J. Org. Chem. 1980, *45*, 1011-1014

Complexation of Arenediazonium Ions by Macrocyclic Multidentate Compounds[1]

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Received October 29, 1979

A kinetic technique is utilized to determine the relative complexing abilities of 40 macrocyclic multidentate compounds for *p-tert*-butylbenzenediazonium tetrafluoroborate in 1,2-dichloroethane. The influence of ligand structure variations, such as ring size, nature of heteroatoms, and substituent effects, upon complexation efficiency is assessed. Maximum complexation is achieved with a 21-membered polyether macrocycle.

In 1976, we reported[2] that the thermal decomposition of *p-tert*-butylbenzenediazonium tetrafluoroborate, 1, in 1,2-dichloroethane was retarded by the presence of the crown ether 18-crown-6. Kinetic investigations established that the entire thermolysis reaction proceeded through the uncomplexed diazonium ion (eq 1). Thus, complexation with crown ethers was demonstrated to be a new method of stabilizing arenediazonium ions.

$$\begin{array}{ll} ArN_2^+BF_4^- + \text{complexing agent} \overset{K}{\rightleftharpoons} \text{complex} & (1) \\ \downarrow k_1 & \\ \text{products} & \end{array}$$

Subsequently, it has been shown that complexation of diazonium ion species with 18-crown-6 produces photochemical stabilization[3] and reduced shock sensitivity.[4] Also, typical aryldiazonium ion reactions, such as azo coupling[5,6] and nucleophilic attack para to the diazonium group,[7] are retarded by the presence of 18-crown-6 or dicyclohexano-18-crown-6. In all of these studies, only minor variation of the macrocyclic complexing agent structure was included.

In order to determine the effects of structural variation within the macrocyclic multidentate ligand upon aryldiazonium ion complexation efficiency, we undertook a study of rate retardations for the thermolysis of 1 produced by a variety of macrocyclic compounds in our laboratories. The results of this investigation are now reported.

In addition to determining which ligands provide the best aryldiazonium ion complexation (stabilization), these studies also are important in identifying appropriate multidentate macrocyclic phase-transfer catalysts for the conduct of aryldiazonium salt reactions in organic solvents of low polarity.[8-11]

Results

Table I. Estimated Cavity Diameters for Crown Ethers

crown ether	diam, Å	crown ether	diam, Å
12-crown-4	1.2-1.5	18-crown-6	2.6-3.2
15-crown-5	1.7-2.2	21-crown-7	3.4-4.3

Kinetics of the thermal decomposition of 1 in 1,2-dichloroethane at 50.0 °C in the absence and presence of multidentate macrocyclic compounds were followed by ultraviolet spectroscopy. In the absence of a potential complexing agent, 1 exhibited an absorption maximum at 285 nm. In the presence of a macrocyclic compound, the absorption maximum usually was shifted to somewhat shorter wavelengths. The reaction products, *p-tert*-butylfluorobenzene, *p-tert*-butylchlorobenzene, and *tert*-butylbenzene,[2,12] are transparent in this region. Excellent first-order kinetic plots covering at least 2 half-lives of the reaction were obtained.[13]

Observed first-order rate constants for the thermal decomposition of 1 in the presence of 1 equiv of different ionophores are presented together with the macrocyclic multidentate compound structures in Figures 1-4. In these figures are listed the results for (a) unsubstituted crown ethers and dicyclohexano crown ethers,[15] (b) monobenzo, dibenzo, mononaphtho, and dinaphtho crown ethers,[15] (c) pyridyl crown ether esters, and (d) furanyl crown ether esters. The observed rate constants were reproducible to ±4% of the reported values.

Discussion

In the absence of complexing agent the first-order rate constant of the thermolysis of 1 in 1,2-dichloroethane at 50.0 °C is 2.51×10^{-4} s^{-1}.[12] Complexation of the diazonium salt by a macrocyclic compound reduces the thermolysis rate since a portion of the diazonium ion is converted into the thermally stable complex (eq 1). More efficient complexation is manifested by a greater retardation of the thermal decomposition rate.

