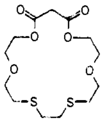
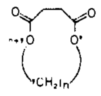
compound	n	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other[a]		
 9	2	H	**9a**			attempted synthesis, only dimer isolated	46
	3	H	**9b**	45-46 (154-166/2)	A,B,E		46
	4	H	**9c**	84-85	A,B,E	forms stable complexes in MeOH with alkali metal ions	46
	5	H	**9d**	liquid	A,B,E		46
 10		X = O, Y = S	**10a**	88-90	A,B,E		46
		X = S, Y = O	**10b**	45-47	A,B,E		46
 11		H	11		A,B,E		76
 12	3	H	**12a**	187	E		3
	4	6,7:14,15-dibenzo	**12b**	233-235	A,B,D		11
 13	1	X = Y = O	**13a**	162.5-164	A,B,E		46
	1	X = O, Y = S	**13b**	195-203	A,B,E		46
	1	X = S, Y = O	**13c**	207.5-210	A,B,E		46
	1	X = Y = S	**13d**	108-109d	A,B		46
	2	X = Y = O	**13e**	68-72	A,B,E		46
Malonates							
 14,15	1	R = H, X = $(CH_2)_{10}$	14a	(117-118/0.5)	E		4
	1	R = Et, X = $-CH(CH_3)-CONHCH_2NHCOCH(CH_3)-$	14b,c			methyl groups are cis on **14b** and trans on **14c**	77
	2	R = H, X = *o*-xylylene	15	215-218	A,B,D		11
 16	2	R = H	**16a**	51.5-52.5	A,B,E		51, 52
	3	R = H	**16b**	67-68	A,B,E		51, 52
	3	R = Et	**16c**	(146-148/0.17)	A,B,E		54
	3	R = phenyl	**16d**	83.5-85	A,B,E		54
	4	R = H	**16e**	65-66	A,B,E	forms stable complexes in MeOH with Na^+, K^+, and Ba^{2+}	17, 51, 52
	4	R = Et	**16f**	(176-182/0.6)	A,B,E		57
	4	R = *n*-heptyl	**16g**	(198-203/1.3)	A,B,E		57
	4	R = phenyl	**16h**	69-70	A,B,E		57
 17		H	**17**	liquid	A,B,E	decomposes on heating	52
 18		H	**18**	liquid	A,B,E		52
Succinates							
 19	3	H	**19a**	81 (94-100/2)	E		5, 6
	4	H	**19b**	42 (95-96/2)	E		5, 6
	5	H	**19c**	19 (88-89/1)	E		5, 6
	6	H	**19d**	−15 (108-110/2)	E		5, 6
	7	H	**19e**	49 (116-118/2)	E		5, 6
	8	H	**19f**	71	E		5, 6
	8	4,7-dithia	**19g**	102-103	A,B,E		57
	9	H	**19h**	71	E		5, 6

TABLE I (*Continued*)

