Syntheses, X-ray Structures, Complexation, and Thermal Stability Studies of Bis(5-carbomethoxy-1,3-phenylene)-(3*x* + 2)-crown-*x* Compounds

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Bis(5-carbomethoxy-1,3-phenylene)-(3x + 2)-crown-x compounds [$x = 6$ (**3a**), $x = 8$ (**3b**), and $x = 10$ (**3c**)] have been synthesized in one step by reaction of methyl 3,5-dihydroxybenzoate (**1**) and the corresponding oligo(ethylene glycol) dichlorides (**2a, 2b**, and **2c**) in the presence of NaH or KH in *N,N*-dimethylformamide (DMF). The smaller monoester, 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4c**), was also isolated along with **3c**. The X-ray crystal structures of these macrocycles (**3b, 3c**, and **4c**) have been determined. Macrocycle **3b** crystallizes in the triclinic space group *P*-1 with unit cell parameters of $a = 8.632(2)$ Å, $b = 10.006(2)$ Å, $c = 11.527(2)$ Å, $\alpha = 78.30(3)°$, $\beta = 71.98(3)°$, $\gamma = 65.00(3)°$. Macrocycle **3c** crystallizes in the triclinic space group *P*-1 with unit cell parameters of $a = 8.911(2)$ Å, $b = 9.497(2)$ Å, $c = 10.140(2)$ Å, $\alpha = 93.66(2)°$, $\beta = 94.03(1)°$, $\gamma = 105.95(1)°$. Macrocycle **4c** crystallizes in the triclinic space group with unit cell parameters of $a = 8.748(2)$ Å, $b = 9.163(2)$ Å, $c = 12.025(3)$ Å, $\alpha = 74.90(2)°$, $\beta = 86.81(2)°$, $\gamma = 61.73(2)°$. The thermal stabilities of these macrocycles and the complexation abilities of the bis(*m*-phenylene)-32-crown-10 derivatives with methyl viologen bis(hexafluorophosphate) (**8**) have been examined by ^{1}H NMR spectroscopy.

Introduction

As Laidler and Stoddart pointed out in their excellent review on the synthesis of crown ethers and analogs,[1] "the synthesis of medium- and large-sized ring compounds is usually a highly inefficient process. Success in crown ether syntheses depends strongly upon preorganized reactants being brought together under some external influence and the acyclic precursor having the "correct" stereochemical orientation in the final cyclization step. Historically, reactions to form macrocyclic compounds have often been performed[2] under high dilution conditions. This meant that all reactions including cyclizations had to be fast in order to maintain very low concentrations of reactants and so supress the formation of acyclic oligomers with respect to cyclic products".

Although optimized procedures for the synthesis of crown ethers in the range up to 18-membered rings[3] and 30–60-membered unsubstituted crown ethers[4] have been developed, we were interested in synthesizing significant quantities of functionalized semirigid medium- to large-sized (20–36-membered) ring compounds; the objective of the present study was to develop a simple method for the preparation of difunctional bis(*m*-phenylene)-(3x + 2)-crown-x molecules, suitable for incorporation into polymeric macrocycles.[5]

The standard strategies for the synthesis of functionalized macrocyclic polyethers are the stepwise construction of intermediates and finally cyclization of these intermediates. Although the yield is usually higher in this approach than the single step method, it is costly and very time consuming.

The general approach we have devised is to use a functionalized resorcinol and choose a proper synthetic procedure to perserve the functionality during a one-step cyclization. Thus, the ring size can be tailored specifically for various applications, such as to complex with different cations or other acceptor species. Here we report the one-step syntheses of bis(5-carbomethoxy-1,3-phenylene)-20-crown-6 (**3a**), bis(5-carbomethoxy-1,3-phenylene)-26-crown-8 (**3b**), and bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**3c**). The complexation of bis(*m*-phenylene)-32-crown-10 derivatives such as bis(5-methyl-1,3-phenylene)-32-crown-10 (**6**),[6] bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**3c**), and bis(5-carboxy-1,3-phenylene)-32-crown-10 (**7**)[5] with paraquat bis(hexafluorophsphate) (**8**) has been studied in acetone solution and compared with the reported[7] results of the bis(*m*-phenylene)-32-crown-10 (**5**)–paraquat $[PF_6]_2$ (**8**) complex.

Results and Discussion

Synthesis. The major problem we encountered in synthesizing the ester-functionalized macrocycles in a stepwise construction as reported for other macrocycles[8] is transesterification, which occurs whenever an alkoxide forms during the reaction pathway. This side reaction prevents cyclic formation and forms mostly polymeric products.[5] Other workers, including Cram et al.[9] and

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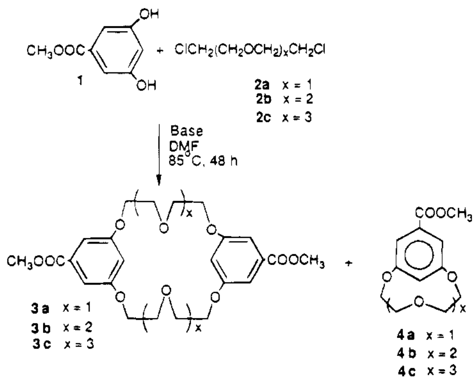
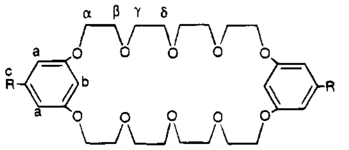
Table 1. Macrocycle Yields in DMF

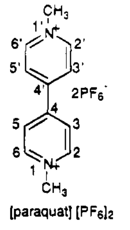
macrocycle	base	% yield
3a	NaH	7
	KH	14.5
3b	NaH	6
3c	NaH	9
4c	NaH	15

Reinhoudt et al.,[10] have applied one-step approaches to synthesize different large ring crown compounds. Therefore, for the synthesis of macrocycles in this study we modified a one-step method, which is simple, fast, and inexpensive and has been used for the synthesis of bis(*p*-phenylene)-34-crown-10,[9] bis(*m*-phenylene)-32-crown-10,[11] and other large ring macrocycles.[12] This approach consists of a single step reaction of methyl 3,5-dihydroxybenzoate (**1**) with the corresponding oligo(ethylene glycol) dichlorides (**2**) and a base in DMF to produce the above-mentioned macrocycles (**3**). The purification of these macrocycles from polymeric and oligomeric byproducts has been achieved by using column chromatography (silica gel with diethyl ether as eluent). The only product that elutes from the column in this condition is the macrocycle, and crystals suitable for X-ray crystallography were then grown from ethyl acetate solution.