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[1] Taken from the Ph.D. Dissertation of P.N.J., Texas Tech University, 1979.

[2] R. A. Bartsch, H. Chen, N. F. Haddock, and P. N. Juri, *J. Am. Chem. Soc.*, **98**, 6753 (1976).

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[4] W. A. Sheppard, G. W. Gokel, O. W. Webster, K. Betterton, and J. W. Timberlake, *J. Org. Chem.*, **44**, 1717 (1979).

[5] A. R. Butler and P. T. Shepherd, *J. Chem. Res. S*, 339 (1978); *J. Chem. Res. M*, 4471 (1978).

[6] P. N. Juri and R. A. Bartsch, *J. Org. Chem.*, **44**, 143 (1979).

[7] G. W. Gokel, S. H. Korzeniowski, and L. Blum, *Tetrahedron Lett.*, 1633 (1977).

[8] G. D. Hartman and S. E. Biffar, *J. Org. Chem.*, **42**, 1468 (1977).

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[11] S. H. Korzeniowski and G. W. Gokel, *Tetrahedron Lett.*, 3519 (1977).

[12] R. A. Bartsch and P. N. Juri, *Tetrahedron Lett.*, 407 (1979).

[13] Normally, first-order kinetic behavior would not be expected for the reaction scheme shown in eq 1. If the overall concentration (free plus complexed) of complexing agent remains constant during the reaction, the disappearance of arenediazonium ion should produce a progressive retardation of the thermal decomposition, and first-order kinetic plots should show a downward curvature. Calculations show that the curvature would be noticeable only if the association constant K is $>10^4$. A compensating factor is the association of the complexing agent with the reaction product BF_3[14] which progressively decreases the effective concentration of complexing agent as the reaction proceeds and should cause an upward curvature in the first-order kinetic plots. The observation of linear first-order kinetic plots over 2 reaction half-lives indicates a fortuitous cancellation of these two factors.

[14] R. A. Bartsch, P. N. Juri, and J. M. Mills, *Inorg. Chim. Acta*, submitted for publication.

[15] Observed first-order rate constants for the thermolysis of 1 in the presence of ionophores **4**, **6**, and **11** were previously reported.[2] Small differences of the present figures from these earlier values result from improved experimental technique.

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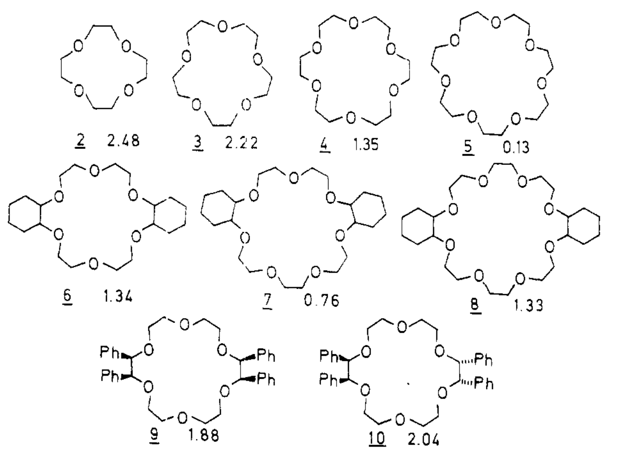

Figure 1. Observed first-order rate constants (×10^4 s^{-1}) for the thermolysis of 1 in 1,2-dichloroethane at 50.0 °C in the presence of 1 equiv of unsubstituted and dicyclohexano crown ethers.

