CH_3O^+ (or CH_2OH^+) was a minor product of the reaction with propionaldehyde (~1%) and with propylene oxide (5%), and not detected for reaction with trimethylene oxide. A larger amount of CH_3O^+ (7%) was observed for reaction of CH_3^+ with acetone but a high degree of H, D isotopic scrambling was noted when CD_3^+ reactant ions were used. This contrasts to the present study in which these C_3H_6O isomers produce a negligible amount of deuterium atom labeling of the CH_3O^+ ionic product. Further studies with double labeling will be required before a definite mechanism can be proposed.

CH_3CO^+ was produced by a direct reaction of methyl cation with acetone (28% abundance), propylene oxide (8% abundance), and propionaldehyde (2% abundance), but not for trimethylene oxide or allyl alcohol. This reaction always occurs without deuterium atom incorporation in the ionic product, implying a direct reaction such as CH_3^- "pickup" from neutral species with a readily available methyl group. An alternative mechanism is dissociative charge transfer, provided one makes the not-unreasonable assumption that the reactant ion beam contains some number of excited CH_3^+ ions and that the excess energy is available to drive the reaction. Again no correlation of reaction exothermicity with products is noted in Table II.

The fact that $C_4H_7^+$ (representing H_2O elimination from the complex) is not observed as a product for any of the C_3H_6O isomers except acetone is best explained as increased competition of alternate channels such as reactions 8-10.

In conclusion, the present work has examined the product distributions for CH_3^+ (CD_3^+) reactions with four C_3H_6O isomers in relation to previous results for acetone. The reactions with allyl alcohol are dissimilar to the other isomers studied, as expected, and are consistent with the reactions of other alcohols with methyl cations.[7,9] Propionaldehyde, propylene oxide, and trimethylene oxide react with CH_3^+ (CD_3^+), with reactions 8-10 being the major pathway (50-60%). Reactions of the alcohol, aldehyde, and oxide isomers are simpler than that of acetone. The fact that a more complex set of reactions occurs with acetone, often involving extensive H, D randomization, is consistent with the complexity of reaction 7, compared to reactions 8-10. A methyl shift or formation of the alternative protonated cyclopropane structure intermediate, followed by C_2H_4 elimination, are undoubtedly slow, rate-determining processes which allow sufficient time for alternate reaction pathways to become important.

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Novel Aromatic Systems. 7.[1a] Benzo- and Dibenzocyclobutadiene Dications[1b]

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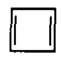
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 18, 1977*

Abstract: Benzo- and dibenzocyclobutadiene dications were prepared in SbF_5-SO_2ClF solution at low temperatures. The dications are characterized from their proton and carbon-13 NMR spectra as fully delocalized closed-shell six and ten π-electron aromatic systems, respectively.

Hückel's "$4n + 2$" rule[2] accurately predicts the enhanced stability of conjugated cyclic polyolefins (annulenes) containing ($4n + 2$) π electrons and thus their "aromaticity".[3] Cyclobutadiene (**1**) is known to be extremely reactive and elusive; its isolation was only achieved by using matrix isolation techniques at low temperatures.[4] Two-electron oxidation of **1** should result in the formation of a closed-shell 2π Huckeloid cyclobutadiene dication (**2**) with aromatic character.[5] Although to date the parent dication **2** has not been directly obtained, a number of substituted cyclobutadiene dications **3** are known.[6] In accord with the theoretical prediction,[5] cyclobutadiene dications are static, nonequilibrating 2π Hückeloid systems.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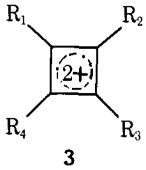

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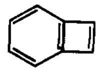
The monobenzo derivative of cyclobutadiene, benzocyclobutadiene (**4**), has also been a subject of extensive search,[3a,5,7]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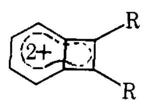