5 R = H
6 R = CH3
7 R = COOH



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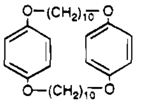

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Comparison of the yields of different macrocycles with different bases is shown in Table 1. The use of sodium hydride as a base produced bis(5-carbomethoxy-1,3-phenylene)-20-crown-6 (**3a**) in lower yield than potassium hydride. The reason for the higher yield in the case of potassium hydride probably is the more efficient template effect[13] of the K^+ ion in comparison to the Na^+ ion. In other words a 20-membered ring dibenzo crown ether has a cavity size closer to the ionic radius of K^+ than to Na^+. Bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**3c**), which is large enough to accommodate two Na^+ cations,[14,15] was obtained in 9% yield with NaH.[5]

The synthesis of **3c** by stepwise construction has also been mentioned by Gunter et al.[16] (no data on yield or characterization). In the process of synthesis of **3c**, a monofunctional 16-membered macrocyclic compound, 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4c**), a result of the 1:1 cyclization reaction, was also isolated in 15% yield. The reason for the higher yield of the smaller crown in comparison to the large one is the fact that the cavity size of the smaller macrocycle better matches the ionic radius of the cation (Na^+).[13] This observation is consistent with our previous results on synthesis of the methyl-functionalized crown compounds, e.g., **6**.[6] The smaller monofunctional compounds **4a** and **4b** were not isolated.

Molecular Structure, Conformation. Single crystal X-ray diffraction was utilized to determine the molecular conformations of the crown ethers in the solid state. Bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**3c**), the largest of these macrocycles, exists in a conformation (Figure 1) similar to the unsubstituted macrocycle **5** as reported by Stoddart et al.[7] That is, the aromatic rings are essentially parallel to each other, but overlap only partially in projection. The carbomethoxy substituents are arranged in an antiparallel or pseudopara orientation in **3c**, as are the 5-protons in **5**. However, in **3c** the cavity is very small, only 0.75 Å from one side of the cavity to the other, taking van der Waals radii into account, in contrast to the 4.9 × 7.8 Å cavity reported for **5**.[7] This difference may arise from the influence of the carbomethoxy moieties on the crystal packing and not necessarily due to large differences in conformational properties of the isolated molecules.

Crystal structural analysis (Figure 2) of the 26-membered macrocyclic diester **3b** reveals the striking effects of ring size on conformation. **3b** exists in the crystals as a puckered structure with sigmoidal edge-on shape reminiscent of 30-crown-10 tetrahydrate[17] in which the aromatic rings are parallel, but do not overlap spatially. The substituents are again arranged in an antiparallel or pseudopara orientation. There is a significant cavity (2.6 × 7.0 Å taking full van der Waals radii into account) in this smaller ring; this is reminiscent of Stoddart's results with similar systems which demonstrated that larger rings because of increased conformational freedom may yield smaller cavities.[18] There is residual electron density that could not be modeled satisfactorily using various solvents and suggests the inclusion of a highly disordered solvent molecule in the lattice. However, this electron density is *not* within the cavity of the macrocycle and cannot account for the size of the cavity.

Interestingly, molecular mechanics calculations[19] predict conformations in which the aromatic rings are essentially in the same plane with no overlap. These calculations do not take into account π-stacking forces which are apparently responsible for the face to face