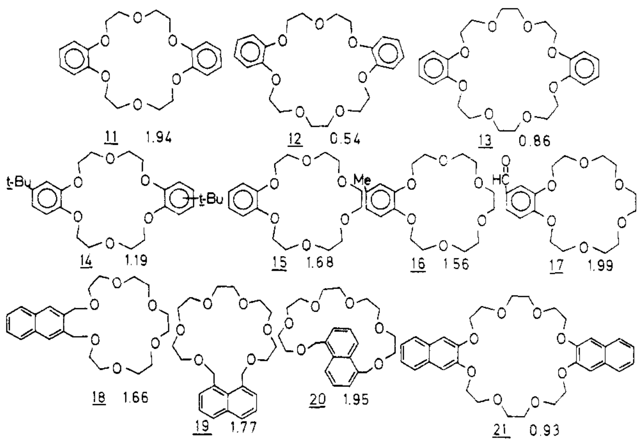

Figure 2. Observed first-order rate constants (×10^4 s^{-1}) for the thermolysis of 1 in 1,2-dichloroethane at 50.0 °C in the presence of 1 equiv of benzo and naphtho crown ethers.

It should be noted that under the conditions employed in this screening study, only relative complexing capabilities of the multidentate macrocyclic compounds are obtained. In order for association constants K (eq 1) for the interactions between 1 and a multidentate macrocyclic ligand to be determined, the complexing agent must be present at concentrations which are in considerable excess of the diazonium ion concentration.[2] For most of the macrocyclic compounds employed in this kinetic study, such concentrations could not be utilized because of overlapping ultraviolet absorptions of the ionophores and 1. In the presence of only 1 equiv of complexing agent, the observed rate retardations are limited, in an absolute sense, because the portion of ionophore-complexed diazonium ion in equilibrium with the uncomplexed diazonium ion is usually rather small. However, the observed rate constants can be determined precisely and are reproducible to ±4% of the stated values. Therefore, the observed rate constant differences are meaningful and allow for comparison of relative complexing efficiencies within a given class of macrocyclic multidentate ligands (e.g., ring size effects for crown ethers) and between different classes of macrocyclic complexing agents (e.g., crown ethers vs. pyridyl crown ether esters).

Unsubstituted and Dicyclohexano Crown Ethers. Thermolysis rates of 1 in the presence of 1 equiv of unsubstituted and dicyclohexano crown ethers are presented in Figure 1. The presence of 12-crown-4, **2**, does not measurably change the thermolysis rate from that observed in the absence of complexing agent. This is consistent with a crown ether cavity[16] (Table I) which is too small to accommodate a diazonium group with an estimated diameter[17] of ~2.4 Å. The slight rate retardation noted for 15-crown-5, **3**, indicates only weak complexation. For 18-crown-6, there is a good match between the estimated diameters of the diazonium group and the crown ether cavity (Table I) which results in an approximately 50% reduction in thermolysis rate. With 21-crown-7, **5**, present, the observed thermolysis rate constant indicates even stronger complexation of the aryldiazonium ion than was obtained with 18-crown-6. Although it might appear that the cavity of 21-crown-7 would be somewhat too large for the diazonium group, the greater ring flexibility may allow for relief of steric interactions between the ortho hydrogens of the benzenediazonium cation and the macrocyclic ring. Of the more than 50 ionophores examined in this study, 21-crown-7 exhibited the strongest complexation with **1**.

It was desired to extend the unsubstituted crown ether series to 24-crown-8. Unfortunately this crown ether could not be obtained. Therefore, the series of dicyclohexano crown ethers **6**, **7**, and **8** was examined. In this series, a preference for complexation involving the 21-membered macrocyclic is clearly evident.

Complexation of 1 by the tetraphenyl-substituted 18-crown-6 derivatives **9** and **10** is weaker than that noted for 18-crown-6 or dicyclohexano-18-crown-6. The reduced complexation efficiency may result from steric interactions of 1 with the phenyl substituents in **9** and **10** or phenyl–phenyl repulsions within the crown ethers themselves which produce crown ether cavities smaller than those in **4** and **6**.