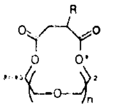
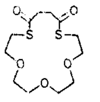
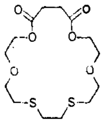
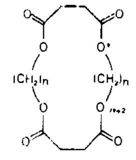
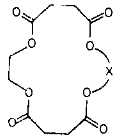
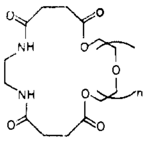
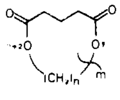
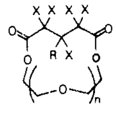
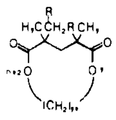
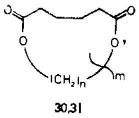
compound	*n*	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other[a]		
	9	4,8-dithia	**19l**	55–56	A,B,E		57
	10	H	**19j**	58 (135–140/2)	E		5, 6
	10	5,8-dithia	**19k**	38.0–38.5	A,B,E		57
	12	H	**19l**	12 (156–159/2)	E		5, 6
	13	H	**19m**	13 (154/2)	E		5,6
	14	H	**19n**	11 (167/2)	E		5
	18	H	**19o**	13 (199–201/2)	E		5, 6
 20	2	R = H	**20a**	57–58 (169–170/2)			78
	3	R = H	**20b**	liquid	A,B,E		52
	3	R = Me	**20c**	(146–154/0.2)	A,B,E		54
	3	R = H, 15,16-cyclohexano	**20d**	liquid	A,B,E		54
	3	R = phenyl	**20e**	liquid	A,B,E		54
	4	R = H	**20f**	30–31	A,B,E		52, 57
 21		H	**21**	liquid	A,B		52
 22		H	**22**	liquid	A,B		52
 23	2	H	**23a**	131	A,B,E		2, 6, 35
	2	6,7:14,15-dicyclobutano	**23b**	185–186.5	E		39
	3	H	**23c**	138	E		5, 6
	4	H	**23d**	121	E		5, 6
	4	3,4:13,14-dibenzo	**23e**	217	A,B,D		11
	5	H	**23f**	87	E		5, 6
	6	H	**23g**	110	E		5, 6
	7	H	**23h**	86	E		5, 6
	8	H	**23i**	109	E		5, 6
	10	H	**23j**	109	E		4, 5
 24		X = $-CH_2(CH_2OCH_2)_2CH_2-$	**24a**	liquid	A,B,E		35
		X = $-CH_2CH_2N(CH_2C_6H_5)-CH_2CH_2-$	**24b**	liquid	A,B,E		35
 25	0	H	**25a**	190–192	A,B,E		35
	1	H	**25b**	167–168	A,B,E		35
	2	H	**25c**	159–161	A,B,E		35
Glutarates							
 26,27	3, *m* = 1	H	**26a**	85	B,E		47
	4, *m* = 1	3,4-dimethylene	**26b**	95–96	C,E		79
	8, *m* = 1	2,3:8,9-dibenzo-4,6-diyne	**26c**	135–136	B,C,E		59, 60
	10, *m* = 1	H	**26d**	14 (136–139/1)	E		5, 6
	4, *m* = 2	3,4:14,15-dibenzo	**27**	173	A,B,D		11
 28	3	R = X = H	**28a**	(155–157/0.65)	A,B,E		54
	3	R = X = F	**28b**	(135–143/0.3)	A,B,E		54
	3	R = Me, X = H	**28c**	(130–142/0.12)	A,B,E		54
	4	R = X = H	**28d**	(175–180/0.8)	A,B,E		52, 57
 29	2	R = $-C(CH_3)_2CN$, 2,3(2′,3′-naphthano)	**29a**		B,E		65
	4	R = $-C(CH_3)_2CN$, 2,3:4,5-dibenzo	**29b**		B,E		65
	5	R = $-C(CH_3)_2CN$, 2,3:5,6-di(4′-methylbenzo)	**29c**	160	A–E		66
Adipates							
 30,31	2, *m* = 1	2,3-*trans*-cyclohexano	**30a**	125–125.5	B		67
	4, *m* = 1	H	**30b**	93	B,E		47
	6, *m* = 1	H	**30c**	70 (117/2)	E		5, 6
	6, *m* = 1	3-ene-5-yne	**30d**	35 (136–145/2)			80
	8, *m* = 1	2,3:8,9-dibenzo-4,6-diyne	**30e**	123.5	B,C,E		59, 60

TABLE I (*Continued*)