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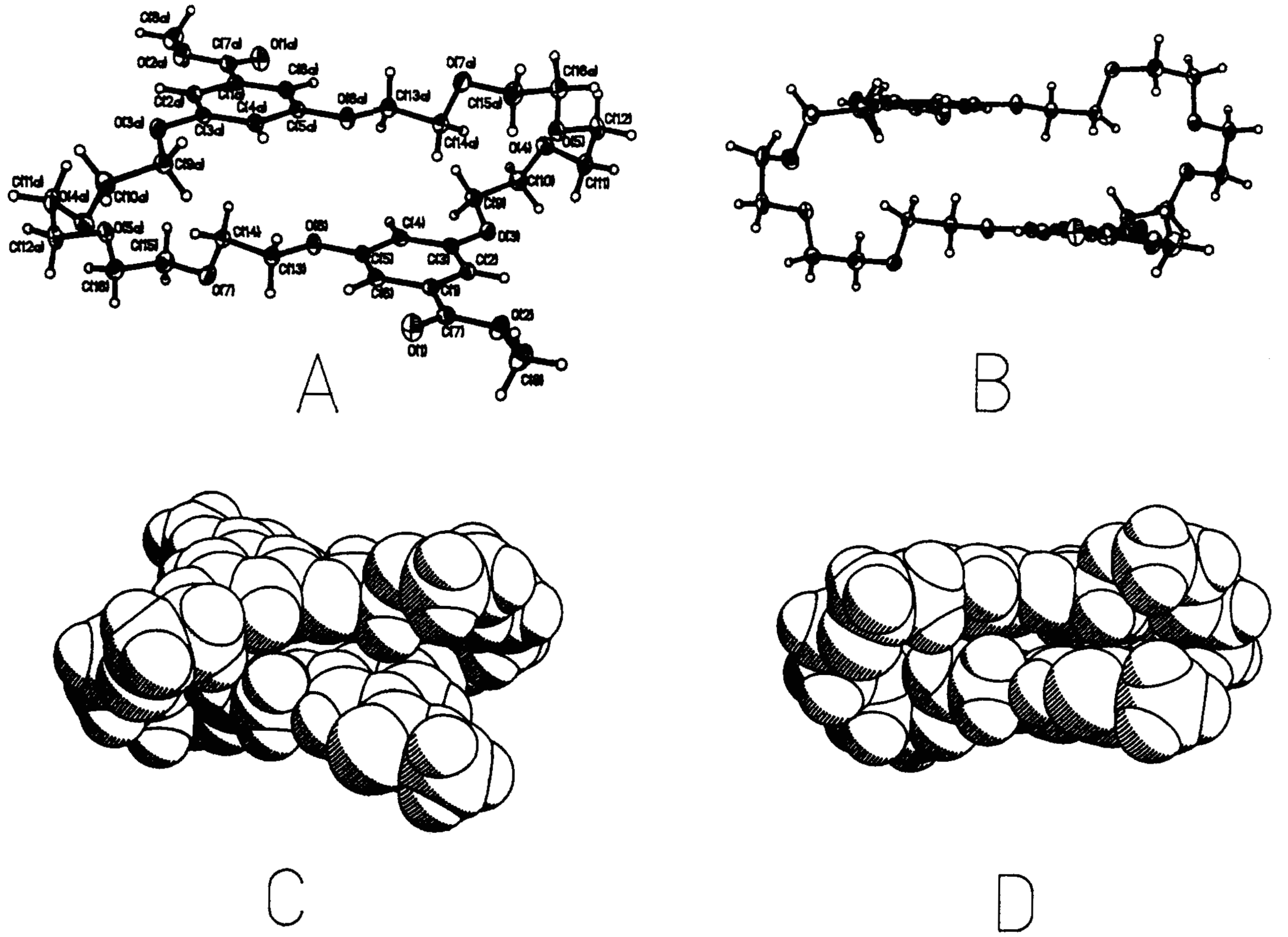

Figure 1. Molecular structure of bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**3c**) as represented by ball and stick (A, B) and full van der Waals space-filling (C, D) structures.

Table 2. ^{1}H NMR Shift Data [δ Values ($\Delta\delta$ Values)][a] in CD_3COCD_3 at 30 °C

compd or complex	2-,6-H	3-,5-H	CH_3	H_a	H_b	α-OCH_2	β-OCH_2	γ/δ-OCH_2	H_c
8	9.35	8.81	4.72						
5[b]				6.48	6.48	4.06	3.78	3.61	7.11
[**5**, **8**][b]	9.12	8.32	4.64	6.11	6.11	3.72	3.72	3.72	6.92
	(−0.23)	(−0.49)	(−0.08)	(−0.37)	(−0.37)	(−0.34)	(−0.06)	(+0.11)	(−0.19)
6				6.32	6.31	4.03	3.76	3.62	2.21
[**6**, **8**][c]	9.20	8.39	4.67	5.89	5.88	3.75	3.68	3.77	2.11
	(−0.15)	(−0.42)	(−0.05)	(−0.43)	(−0.43)	(−0.28)	(−0.08)	(+0.15)	(−0.10)
7				7.14	6.74	4.13	3.81	3.62	7.34
[**7**, **8**][d]	9.26	8.55	4.70	6.83	6.39	3.90	3.76	3.72	
	(−0.09)	(−0.26)	(−0.02)	(−0.31)	(−0.35)	(−0.23)	(−0.05)	(+0.10)	
3c				7.08	6.71	4.11	3.80	3.62	3.83
[**3c**, **8**][e]	9.23	8.50	4.69	6.80	6.37	3.89	3.76	3.73	3.82
	(−0.11)	(−0.31)	(−0.03)	(−0.28)	(−0.34)	(−0.22)	(−0.04)	(+0.11)	(−0.01)
9				6.79[f]		3.91[g]	1.68[g]	1.43[g]	1.31[g]
[**9**, **8**][h]	9.34	8.81	4.72	6.79[f]		3.91[g]	1.68[g]	1.42[g]	1.30[g]
	(−0.01)	(0.0)	(0.0)	(0.0)		(0.0)	(0.0)	(0.0)	(−0.01)

[a] The $\Delta\delta$ values indicated in parentheses under the respective δ values relate to the chemical shift changes experienced in equimolar solutions. The chemical shift assignments for **8** are based on ref 7. The chemical shifts assigned to the H_b protons of **3a**, **6**, and **7** are based on the multiplicity (triplet). Likewise, H_a signals of **3c**, **6**, and **7** are assigned on the basis of multiplicity (doublet) and coupling to H_a. The CH_3 signals of **3c** and **6** were assigned on the basis of chemical shift and singlet character. The α, β, γ, and δ protons of **3c**, **6**, and **7** were based on assignments for **5** given in ref 7. Assignments for **9** were made on the basis of chemical shifts and multiplicity [singlet for aromatics, triplet for OCH_2 and multiplets for $OC(CH_2)_4$]. [b] Data from ref 7, concentrations unknown. [c] 17.7 mM. [d] 4.0 mM. [e] 16.0 mM. [f] Ar-H. [g] α,β, γ/δ of $O(CH_2)_5$. [h] 2.1 mM.

arrangement of the aromatic rings in the crystals of **5** and its diester **3c** (Figure 1).