5, R = H
6, R = CH_3

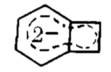

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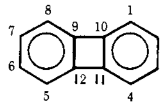
Table I. Proton and Carbon-13 NMR Parameters of Benzocyclobutadiene Dications[a]

Compd	Chemical shifts	1,2	3,6	4,5	7,8	Other
6	$\delta\ ^1$H		9.70	10.08		CH_3: 4.42
	$\delta\ ^{13}$C	186.9	136.2	169.7	178.8	CH_3: 27.9
		(s)	(d, 172.4)	(d, 182.8)	(s)	(q, 136.8)
20	$\delta\ ^1$H		8.08	7.86		
	$\delta\ ^{13}$C	194.2	136.8	123.8	173.2	
		(s)	(d-d, 163.8; 6.5)	d-d, 174.4; 4.6)	(s)	
21	$\delta\ ^1$H		8.82	8.82		OH^+; 11.4
	$\delta\ ^{13}$C	196.9	146.0	127.5	169.8	
		(s)	(d, 170.4)	(d, 181.4)	(s)	

[a] Proton and carbon-13 shifts are in parts per million from external tetramethylsilane (capillary). Multiplicities and coupling constants (J_{CH}) are given in parentheses; d = doublet; d-d = doublet of doublets; s = singlet; q = quartet.

but its isolation was only successful recently[8] despite the fact that several of its substituted derivatives have been known for years.[3a,9] Benzocyclobutadiene, in principle, should also give a stable 6π aromatic dication **5** by two-electron oxidation. The 10π benzocyclobutadiene dianion (**7**) has also been predicted to be aromatic.[3,7,10] On the other hand, biphenylene (**8**)[11] and



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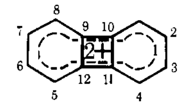

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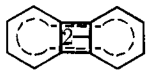

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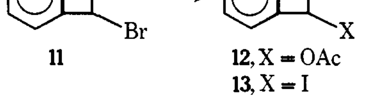
its derivatives are interesting 12 π-electron systems which can be regarded as weakly coupled benzenoid systems rather than derivatives of cyclobutadiene, as supported by x-ray structure analysis[12] and theoretical calculations.[3,13] The calculated highest occupied MO energy levels of biphenylene (**8**) have been shown to be bonding and not degenerate.[3,13] According to the Hückel rule, the removal of two electrons from or their addition to biphenylene (a 12 π system) should give stable dication **9** (a ten π system) or dianion **10** (a 14 π system), respectively. Although the biphenylene dianion (**10**) has been previously studied and characterized as the dibenzocyclobutadiene dianion possessing a fully delocalized 14 π-electron closed-shell system,[14] dication **9** has thus far not been directly observed.[15]

In continuation of our work on novel aromatic systems, which included inter alia the preparation and study of 2π cyclobutadiene dications,[6] we now report the preparation and NMR spectroscopic study of benzo- and dibenzocyclobutadiene dications, showing them to be fully delocalized closed-shell six and ten π-electron aromatic systems, respectively.

Results and Discussion

I. **Benzocyclobutadiene Dications.** Acetolysis of *trans*-1,2-dibromobenzocyclobutene (**11**), in the absence of water, gave the corresponding *trans*-1,2-diacetate **12**.[16] Ionization of 1,2-dibromo- (**11**), 1,2-diiodo- (**13**), and 1,2-dihydroxybenzocyclobutenes (**14**) in either SbF_5-SO_2ClF, FSO_3H-SbF_5-SO_2ClF, or HF-SbF_5-SO_2ClF solutions at −120 °C failed to give any evidence for the formation of the parent 1,2-benzocyclobutadiene dication **5**, and resulted only in the formation of unidentifiable polymeric products.[17] The 1,2-dimethylbenzocyclobutadiene dication **6**, however, could be prepared by careful addition of a suspension of *cis*- or *trans*-1,2-dimethylbenzocyclobutene-1,2-diol (**15** and **16**)[18] in SO_2ClF to a saturated solution of SbF_5 in SO_2ClF at dry ice-acetone bath temperature (ca. −78 °C).[17] The resulting deep red solution of **6** is stable up to −30 °C and decomposes at higher temperatures. Quenching of the solution with $NaOCH_3/CH_3OH$ at −60 °C gave as the only detectable product the corresponding dimethyl ether (~15% by ^{1}H NMR). The low yield is due to the formation of considerable amount of polymeric materials.