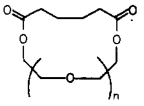
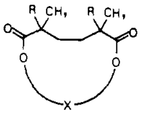
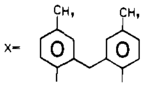
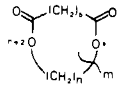
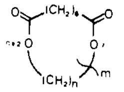
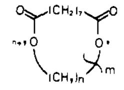
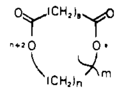
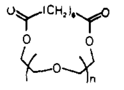
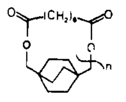
compound	*n*	substituents	compd no.	physical data: mp (bp/mm), °C	physical data: other^a	general comments	ref
	9, *m* = 1	H	**30f**	26 (144–146/2)	E		5
	10, *m* = 1	5-ene-7-yne	**30g**	(130–140/0.2)			81
	4, *m* = 2	3,4:15,16-dibenzo	**31**	144	A,B,D		11
 **32**	1	H	**32a**				82
	2	H	**32b**	59 (162/2)	A,B,E		5, 54, 78
	3	H	**32c**	(154–155/0.07)	A,B,E		54
 **33**		R = –C(CH$_3$)$_2$CN X = *p*-phenylene	**33a**	93.3	B,E		65
		R = –C(CH$_3$)$_2$CN X = 2,3-naphthylene	**33b**		B,E		65
		R = –C(CH$_3$)$_2$CN X = 2,2′-biphenylene	**33c**		B,E		65
		R = –C(CH$_3$)$_2$CN X= 	**33d**	132	A–E		66
Pimelates							
 **34, 35**	5, *m* = 1	H	**34a**	59	B,E		47
	8, *m* = 1	2,3:8,9-dibenzo-4,6-diyne	**34b**	120.5–121.5	B,C,E		59, 60
	4, *m* = 2	3,4:16,17-dibenzo	**35**	121	A,B,D		11
Suberates							
 **36, 37**	6, *m* = 1	H	**36a**	64	B,E		47
	7, *m* = 1	H	**36b**	47 (158–160/2)	E		5, 6
	4, *m* = 2	3,4:17,18-dibenzo	**37**	134	A,B,D		11
Azelates							
 **38,39**	2, *m* = 1	H	**38a**	52	E		5, 6
	2, *m* = 1	2-phenyl	**38b**				64
	4, *m* = 1	H	**38c**	9 (123–124/2)	E		5
	6, *m* = 1	H	**38d**	59	E		5
	7, *m* = 1	H	**38e**	62	B,E		47
	8, *m* = 1	2,3:8,9-dibenzo-4,6-diyne	**38f**	125–127	B,C,E	forms two polymorphs (lower melting form 111 °C)	60
	9, *m* = 1	H	**38g**	10–12 (147–148/0.01)			38
	2, *m* = 2	H	**39a**	145	E		5, 6
	4, *m* = 2	3,4:18,19-dibenzo	**39b**	119	A,B,D		11
	9, *m* = 2	H	**39c**	70			38
Sebacates							
 **40,41**	2, *m* = 1	H	**40a**	42 (119–123/2)	E		4, 5, 83, 84
	2, *m* = 1	2-phenyl	**40b**				64
	3, *m* = 1	H	**40c**	7 (130–133/2)	E		5, 6, 38, 78
	4, *m* = 1	H	**40d**	6 (136–138/2)	E		5
	5, *m* = 1	H	**40e**	37 (159–160/2)	E		5
	6, *m* = 1	H	**40f**	47	E		5, 85
	6, *m* = 1	3-ene-5-yne	**40g**	(140–145/0.3)			81
	8, *m* = 1	H	**40h**	68	B,E		47
	8, *m* = 1	4,6-diyne	**40i**	54–55	B,C,E		61, 62
	10, *m* = 1	5-ene-7-yne	**40j**	(140/10.5)			81
	10, *m* = 1	3,9-diene-5,7-diyne	**40k**	200	B,C		63
	2, *m* = 2	H	**41a**	81	E		4, 5
	3, *m* = 2	H	**41b**	113–113.5	E		4, 5, 38
	4, *m* = 2	3,4:19,20-dibenzo	**41c**	135	A,B,D		11
	8, *m* = 2	4,6,24,26-tetrayne	**41d**	109–110	B,C,E		61,62
 **42**	1	H	**42a**	15 (156–157/2)	E		5, 78
	2	H	**42b**	(202–204/3)			78
 **43,44**	1	H	**43**			attempted synthesis only dimer isolated	37
	2	H	**44**	50–52	A,B		37

TABLE I (*Continued*)