The structure of 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4c**) as shown in Figure 3 reflects the conformational limitations of the smaller ring coupled to the resorcinol nucleus. The ring is actually disordered. The disorder could be modeled satisfactorily with two different atomic positions for atom O3 (O3A) with the system refining to a 75% occupancy at position O3 and a 25% occupancy at position O3A. The result is a bent, almost v-shaped structure, the crown ether ring being nearly planar but at ca. 120° relative to the aromatic ring. The cavity is small: 1.2 Å from H_2 to O(3) and 3 Å along the other elliptical axis from O(2) to C(7).

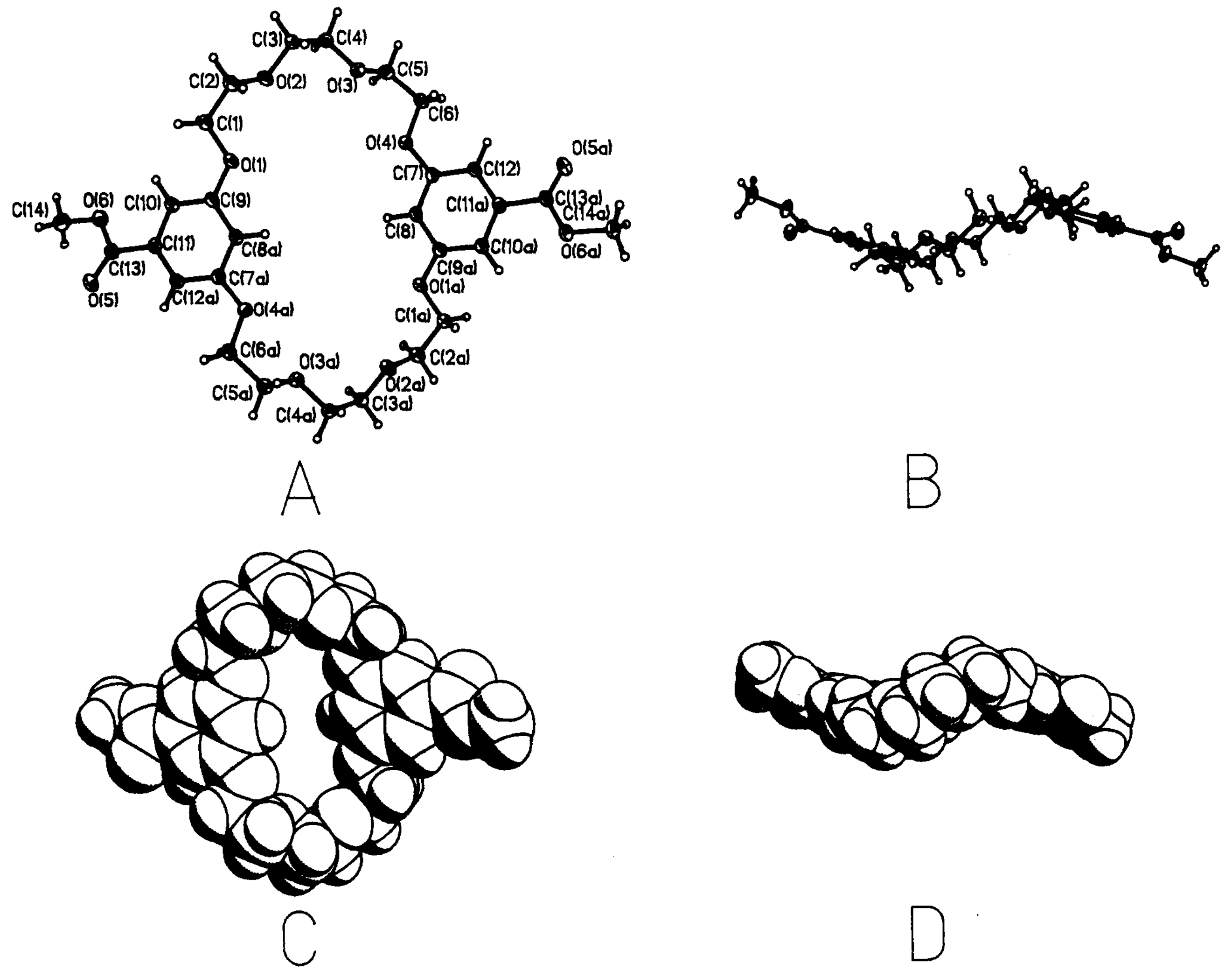

Figure 2. Molecular structure of bis(5-carbomethoxy-1,3-phenylene)-26-crown-8 (**3b**) as represented by ball and stick (A, B) and full van der Waals space-filling (C, D) structures.

Solution Complexation with Paraquat $[PF_6]_2$. Stoddart and co-workers[7] studied the complexation of bis(*m*-phenylene)-32-crown-10 (BMP32C10) (**5**) with paraquat (**8**) or diquat bis(hexafluorophosphate)s. They found that BMP32C10 forms a 1:1 complex (K_a = 760 M^{-1}) with paraquat $[PF_6]_2$ (**8**) in acetone.

When a colorless acetone solution of a BMP32C10 derivative is mixed with a colorless solution of paraquat $[PF_6]_2$ on an equimolar basis, a yellow-orange solution is formed immediately. ^1H NMR has been used to investigate the effects of substituents on the complexation ability of these macrocycles with paraquat bis(hexafluorophosphate). Complex formation is a dynamic equilibrium. Consequently, all of the NMR signals are time averaged at room temperature. The observed chemical shifts are a function of the chemical shifts of the particular proton in question in the uncomplexed (δ_u) and complexed (δ_c) states and the equilibrium constant for association (K_a). Under the simplifying assumption that the chemical shift changes ($\Delta\delta$) upon complexation, $\delta_c - \delta_u$, are not a function of structure, we proceed to use the magnitude of the observed chemical shift changes between the isolated host (the macrocycles) and guest (**8**) vs the 1:1 solutions as a semiquantitative measure of K_a.