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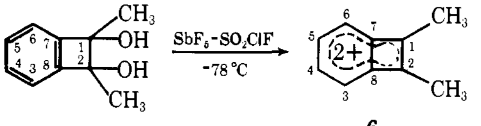
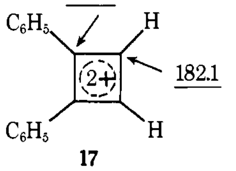
12, X = OAc
13, X = I
14, X = OH



15, cis-
16, trans-
6

The 60-MHz proton NMR spectrum of **6** displays the methyl absorption at δ 4.42 (six protons, singlet), and two broad deshielded two-proton aromatic resonances at δ 9.70 (overlapping with the hydronium ion peak) and at δ 10.08.[11] The natural abundance carbon-13 NMR spectrum obtained by Fourier transform technique consists of five carbon resonances at $\delta_{^{13}C}$ 27.9 (quartet, J_{CH} = 136.8 Hz), 136.2 (doublet, J_{CH} = 172.4 Hz), 169.8 (doublet, J_{CH} = 182.2 Hz), 178.8 (singlet), and 186.9 (singlet). Comparing the chemical shifts of the cyclobutadiene ring carbons, $\delta_{^{13}C}$ 178.8 (C(7) and C(8)) and 186.9 (C(1) and C(2)) obtained for the 1,2-dimethylbenzocyclobutadiene dication (**6**) to those for the 1,2-diphenyl- (**17**, $\delta_{^{13}C}$ 182.1 and 190.9), tetraphenyl- (**18**, $\delta_{^{13}C}$ 173.4) and tetramethylcyclobutadiene dications[1] (**19**, $\delta_{^{13}C}$ 209.7) confirms that ion **6** is indeed a fully delocalized aromatic system, as are the compared cyclobutadiene dications.[6c]



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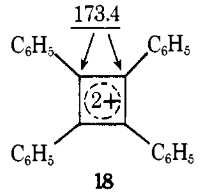

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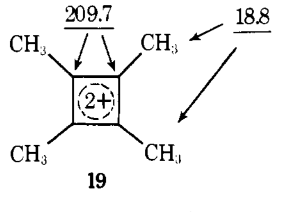

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Diprotonation of the benzocyclobutenedione (**20**)[18] with FSO_3H-SO_2ClF solution at −78 °C gives the dication **21** whose carbon-13 NMR spectrum displays four carbon resonances which are not much different from the corresponding shifts in the parent diketone **10**. The ^{1}H NMR spectrum of **21** in FSO_3H-SbF_5 (5:1)-SO_2ClF solution at −85 °C shows two singlet absorptions at δ 8.82 (four aromatic protons) and 11.4 (OH) in a ratio of 2:1. The proton decoupled ^{13}C NMR spec-