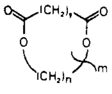
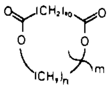
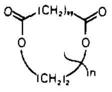
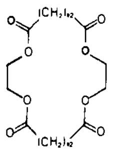
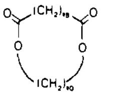
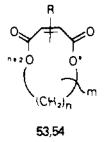
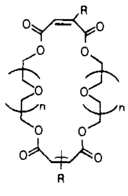
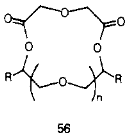
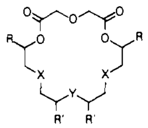
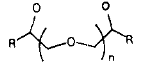
compound	*n*	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other[a]		
Undecanedioates							
 45,46	2, *m* = 1	H	**45a**	35			4
	9, *m* = 1	H	**45b**	73	B,E		47
	2, *m* = 2	H	**46**	143	E		4
Dodecanedioates							
 47,48	2, *m* = 1	H	**47a**	18 (139–141/2)	E		4, 5
	3, *m* = 1	H	**47b**				85
	0, *m* = 1	H	**47c**	80	B,E		47
	2, *m* = 2	H	**48**	95–96	E		4, 5
Tridecanedioates							
 49,50	1	H	**49**	−8 (139–142/1)	E		5, 83, 85, 86
	2	H	**50**	145–146	E		4, 5
Tetradecanedioates							
 51		H	**51**	102–103			4
Octadecanedioates							
 52		H	**52**	60	E		5
Maleates, Fumarates, and Citraconates							
 53,54	4, *m* = 1	R = H, 3,4-benzo	**53a**	160	A,B,D		11
	4, *m* = 1	R = Me, 3,4-benzo	**53b**	108	A,B,D		11
	4, *m* = 2	R = H	**54a**				87
	4, *m* = 2	R = H, 3,13-diyne	**54b**	184	A,B,C,D		10
	4, *m* = 2	R = Me, 3,13-diyne	**54c**	254	A,B,C,D		10
	6, *m* = 2	R = H, 3,5,15,17-tetrayne	**54d**	160 d	A,B,C,D		10
	6, *m* = 2	R = Me, 3,5,15,17-tetrayne	**54e**	160 d	A,B,C,D		10
 55	1	R = H	**55a**	127.5–128	A,B,E		35
	1	R = Me	**55b**	liquid	A,B,E		35
	3	R = H	**55c**	67–71	A,B,E	forms from fumaroyl dichloride, double bonds are trans	54
Diglycolates							
 56	2	R = H	**56a**	100.5–101.5 (145/0.2)	A,B,E		53
	2	R = Me	**56b**	116–118	A,B,E		57
	3	R = H	**56c**	78.5–79.5 (148/0.16)	A,B,E	forms stable complexes in MeOH with Na^+, K^+, Ba^{2+} and Ag^+ (KSCN complex mp 169–169.5 °C)	17, 18, 53
	3	R = Me	**56d**	(172/1)	A,B,E		57
	4	R = H	**56e**	(200/0.2)	A,B,E		53
 57		R = H, R′ = Me, X = Y = O	**57a**	(163–166/1)	A,B,E		57
		R = R′ = Me, X = Y = O	**57b**	(150/0.8)	A,B,E		57
		R = R′ = H, X = O, Y = S	**57c**	113.5–115	A,B,E		53
		R = R′ = H, X = S, Y = O	**57d**	36–36.5	A,B,E		53
Thiodiglycolates							
 58	1	R = H	**58a**	93.5–94.5 (155/1)	A,B,E		53
	2	R = H	**58b**	85.5–86.5 (156/0.15)	A,B,E		53
	2	R = Me	**58c**	120–121	A,B,E		57
	3	R = H	**58d**	43.5–44.5 (181/0.4)	A,B,E	forms a stable complex in MeOH with Ag^+	18, 53

TABLE I (*Continued*)