$$H + G \overset{K_a}{\rightleftharpoons} H{:}G$$

Comparison (Table 2) of the ^1H NMR spectra of complexes of BMP32C10 derivatives with [paraquat] $[PF_6]_2$ (**8**) reveals upfield shifts (shielding) on complexation for most protons; in particular, the pyridinium ring proton (3-, 5-H) and H_a, H_b, and α-OCH_2 of the BMP32C10 derivatives experience the largest changes. These observations as mentioned by Stoddart and co-workers[7] can be interpreted "in terms of 1:1 complexes in which the bipyridinium unit in the substrates becomes sandwiched between the two resorcinol rings of BMP32C10 derivatives, such that the anisotropic diamagnetic susceptibility of one aromatic ring reduces the local magnetic field experienced by ^1H nuclei attached to neighboring stacked aromatic rings. A combination of [C- -H- - - -O] hydrogen bonding, [N^+- - - - -O] electrostatic interactions, and charge transfer between the π-electron-rich resorcinol rings π-electron-deficient bipyridinium dication, clearly stabilize the 1:1 complex. The charge transfer interactions account for the yellowish-orange color of the complex."

With regard to the effects of substituents, electron-withdrawing groups such as carbomethoxy and carboxy decrease the π-donor capabilities, in comparison to their unsubstituted analog. This can be seen from the smaller upfield chemical shift changes on protons of the bipyridinium salt and the α-OCH_2 of the crowns (Table 2). Although the bipyridinium protons 3,5-H of the complex with **3c** undergo larger negative shifts than the complex

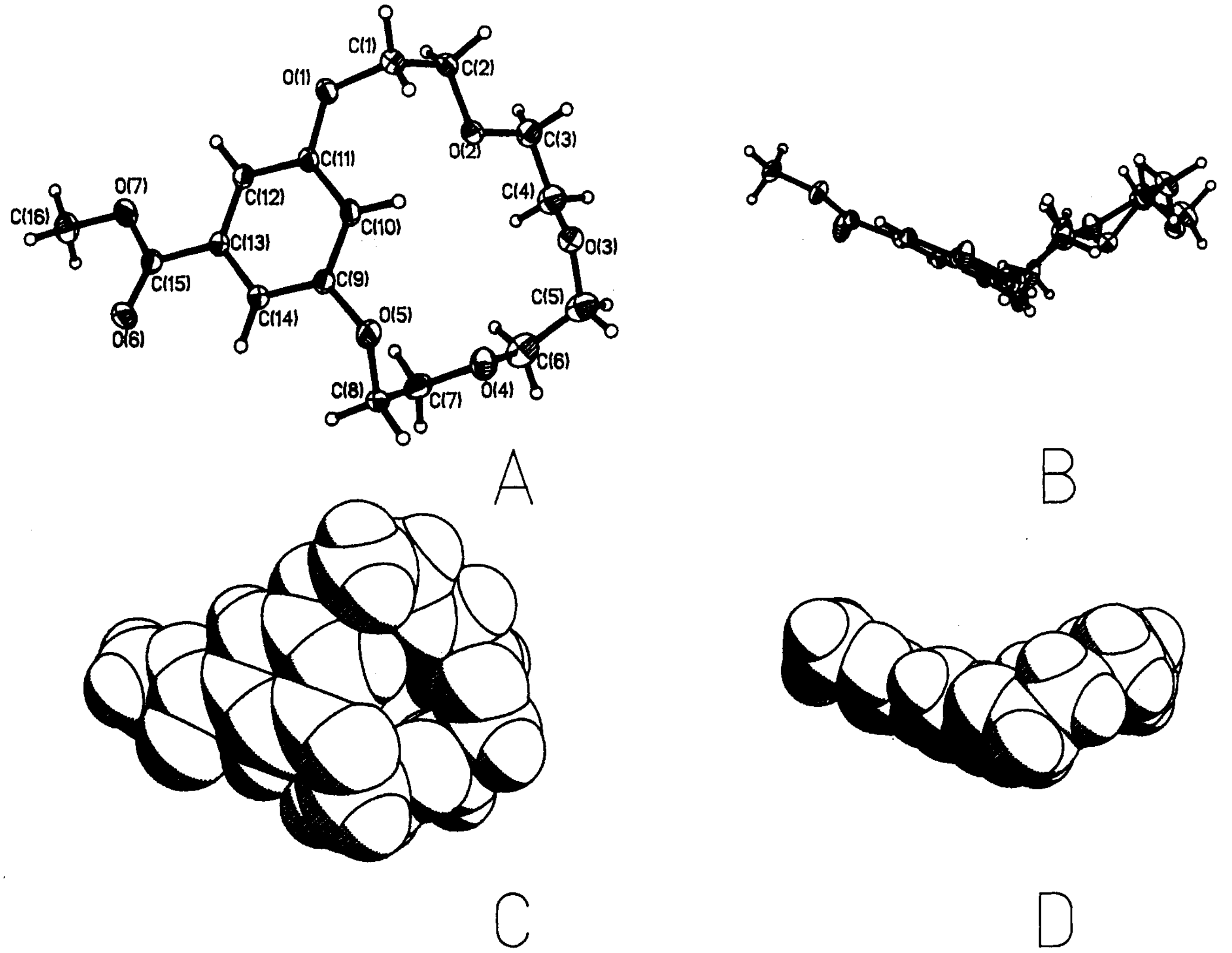

Figure 3. Molecular structure of 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4c**) as represented by ball and stick (A, B) and full van der Waals space-filling (C, D) structures.