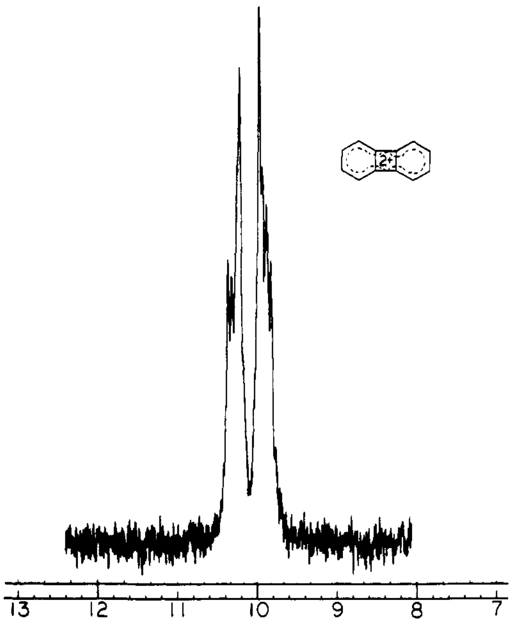
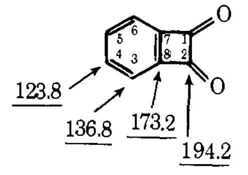


Figure 1. 60-MHz proton NMR spectrum of **8**.

trum of **21** obtained at −85 °C indicates that the ring carbons are hardly deshielded to any substantial extent as is found in the case of 1,2-dimethylbenzocyclobutadiene dication (**6**). The lack of deshielding and splitting of the aromatic protons in the diprotonated diketone **21** also indicates that little positive charge has been delocalized into the benzo ring. Both proton and carbon-13 NMR spectroscopic data thus indicate that observed diprotonated benzocyclobutenedione exists predominantly in the dioxonium ion form **22**, instead of the dihydroxycyclobutadiene dication form **21**.



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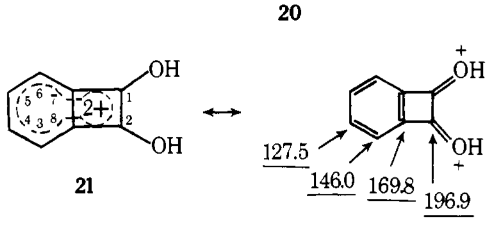

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II. Dibenzocyclobutadiene Dications. A suspension of biphenylene (**8**)[19] in SO_2ClF at dry ice-acetone bath temperature was slowly added to excess SbF_5-SO_2ClF at the same temperature. The initially dark green mixture was allowed to warm to −10 °C. The resulting dark brown solution displayed a complex AB coupling pattern, centered at δ 10.1, in its ^{1}H NMR spectrum taken at −10 °C (Figure 1). The same solution showed three carbon resonances at $\delta_{^{13}C}$ 135.5 (doublet, J_{CH} = 190.4 Hz), 169.6 (doublet, J_{CH} = 186.9 Hz), and 177.7 (singlet) in the ratio of 1:1:1 (Figure 2). Characteristic deshielding of ^{1}H and ^{13}C NMR spectra were also observed for the 1,4,5,8-tetramethyldibenzocyclobutadiene dication (**24**) prepared from its precursor **23** under the same condition (Figure 3). We have summarized the NMR parameters for biphenylenes and their dications in Table II.

We believe the species obtained from biphenylenes in SbF_5-SO_2ClF are dibenzocyclobutadiene dications, since (a) they give rise to very deshielded ^{1}H and ^{13}C chemical shifts for all positions, (b) they show symmetrical NMR spectra, and (c) quenching the solutions of the ions with cold pentane-$NaHCO_3$ mixture regenerates the original neutral biphenylenes. For the parent dication **9**, both H(1) and H(2) are deshielded by about 3-4 ppm, while all the ring carbons, C(1), C(2), and C(9) are deshielded, by about 18, 40, and 25 ppm, respectively. According to the ^{13}C NMR data summarized in Table II, a total deshielding of 342.4 ppm has been observed in going from the neutral biphenylene **8** ((4 × 117.1) + (4 × 128.4) + (4 × 151.7) = 1588.8 ppm) to the dicationic biphenylene ((4 × 135.5) + (4 × 169.6) + (4 × 177.7) = 1931.2 ppm). This corresponds to the formation of a dicationic species. A similar degree of deshielding (432.4 ppm) is also noticed in the tetramethyl dication **24**. The fact that both ring positions