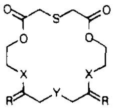
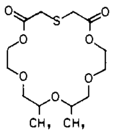
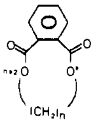
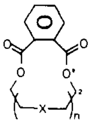
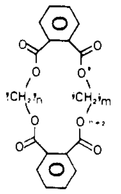
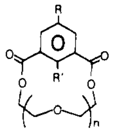
compound	n	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other^a		
	3	R = Me	**58e**	(180/0.7)	A,B,E		57
	4	H	**58f**	(204/0.2)	A,B,E		53
 59		R = H$_2$, X = O, Y = S	**59a**	106-107	A,B,E		53
		R = O, X = O, Y = S	**59b**	150.5-151.5			71
		R = H$_2$, X = S, Y = O	**59c**	liquid	A,B,E		53
 60		H	**60**	(163-165/0.7)	A,B,E		57
Phthalates							
 61	3	2-Me	**61a**	78.6-78.8	B,E		48
	4	H	**61b**	111	A,B,D		7, 8
	4	3,4-dibenzo	**61c**	148	A,B,D		11
	5	H	**61d**	101	A,B,D,E		7, 8, 48
	6	H	**61e**	64	A,B,D,E		8, 48
	8	H	**61f**	liquid	A,B,D		8
	10	H	**61g**	liquid	A,B,D		8
	12	H	**61h**	liquid	A,B,D		8
 62	1	X = O	**62a**	61.5-62.5	B,E		48, 88
	1	X = S	**62b**	107.2-107.7	B,E		48
	1	X = O, 2,5-diMe	**62c,d**	130.5-131.5 105.8-107.1		two diasteromers	48, 88
	2	X = O	**62e**	119.5-121	B,E		48, 88, 98
	3	X = O	**62f**	70-75	A,B,E		54
	4	X = O	**62g**	liquid	A,B,E		55
	5	X = O	**62h**	liquid	A,B,E		55
 63	$n = m = 2$	H	**63a**	198	A,B,D		6, 8
	$n = 2$, $m = 4$	H	**63b**	104	A,B,C,D		9
	$n = 2$, $m = 6$	H	**63c**	147	A,B,C,D		9
	$n = m = 3$	H	**63d**	193	A,B,D		8
	$n = 3$, $m = 4$	H	**63e**	131	A,B,C,D		9
	$n = 3$, $m = 5$	H	**63f**	165	A,B,C,D		9
	$n = m = 4$	H	**63g**	140	A,B,C,D		9
	$n = m = 4$	3-ene	**63h**	149	A,B,C,D		9
	$n = m = 4$	3,13-diyne	**63i**	280	A,B,C,D		10
	$n = 4$, $m = 5$	H	**63j**	100	A,B,C,D		9
	$n = 4$, $m = 6$	H	**63k**	108	A,B,C,D		9
	$n = 4$, $m = 7$	H	**63l**	115-117	A,B,C,D		9
	$n = 4$, $m = 8$	H	**63m**	138	A,B,C,D		9
	$n = 4$, $m = 9$	H	**63n**	112	A,B,C,D		9
	$n = m = 5$	H	**63o**	139	A,B,C,D		9
	$n = m = 6$	H	**63p**	66	A,B,C,D		9
	$n = m = 6$	3,5,15,17-tetrayne	**63q**	160 d	A,B,C,D		10
	$n = 6$, $m = 7$	H	**63r**	60	A,B,C,D		9
	$n = 6$, $m = 8$	H	**63s**	93	A,B,C,D		9
	$n = m = 7$	H	**63t**	163	A,B,D		8
	$n = 7$, $m = 8$	H	**63u**	89	A,B,C,D		9
	$n = m = 8$	H	**63v**	64-65	A,B,C,D		9
	$n = 8$, $m = 9$	H	**63w**	75	A,B,C,D		9
	$n = 8$, $m = 12$	H	**63x**	95	A,B,C,D		9
	$n = m = 9$	H	**63y**	140-141	A,B,D		8
	$n = 9$, $m = 10$	H	**63z**	56	A,B,C,D		9
	$n = m = 10$	H	**63aa**	78-79	A,B,C,D		9
	$n = 10$, $m = 11$	H	**63bb**	64	A,B,C,D		9
	$n = m = 11$	H	**63cc**	138-139	A,B,D		8
	$n = 11$, $m = 12$	H	**63dd**	75	A,B,C,D		9
	$n = m = 12$	H	**63ee**	84	A,B,C,D		9
Isophthalates							
 64	2	R = R′ = H	**64a**	138-140	A,B,E		55
	2	R = NO$_2$, R′ = H	**64b**	161-163	A,B,E		55
	3	R = R′ = H	**64c**	95.5-96	A,B,E	(NaSCN complex mp 173.5-174.5 °C)	19, 55, 98
	3	R = NO$_2$, R′ = H	**64d**	157-158	A,B,E		55
	3	R = NH$_2$, R′ = H	**64e**	140 d	A,B,E		57
	3	R = H, R′ = NO$_2$	**64f**	124-126		(NaSCN complex mp 158-162 °C)	19