Table 3. Thermogravimetric Analyses (TGA). Temperature (°C) of 5% Weight Loss of Crown Compounds in Air and Nitrogen Atmospheres at a Scan Rate of 10 °C/min

crown ether	air	nitrogen
18-crown-6	122	131
30-crown-10	213	265
dibenzo-18-crown-6	255	255
3a	293	293
3b	317	326
3c	292	293
4c	227	233
5	318	339
6	298	321
7	352	394
9	259	216

with **7**, the changes in the chemical shifts of the rest of the protons do not show significant differences between the carboxy (**7**) or carbomethoxy (**3c**) group substitutents (Table 2). The presence of the electron-donating CH_3 groups in **6** on the other hand is expected to enhance the ability of the resorcinol moiety to act as a π-donor toward the π-electron deficient bipyridinium dication. Comparison of the chemical shift changes of the protons of the complexes of paraquat with BMP32C10 (**5**), dimethyl analog **6**, and diester **3c**, respectively, reveals the fact that indeed there are larger changes in the chemical shifts of the crown protons H_a, H_b, β-OCH_2, and γ/δ OCH_2 as a result of the electron-donating CH_3 substituents of **6** (Table 2), but the shifts of the paraquat protons 2,6-H, 3,5-H, and CH_3 and the α-OCH_2 of **6** are greater than those of the diester **3c**, but less than those of unsubstituted **5**. Perhaps steric factors of the substituents influence the stability of the complex.

We also synthesized the mostly hydrocarbon macrocycle bis(*p*-phenylene)-32-crown-4 (**9**) (BPP32C4)[12] with the same number of atoms in the ring as the BMP32C10 derivatives **3**, **5–7**. The ^1H NMR spectrum of an equimolar solution of this macrocycle with [paraquat] $[PF_6]_2$ in acetone shows no change in the chemical shifts of the protons of the bipyridinium dication or the macrocycle, and the color of the solution was barely yellow. This result indicates the fact that the presence of ethylenoxy linkages is a necessary factor in stabilizing the donor–acceptor complexes derived from the crown ethers through hydrogen bonding between the ethylenoxy oxygen atons and the 2- and 6-protons of the pyridinium rings, as suggested by Stoddart and co-workers.[7]

Thermal Stabilities. In order to ascertain the thermal stability of the macrocycles, they have been subjected to dynamic thermogravimetric analyses in air and nitrogen atmospheres, and the results are shown in Table 3. As expected, the presence of phenylene moieties increases the apparent thermal stability of crown compounds significantly relative to unsubstituted crown ethers such as 18-crown-6 and 30-crown-10. For example, dibenzo-18-crown-6 and BMP32C10 (**5**) are 100 °C more stable

Table 4. Summary of Experimental Data for X-ray Diffraction Studies

compd	**3b**	**3c**	**4c**
crystal data			
emp formula	$C_{28}H_{36}O_{12}$	$C_{32}H_{44}O_{14}$	$C_{16}H_{22}O_7$
color; habit	clear irregular prism	clear prism	clear rectangular prism
cryst size (mm)	0.4 × 0.4 × 0.6	0.4 × 0.4 × 0.6	0.8 × 0.8 × 0.4
cryst syst	triclinic	triclinic	triclinic
space grp	*P*-1	*P*-1	*P*-1
unit cell dimens	a = 8.632(2) Å b = 10.006(2) Å c = 11.527(2) Å α = 78.30(3)° β = 71.98(3)° γ = 65.00(3)°	a = 8.9113(15) Å b = 9.497(2) Å c = 10.140(2) Å α = 93.658(14)° β = 94.030(14)° γ = 105.946(14)°	a = 8.748(2) Å b = 9.163(2) Å c = 12.025(3) Å α = 74.90(2)° β = 86.81(2)° γ = 61.73(2)°
volume	855.1(3) Å^3	820.0(2) Å^3	817.1(3) Å^3
Z	1	1	2
formula wt	609.6	652.7	326.3
density (calcd)	1.184 g/cm^3	1.322 g/cm^3	1.326 mg/m^3
absorption coeff	0.093 mm^{-1}	0.097 mm^{-1}	0.097 mm^{-1}
F(000)	325	348	348
data collection			
2θ range	3.5–50.0°	3.5–55.0°	3.5–55.0°
scan type	2θ-θ	2θ-θ	Wyckoff
scan speed (in ω)	3.50–15.00°/min	3.00–15.00°/min	3.00–19.53°/min
standard reflns	3 every 200 reflns	3 every 200 reflns	3 every 200 reflns
index ranges	$0 \le h \le 11$ $-11 \le k \le 12$ $-14 \le l \le 14$	$0 \le h \le 11$ $-12 \le k \le 11$ $-13 \le l \le 13$	$0 \le h \le 11$ $-10 \le k \le 11$ $-15 \le l \le 15$
reflns collected	4189	4043	3987
independent reflns	3926 (R_{int} = 1.29%)	3784 (R_{int} = 1.31%)	3739 (R_{int} = 0.80%)
obsd reflns	2657 ($F > 3.0\sigma(F)$)	3261 ($F > 3.0\sigma(F)$)	2821 ($F > 4.0\sigma(F)$)
solution and refinement			
solution	direct methods	direct methods	direct methods
refinement method	full-matrix least squares	full-matrix least squares	full-matrix least squares
quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
extinction correction, χ, where ($F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$)	0.0089(10)	0.0095(16)	χ = 0.0066(7)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$	$w^{-1} = \sigma^2(F) + 0.0005F^2$	$w^{-1} = \sigma^2(F) + 0.0001F^2$
final R indices (obsd data)	R = 8.44%, wR = 8.24%	R = 4.89%, wR = 7.16%	R = 5.22%, wR = 6.16%
goodness-of-fit	3.87	2.27	3.48
largest and mean Δ/σ	0.423, 0.024	0.183, 0.022	0.001, 0.000
data-to-param ratio	12.9:1	15.6:1	12.9:1
largest diff peak	0.68 eÅ^{-3}	0.26 eÅ^{-3}	0.28 eÅ^{-3}
largest diff hole	−0.42 eÅ^{-3}	−0.19 eÅ^{-3}	−0.32 eÅ^{-3}

than their fully aliphatic analogs 18-crown-6[4] and 30-crown-10.[4] The dibenzocrowns with ethylenoxy linkages are also more stable than the fully hydrocarbon analogs with the same ring sizes; i.e., BMP32C10 (**5**) is more stable than BPP32C4 (**9**). In terms of the effects of the functionality, the crown containing carboxy groups (**7**) is more stable than those containing carbomethoxy (**3a**, **3b**, **3c**) or methyl groups (**6**) (Table 3). Thermogravimetric analysis–mass spectrometry (TGA–MS) was used to examine the stabilities more carefully, and the results were published elsewhere.[4]