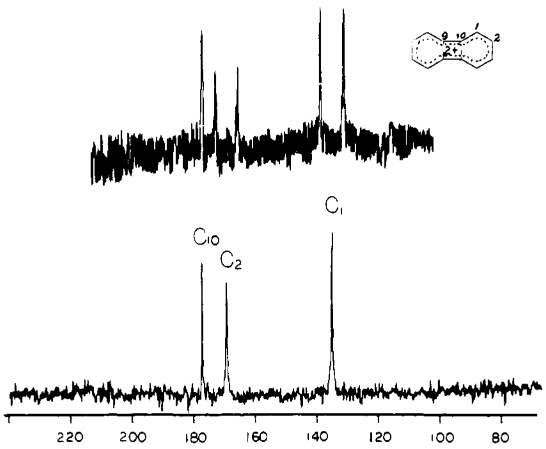

Figure 2. ^{13}C NMR spectra of **8**: bottom trace, proton decoupled; upper trace, proton coupled.

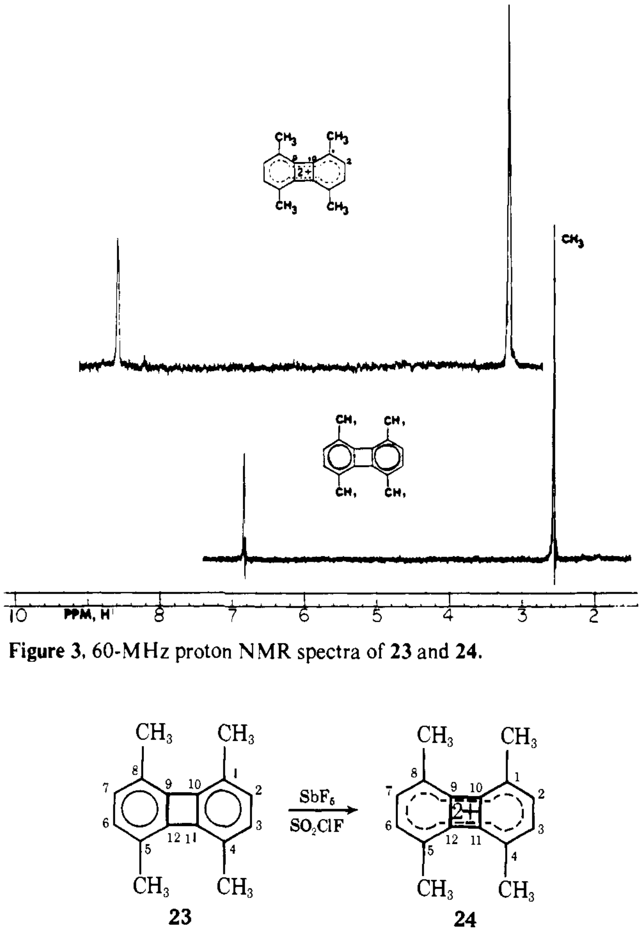

Figure 3. 60-MHz proton NMR spectra of **23** and **24**.

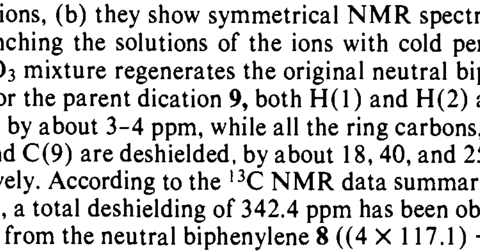

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Table II. ^1H and ^{13}C NMR Parameters of Dibenzocyclobutadiene Dications and Their Precursors[a,b]