TABLE I *(Continued)*

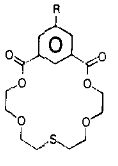
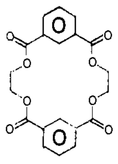
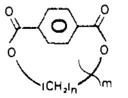
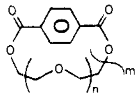
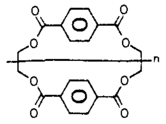
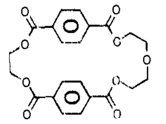
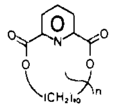
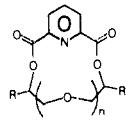
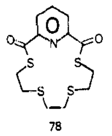
compound	n	substituents	compd no.	physical data: mp (bp/mm), °C	physical data: other[a]	general comments	ref
	4	R = R′ = H	**64g**	103.5–104.5	A,B,E		55
	4	R = NO_2, R′ = H	**64h**	104–105	A,B,E		55
	4	R = NH_2, R′ = H	**64i**	128–129	A,B,E		55
	4	R = $NHCOCH_3$, R′ = H	**64j**	148.5–150.5	A,B		55
	5	R = R′ = H	**64k**	106.5–108.5	A,B,E		55
	5	R = NO_2, R′ = H	**64l**	90–92	A,B,E		55
 65		R = H	**65a**	liquid	A,B,E		55
		R = NO_2	**65b**	liquid	A,B,C,E		55
 66		H	**66**	325–327	E		89
Terephthalates  67,68,69	12, *m* = 1	6,8-diyne	**67**	145–148	C		62
	12, *m* = 2	6,8,26,28-tetrayne	**68**	210–211	B,C,E		62
	4, *m* = 4	H	**69**	247–249	B		49
 70,71	3, *m* = 1	H	**70a**	96		(NaSCN complex mp 174–176.5 °C)	19
	4, *m* = 1	H	**70b**	108–109.5	A,B,E		55, 98
	5, *m* = 1	H	**70c**	69–70	A,B,E		55, 98
	3, *m* = 2	H	**71**	93.5–95	A,B,E		55
 72	1	H	**72a**	229	B,D,E		90
	2	H	**72b**	314–316	B,E		49, 50
	3	H	**72c**	324–325	B,E		49, 50
	4	H	**72d**	264	B,E		50
	5	H	**72e**	304–305	B,E		50
	6	H	**72f**	238–240	B,E		50
 73		H	**73**	165–167	B,E		49, 91
Pyridinedicarboxylates  74	1	H	**74a**			attempted synthesis only dimer isolated	19
	2	H	**74b**	156–158			19
 75	2	R = H	**75a**	139–140	A,B,E		56
	2	R = Me	**75b**	(165/1)	A,B,E		57
	3	R = H	**75c**	86.5–87.5	A,B,E	forms stable complexes in MeOH with Na^+, K^+, Ba^{2+}, and Ag^+ (NaSCN complex mp 170.5–172.5 °C; KSCN complex mp 198.5–200.5 °C; $Ca(SCN)_2{\cdot}H_2O$ complex mp 203–206 °C)	18, 19, 56
	3	R = Me	**75d**	80–83	A,B,E		57
	4	R = H	**75e**	143–144.5	A,B,E		56
	5	R = H	**75f**	110–111	A,B,E		56
 78		H	**76**	135–138			19

TABLE I (*Continued*)

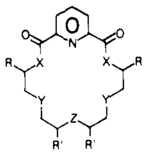
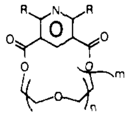
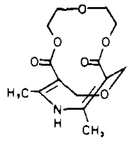
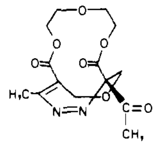
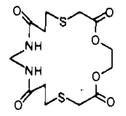
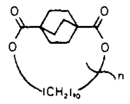
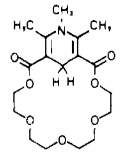
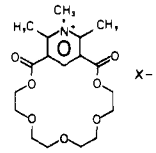
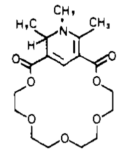
compound	n	substituents	compd no.	physical data		general comments	ref
				mp (bp/mm), °C	other[a]		
 77		R = H, R′ = Me, X = Y = Z = O	**77a**	97–100	A,B,E		57
		R = R′ = Me, X = Y = Z = O	**77b**	(175/1)	A,B,E		57
		R = R′ = H, X = O, Y = O, Z = S	**77c**	96–97.5	A,B,E		56
		R = R′ = H, X = O, Y = S, Z = O	**77d**	127–129	A,B,E		56
		R = R′ = H, X = S, Y = O, Z = O	**77e**	146–148			19
 78,79	2, m = 1	R = H	**78a**	137–137.5	A,B,D,E		56, 98
	2, m = 1	R = Me	**78b**	167–169	A,C,D		68
	3, m = 1	R = H	**78c**	112–113	A,B,E		56, 98
	3, m = 1	R = Me	**78d**	90–92	A,C,D		68, 69, 98
	4, m = 1	R = H	**78e**	54.5–55.5	A,B,E		56, 98
	5, m = 1	R = H	**78f**	50–51	A,B,E		56, 98
	0, m = 2	R = Me	**79a**	196–198	A,C,D		68
	1, m = 2	R = Me	**79b**		A,C		68
	2, m = 2	R = Me	**79c**		A,C		68
	3, m = 2	R = Me	**79d**		A,C		68
Miscellaneous							
 80		H	**80**	141–145	A		68
 81		H	**81**	124–126	A,B,C	^{13}C NMR	68
 82		H	**82**	177–178			71
 83,84	1	H	**83**			attempted synthesis only dimer isolated	37
	2	H	**84**	57.5–58	A,B		37
 85		H	**85**	110–113,[68] 90–92[69]	A,C,D	forms a complex with $Na^+ ClO_4^-$ which cocrystallizes with one molecule of solvent,[69] mp of complex: (acetonitrile) 176–180 °C, (acetone) 172.5–175 °C (methyl acetate) 169.5–171.5 °C	68, 69
 86		$X^- = BF_4^-$	**86a**				69
		$X^- = ClO_4^-$	**86b**	190–193	A,C,D		68
 87		H	**87**	131.5–133	D		68