Conclusions

A convenient procedure for the synthesis of bis(5-carbomethoxy-1,3-phenylene)-(3*x* + 2)-crown-*x* molecules has been developed. This methodology is general, and the size of the ring of the macrocycle can be tailored for various applications. Work is underway in our laboratory for investigating the factors influencing yields in syntheses of these macrocycles, such as the nature of leaving groups, the solvent, and the temperature of the reaction.

The solution complexation of BMP32C10 derivatives with paraquat $[PF_6]_2$ based on 1:1 molar ratio in acetone has been studied. The substituents on the resorcinol rings affect the overall complexation abilities of the macrocycles; electron-withdrawing groups such as carbomethoxy and carboxy decrease the π-donor capabilities, and electron-donating CH_3 groups enhance the ability of resorcinol moieties as a π-donor toward the π-electron deficient bipyridinium dication.

We also found that there was not a significant interaction between the mostly hydrocarbon macrocycle BPP32C4 (**9**) and paraquat $[PF_6]_2$. This result indicates that electrostatic stabilization of the positively charged bipyridinium moiety by the lone pair electrons of the oxygen atoms in the ethyleneoxy linkages of the macrocycle and hydrogen binding to the 2- or 6-protons of the pyridinium nuclei are requirements for the stability of the complexes.

Experimental Section

Materials. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. Di(ethylene glycol) dichloride (**2a**) and tri(ethylene glycol) dichloride (**2a**) were distilled over calcium hydride prior to use; tetra(ethylene glycol) (**2c**) dichloride was synthesized according to a literature procedure.[20] Reaction of 4,4′-dipyridyl with iodomethane (excess) in acetonitrile formed methyl viologen diiodide, which was further reacted with ammonium hexafluorophosphate in water to form methyl viologen bis(hexafluorophosphate) (**8**) in quantitative yield; the spectroscopic data were as reported.[7]

Measurements. Melting points were taken in capillary tubes with a Haake–Buchler melting point apparatus and have been corrected. ^{1}H NMR spectra were obtained at ambient temperature on a Varian Unity 400 MHz spectrom-

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

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Compounds 3b, 3c, and 4c

compd	*x*	*y*	*z*	*U*(eq)[a]
3b				
O(1)	14 052(3)	8993(3)	4388(2)	60(1)
C(1)	13 733(5)	10 314(4)	3583(3)	52(2)
C(2)	15 318(5)	10 046(4)	2520(3)	54(2)
O(2)	15 347(3)	9077(3)	1769(2)	55(1)
C(3)	16 825(5)	8770(4)	740(3)	54(2)
C(4)	16 785(5)	7712(4)	33(3)	54(2)
O(3)	17 465(3)	6251(3)	596(2)	52(1)
C(5)	17 301(6)	5209(4)	30(3)	60(2)
C(6)	18 150(6)	3690(4)	609(3)	59(2)
O(4)	17 084(3)	3560(3)	1812(2)	62(1)
C(7)	17 686(5)	2273(4)	2517(3)	50(2)
C(8)	16 646(5)	2214(4)	3708(3)	51(2)
C(9)	12 872(5)	9030(4)	5512(3)	50(2)
C(10)	11 312(5)	10 243(4)	5874(3)	48(2)
C(11)	10 307(4)	10 180(4)	7072(3)	45(2)
C(12)	19 200(5)	1052(4)	2115(3)	49(2)
C(13)	8653(5)	11 476(4)	7540(4)	52(2)
O(5)	7978(4)	11 657(3)	8604(3)	72(1)
O(6)	8025(3)	12 382(3)	6638(3)	69(1)
C(14)	6369(6)	13 622(5)	6994(5)	82(2)
3c				
C(1)	7149(2)	−430(1)	3227(1)	38(1)
C(2)	8498(2)	685(1)	3124(1)	41(1)
C(3)	8923(2)	1048(1)	1865(1)	38(1)
C(4)	8034(2)	279(1)	740(1)	39(1)
C(5)	6687(2)	−852(1)	865(1)	37(1)
C(6)	6223(2)	−1210(1)	2104(1)	40(1)
C(7)	6597(2)	−842(2)	4543(1)	45(1)
C(8)	7152(2)	−466(2)	6853(2)	70(1)
C(9)	10 545(2)	2809(2)	600(2)	45(1)
C(10)	11 855(2)	4204(2)	855(2)	56(1)
C(11)	11 644(2)	5526(2)	2895(2)	63(1)
C(12)	10 527(2)	6263(2)	3446(2)	70(1)
C(13)	4445(2)	−2637(2)	−223(2)	45(1)
C(14)	3684(2)	−3173(2)	−1590(2)	46(1)
C(15)	3755(2)	−4797(2)	−3456(2)	64(1)
C(16)	2191(2)	−5916(2)	−3580(2)	65(1)
O(1)	5364(2)	−1718(1)	4677(1)	70(1)
O(2)	7618(1)	−145(1)	5548(1)	60(1)
O(3)	10 233(1)	2194(1)	1839(1)	48(1)
O(4)	11 377(2)	5358(1)	1487(1)	64(1)
O(5)	9010(1)	5251(1)	3328(1)	62(1)
O(6)	5901(1)	−1546(1)	−306(1)	48(1)
O(7)	4352(1)	−4249(1)	−2130(1)	57(1)
4c				
O(1)	5265(2)	1021(2)	6392(1)	66(1)
C(1)	5840(3)	1648(3)	5318(2)	55(1)
C(2)	7633(2)	1398(2)	5447(2)	52(1)
O(2)	7650(2)	2622(2)	5945(1)	57(1)
C(3)	9233(3)	2671(3)	5865(2)	63(1)
C(4)	9265(3)	3879(3)	6435(2)	76(1)
O(3)	8013(2)	5502(2)	6046(2)	55(1)
C(5)	7917(3)	6590(3)	6745(3)	84(1)
C(6)	7055(3)	6497(4)	7831(3)	87(2)
O(4)	5239(2)	7028(2)	7583(1)	70(1)
C(7)	4434(4)	6545(3)	8516(2)	72(1)
C(8)	2586(3)	7179(3)	8159(2)	74(1)
O(5)	2398(2)	6473(2)	7259(1)	60(1)
C(9)	2854(2)	4747(2)	7576(2)	46(1)
C(10)	3875(2)	3802(2)	6835(2)	48(1)
C(11)	4282(2)	2091(2)	7049(2)	47(1)
C(12)	3695(2)	1330(2)	8010(2)	46(1)
C(13)	2690(2)	2297(2)	8742(2)	44(1)
C(14)	2252(2)	4020(2)	8533(2)	47(1)
C(15)	1984(3)	1560(2)	9762(2)	49(1)
O(6)	911(2)	2400(2)	10321(2)	83(1)
O(7)	2647(2)	−132(2)	9995(1)	64(1)
C(16)	2095(3)	−950(3)	11007(2)	72(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