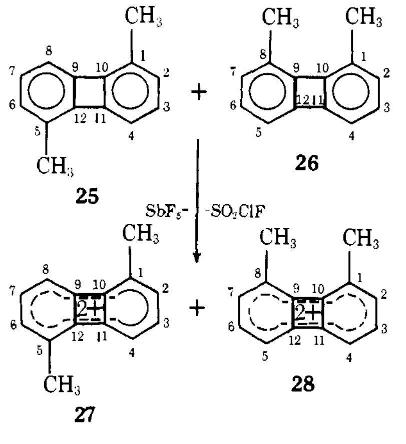
Compd		1,4,5,8	2,3,6,7	9,10,11,12	CH_3
8	$\delta\ ^1H$[a]	6.60	6.70		
	$\delta\ ^{13}C$	117.1	128.4	151.7	
9	$\delta\ ^1H$	9.92	10.30		
	$\delta\ ^{13}C$	135.5	169.6	177.7	
		(d, 190.4)	(d, 186.9)	(s)	
23	$\delta\ ^1H$		6.83		2.58
	$\delta\ ^{13}C$	125.3	131.6	149.8	18.9
24	$\delta\ ^1H$		8.63		3.20
	$\delta\ ^{13}C$	147.7	167.5	174.8	18.5
		(s)	(d, 187.8)	(s)	(q, 134.8)
25 and **26**	$\delta\ ^1H$		7.8–8.1		3.48; 3.58
27 and **28**	$\delta\ ^1H$		9.36–10.0		3.40; 3.50
	$\delta\ ^{13}C$	176.5 (s), 168.0 (d),	176.3 (s), 175.4 (s), 166.2 (d), 152.3 (s),	170.9 (d), 169.3 (d), 152.1 (s), 132.5 (d)	18.5 and 19.7

[a] ^1H NMR shifts are in parts per million from external Me_4Si (capillary) (60 MHz, $CDCl_3$). [b] Carbon-13 NMR shifts are in parts per million from external Me_4Si. Coupling constants. (J_{CH}) and multiplicity are given in parentheses: d = doublet, s = singlet, q = quartet.

(1 and 2) show deshielded chemical shifts indicates that considerable positive charge has been delocalized into the fused benzo rings. Furthermore, the carbon shifts for the central four-membered ring (C(9)) in **9** and **24** are deshielded by an extent very similar to those in the tetraphenylcyclobutadiene (**18**) and dimethylbenzocyclobutadiene (**6**) dications.[6] These comparisons clearly ascertain that in the present systems the two-electron oxidation of biphenylenes has indeed taken place in SbF_5-SO_2ClF solution,[20] giving rise to the corresponding dication **9** and **24**.

Another interesting feature of the carbon-13 NMR spectrum of **9** is that the methyl carbon is unexpectedly not very deshielded, even though the methyl protons are deshielded by about 0.7 ppm from the neutral species **5**. Going from **8** to **9** and from **23** to **24** we are changing the 12 π-electron neutral biphenylene systems to the ten π-electron dications. According to Hückel's $4n + 2$ rule, the latter should be aromatic. Originally, the high-field position of the protons (relative to benzene) in the ^1H NMR spectrum of biphenylene (**8**) and the low-field position of the carbon atoms of the four-membered ring in the ^{13}C NMR spectrum have both been attributed to a paramagnetic ring current contribution from the central cyclobutadiene ring.[21] The removal of two electrons from the biphenylene molecule (a $4n$ π system) gives rise to the corresponding dication (a $(4n + 2)$ π system). Whether the deshielding due to the positive charge and the effect from the ring current would be overshadowed by the effect arising from the change in charge density cannot be answered at the present time. Substantial deshielding at alternate carbons C(2) and C(9), and less at C(1) indicates, however, that **9** and **24** are indeed fully delocalized closed-shell ten π-electron aromatic dibenzocyclobutadiene dications.

We have also prepared the 1,5- and 1,8-dimethylbiphenylenes (**25** and **26**) according to Wilcox's method.[22] Two-electron oxidation of a mixture of these two compounds with SbF_5-SO_2ClF at −10 °C clearly generates their corresponding dications **27** and **28**. The proton and carbon-13 NMR parameters of the mixture of these dications are summarized in Table II, showing comparable deshieldings as in case of **9** and **24**. Ring carbon atoms of the dications are deshielded corresponding to the presence of two formal positive charges.