TABLE I (*Continued*)

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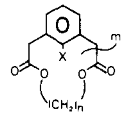
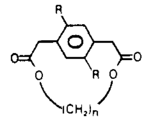
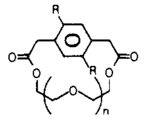
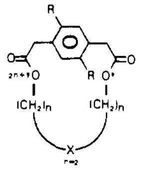
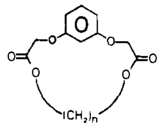
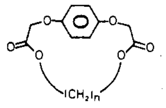
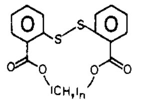
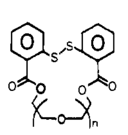
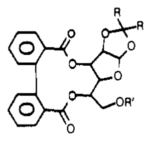
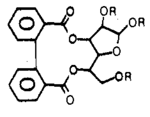
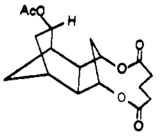
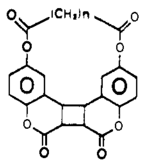
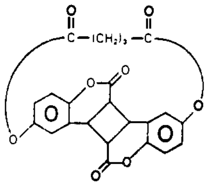
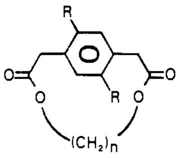
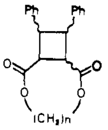
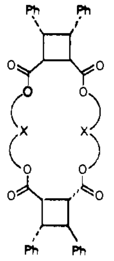
				mp (bp/mm), °C	other[a]		
 **88,89**	5, *m* = 1	X = H	**88**	80–81	A		36
	4, *m* = 2	X = H	**89a**	92–93	A		36
	4, *m* = 2	X = Cl	**89b**	163–164	A		36
 **90**	5	R = H	**90a**	147–148	A,B,D		14
	5	R = Me	**90b**	80–81	A,B,D		14
	6	R = H	**90c**	135.5–136.5	A,B,D		14
	6	R = Me	**90d**	92.5–93.5	A,B,D		14
	7	R = H	**90e**	110–111	A,B,D		14
	7	R = Me	**90f**	51.5–53	A,B,D		14
	8	R = H	**90g**	94–95	A,B,D		14
	8	R = Me	**90h**	78–79	A,B,D		14
	9	R = H	**90i**	45–46	A,B,D		14
	9	R = Me	**90j**	87–88	A,B,D		14
	10	R = H	**90k**	38–39	A,B,D		14
	10	R = Me	**90l**	89–90	A,B,D		12, 14
	10	R = OMe	**90m**	63–64	A,B,D		12
 **91**	1	R = H	**91a**	158.5–159.5	A,B,D		16
	1	R = Me	**91b**	96–97	A,B,D		16
	2	R = H	**91c**	39–40	A,B,D		16
	2	R = Me	**91d**	70.5–71	A,B,D		16
	3	R = H	**91e**	95.5–96.5	A,B,D		16
	3	R = Me	**91f**	85.5–86.5	A,B,D		16
	3	R = OMe	**91g**	94.5–95	A,B,D		16
 **92**	1	R = H, X = *p*-phenylene	**92a**	238–239	A,B,C,D		42
	4	R = Me, X = S	**92b**	70–71	A,B,D		13
	4	R = Me, X = SO	**92c**	134–134.5	A,B,D		13
	4	R = Me, X = SO_2	**92d**	123–124	A,B,D		13
	5	R = H, X = S, 4,5:9,10-dibenzo	**92e**	125–125.5	A,D		15
 **93**	2	H	**93a**	100	E		45
	3	H	**93b**	134	E		45
	4	H	**93c**	112	E		45
	6	H	**93d**	115	E		45, 85
	9	H	**93e**	86	E		45
	10	H	**93f**	86	E		45
 **94**	4	H	**94a**	140	E		45
	6	H	**94b**	124	E		45, 85
	10	H	**94c**	58	E		45
 **95**	4	H	**95a**	157	A,D		58
	4	3-yne	**95b**	148–150	A,D		58
	5	H	**95c**	85–87	A,D		58
	6	H	**95d**	147	A,D		58
	7	H	**95e**	117	A,D		58
	8	H	**95f**	186	A,D		58
 **96**	2	H	**96a**	193	A,D		58
	3	H	**96b**	141–142	A,D		58
 **97**		R = Me, R′ = H	**97a**		E		92
		R = R′ = Me	**97b**				92
		R = Me, R′ = Ac	**97c**	216–217			92
 **98**		R = H	**98a**				92
		R = Ac	**98b**	208–209			92

[a] A = NMR, B = IR, C = UV, D = MS, E = mol wt.