eter using deuterated acetone or chloroform solutions with CD_2HCOCD_3 (δ = 2.04 ppm) or TMS (δ = 0 ppm) as internal standards, respectively. Thermogravimetric analyses were carried out using a DuPont TGA 951 or a Perkin-Elmer TGA-7. Infrared spectra were recorded on a Nicolet MX-1 FTIR spectrometer. Mass spectra were measured with a VGA 7070E analytical mass spectrometer. Elemental analyses were performed by Atlantic Microlab of Norcross, GA.

X-ray crystallographic data were obtained using a Siemens R3m/v single crystal diffractometer, and the structures were solved and refined using the SHELXTL PLUS software package on a MicroVax II computer.[21] Table 4 summarizes the experimental details for the data collection, structure solution and refinement for compounds **3c**, **3b**, and **4c**. In all cases, data collection was carried out at room temperature using Mo Kα radiation with a graphite monochromator. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added in at calculated positions and allowed to ride on the carbon atom to which they were attached. Table 5 lists the positions for the non-hydrogen atoms in **3b**, **3c**, and **4c**. Additional information such as bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions has been deposited with the Cambridge Crystallographic Data Centre.[21]

General Procedure. The oligo(ethylene glycol) dichloride (**2**, 57 mmol) in DMF (250 mL) was added in one portion to a DMF solution (225 mL) containing methyl 3,5-dihydroxybenzoate (**1**, 9.58 g, 57 mmol) and sodium hydride or potassium hydride (115 mmol). The mixture was stirred vigorously at 85 °C for 24 h under a blanket of nitrogen, cooled, filtered, and evaporated to give a brown viscous oily residue. This was dissolved in dichloromethane, filtered, and then chromatographed on silica gel (7 g per g crude product) with diethyl ether as eluent to produce the corresponding macrocyles **3**.

Bis(5-carbomethoxy-1,3-phenylene)-20-crown-6 (3a) was obtained as a crystalline solid, mp 179−181 °C. IR (KBr pellet) *ν*: 1723 (C═O), 1600 (C═C) and 1142 (COC) cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ: 7.14 (4H, d, *J* = 2.4 Hz), 6.72 (2H, t, *J* = 2.4 Hz), 4.16 (8H, t, *J* = 4.4 Hz), 3.90 (8H, t, *J* = 4.4 Hz) and 3.87 (6H, s). (EI) *m/z*: 476 (M^+) and 445 ($M^+ - CH_3O$). Anal. Calcd for $C_{24}H_{28}O_{10}$ (MW 476.48): C, 60.49; H, 5.92. Found: C, 60.39; H, 5.88.

Bis(5-carbomethoxy-1,3-phenylene)-26-crown-8 (3b) was obtained as a crystalline solid, mp 131.2−133.2 °C. IR (KBr pellet) *ν*: 1723 (C═O), 1607 (C═C) and 1129 (COC) cm^{-1}. ^1H NMR ($CDCl_3$/TMS) δ: 7.15 (4H, d, *J* = 2.0 Hz), 6.67 (2H, t, *J* = 2.0 Hz), 4.12 (8H, t, *J* = 4.4 Hz), 3.87 (6H, s), 3.85 (8H, t, *J* = 4.4 Hz) and 3.73 (8H, s). (EI) *m/z*: 564 (M^+) and 533 ($M^+ - CH_3O$). Anal. Calcd for $C_{28}H_{36}O_{12}$ (MW 564.58): C, 59.56; H, 6.43. Found: C, 59.38; H, 6.49.

Bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (3c) and 5-Carbomethoxy-1,3-phenylene-16-crown-5 (4c). The characterization data for these two crowns have been reported elsewhere.[5]

Bis(5-carboxy-1,3-phenylene)-32-crown-10 (7). This compound was made by hydrolysis[5] of **3c**.

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[21] The authors have deposited complete atomic coordinates for **3b**, **3c**, and **4c** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.