Experimental Section

Materials. 1,2-Dibromo-, 1,2-diiodo-, 1,2-dihydroxy-, and 1,2-diketobenzocyclobutanes were prepared according to Cava's method.[18] The preparation of tertiary alcohols **15** and **16** was also according to Cava.[18] Biphenylenes were prepared according to literature methods.[19,22] Analyses and physical properties of these compounds were satisfactory.

Preparation of Dications. A suspension of the desired precursor in SO_2ClF at −78 °C was slowly added to a well-stirred saturated solution of SbF_5 (fourfold excess) in SO_2ClF at either −78 or −10 °C to give an approximately 10% solution of the dications, which was then carefully transferred to a precooled NMR tube for analysis.

Quenching of Dications. A nearly quantitative recovery of biphenylenes was achieved when the solutions of biphenylene dications were quenched with pentane-$NaOCH_3$ at −60 °C. Quenching of benzocyclobutadiene dication (**6**) with $NaOCH_3$-CH_3OH at −60 °C gave only a 15% yield of the corresponding dimethyl ether, the balance being polymeric material. All products were identified by NMR.

Proton and carbon-13 NMR spectra of the studied dications were obtained on a Varian A56/60A and XL-100-15 FT NMR spectrometers equipped with a variable temperature probe as previously described.[6c]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

References and Notes

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Structure and Binding in Molecular Complexes of Cyclic Polyethers. 4. Crystallographic Study of a Chiral System: an Inclusion Complex of a Macrocyclic Ligand with Phenylglycine Methyl Ester[1]

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Abstract: The crystal and molecular structures of the 1:1 complex between an optically pure macrocyclic polyether host (*S*,*S*)-I ($C_{48}H_{40}O_6$) and a hexafluorophosphate salt of (*R*)-phenylglycine methyl ester has been determined by x-ray diffraction methods at low temperature (−160 °C). The inclusion complex crystallizes with 1 mol of chloroform in the orthorhombic space group $P2_12_12_1$ with $a = 11.885$ (1), $b = 17.039$ (2), $c = 26.749$ (4) Å, and $Z = 4$. The structure was solved by Fourier and tangent formula techniques and refined to $R = 0.049$ for 3204 independent reflections measured by counter diffractometry. The geometry of the intermolecular "host-guest" type association is described in detail. The hydrophilic alkylammonium substrate is included in and hydrogen bonded to the macrocyclic cavity of the ligand. Steric repulsions involving the rigid aromatic substituents of the interacting host and guest moieties play an important role in determining the overall conformation of the complex. In the crystal, the adduct molecules are arranged in a face-to-face manner; the space between the host-guest entities is filled with chloroform molecules and hexafluorophosphate ions. The structural results are correlated with those of a recent solution study of chiral recognition in α-amino acid and ester complexation.

Recent investigations on multidentate macrocyclic systems have aroused considerable interest in several unique properties of these compounds.[2-4] For example, much attention has been given to macrocyclic polyethers,[5] macroheterobicyclic diamines,[6] and naturally occurring cyclodextrins,[7,8] and to their remarkable capability of forming stable inclusion complexes with a variety of guest molecules and ions of appropriate size. Selected series of the inclusion compounds have also been used as models for interacting biological systems in order to understand better the selective binding of substrate molecules to enzyme sites and ion carriers in biological reactions.[9,10]

Among the most interesting problems of stereochemical relationships in host-guest chemistry, those associated with properties of chiral recognition exhibited by macrocyclic ligands toward natural compounds are particularly attractive. Most recently, the cyclic polyethers have been the subject of an extensive synthetic research in which a series of chiral "crown" ethers are being developed.[11] The ability of these li-