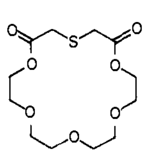
TABLE II. Addendum Table

Compound	n	substituents	compd no.[a]	physical data		general comments	ref
				mp (bp/mm), °C	other[b]		
			**26e**	158-159		Baeyer-Villiger oxidation	99
	4		**30h**	215-217.5	A,B,D	[2 + 2] photocyclization of the bis(7-coumarinyl) ester	100
	5		**34c**	229-233	A,B,D	[2 + 2] photocyclization of the bis(7-coumarinyl) ester	100
	6		**36c**	229.5-232	A,B,D	[2 + 2] photocyclization of the bis(7-coumarinyl) ester	100
	7		**38h**	216.5-218	A,B,D	[2 + 2] photocyclization of the bis(7-coumarinyl) ester	100
			**34d**	237-241	A,B,D	[2 + 2] photocyclization 100 of the bis(7-coumarinyl) ester	100
	9	R = OMe	**90n**	61.5-62.5	A,B,D		101
	10	R = OEt	**90o**	oil	A,B,D		101
	11	R = OMe	**90p**	74.5-75.0	A,B,D		101
	11	R = OMe	**90q**	50.0-51.0	A,B,D		101
	11	R = O-*n*-Pr	**90r**	oil	A,B,D		101
	12	R = OEt	**90s**	oil	A,B,D		101
	12	R = O-*n*-Pr	**90t**	oil	A,B,D		101
	3		**99a**	β-isomer 162-163	B	mixt of β and δ truxinic acid moieties	102
	4		**99b**		B	exclusively the δ truxinic acid moiety	102
		X = $(CH_2)_3$	**100a**	159-161	A,D		103
		X = $(CH_2)_{10}$	**100b**		A		104
		X = $(CH_2)_{12}$	**100c**		A		104
		X = $CH_2CH_2OCH_2CH_2$	**100d**		A		104
		X = $CH_2(CH_2OCH_2)_2CH_2$	**100e**		A		104

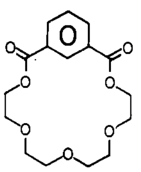
[a] See Table I. [b] A = NMR, B = IR, C = UV, D = MS, E = molecular weight.

and Ag^+ in methanol (log K = 4.3 to 4.9).[18,19] The macrocyclic polyether, pyridino-18-crown-6, formed even stronger complexes in the cases of K^+, Ba^{2+}, and Ag^+.[18] That the pyridine nitrogen is an integral part of the complex was shown by the fact that compound **78c** which has the nitrogen outside the polyether cavity does not complex with the alkali metal cations in methanol.[95] It is interesting that the infrared spectra of compound **75c** and its potassium ion complex were almost identical.[56] X-ray analyses of compound **75c** show that all the oxygen atoms and the pyridine nitrogen atom are in about the same plane and that the cavity is almost symmetrical.[96] No complex of potassium ion and compound **78c** could be isolated.[56]

Metal cation complexation properties for compounds **58d** and **64c** have also been investigated.[18,95] Compound **58d** formed a strong complex with Ag^+ in methanol with a 1:1 ligand-metal ion complex being reported.[18] No complexes with the alkali and alkaline earth cations were formed.[18] These results are much the same as the complexation data found for the metal cation-thiacrown interactions.[97] Compound **64c** does not complex with metal cations in methanol.



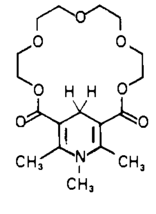
58d



64c

van Bergen and Kellogg have prepared a macrocyclic multidentate polyether diester compound with an NAD(P)H mimic formed from a Hantzsch 1,4-dihydropyridine segment.[68,69] They found that compound **85** would transfer a hydride to a sulfonium salt much the same as NAD(P)H does.[69] These types of enzymatic reactions are certain to receive future attention as new macrocyclic multidentate polyether-diester compounds are prepared.

85



V. Addendum

A number of compounds have been reported since this review was submitted. These compounds are listed in Table II.

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VI. References

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