Benzo, Dibenzo, Naphtho, and Dinaphtho Crown Ethers. Observed thermal decomposition rates of 1 in the presence of 1 equiv of macrocyclic compounds which contain an aromatic group as a portion of the crown ether ring are recorded in Figure 2. Comparison of the results for mono- and dibenzo-18-crown-6, **15** and **11**, respectively (Figure 2), with those for 18-crown-6, **4**, and dicyclohexano-18-crown-6, **6** (Figure 1), reveals that complexation of 1 decreases in the order **4** ≃ **6** > **15** > **11**. This ordering is consistent with a diminished basicity of two and four ether oxygen atoms in **15** and **11**, respectively.

The optimal ring size for complexation of 1 by dibenzo crown ethers is again the 21-membered-ring macrocycle. It is interesting to note that dibenzo-21-crown-7 and dibenzo-24-crown-8, **12** and **13**, respectively, are better complexing agents than the corresponding dicyclohexano compounds **7** and **8** (Figure 1). This contrasts sharply with the results obtained for dibenzo- and dicyclohexano-18-crown-6 which were discussed in the preceding paragraph. Apparently for **12** and **13** some factor counteracts an anticipated diminution of complexing ability due to decreased oxygen basicity. It is postulated that this factor is reduced steric interactions of the benzenediazonium ion ortho hydrogens with the more planar dibenzo crown ether ligands. Consistent with this argument is the similarity of complexation of 1 by dibenzo-24-crown-8, **13**, and 2,3-dinaphtho-24-crown-8, **21**, for which the ligand planarity should be the same.

Electronic effects of substituents upon complexing efficiency are apparent when results for macrocyclic compounds **11** and **14** and the series **15**, **16**, and **17** are compared. Electron-donating alkyl groups enhance complex-

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[16] C. J. Pederson in "Synthetic Multidentate Macrocyclic Compounds", R. M. Izatt and J. J. Christensen, Eds., Academic Press, New York, 1978, p 25.

[17] D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 11, 8 (1978).

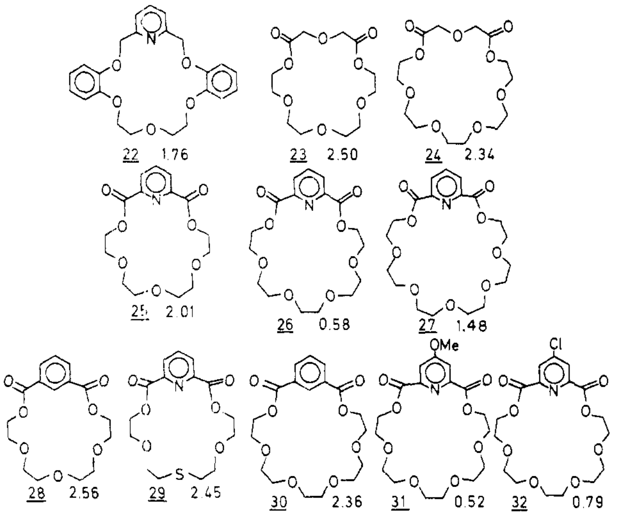

Figure 3. Observed first-order rate constants ($\times 10^4$ s^{-1}) for the thermolysis of 1 in 1,2-dichloroethane at 50.0 °C in the presence of 1 equiv of pyridyl crown ether esters.

ation, whereas the electron-withdrawing formyl group in **17** produces decreased complexation when compared with the corresponding unsubstituted monobenzo crown ether **15**.

Larson and Sousa[18] prepared the series of crown ether naphthalene derivatives **18**, **19**, and **20**. Although the apparent diazonium ion complexation by **20** in which the crown ether ring passes over the face of the naphthalene ring is less than that by **18** and **19**, it is noteworthy that **20** does complex **1**. The reaction solution of **20** and **1** in 1,2-dichloroethane did not exhibit the charge-transfer colors reported by Cram and co-workers[19,20] for solutions of benzenediazonium tetrafluoroborates with binaphtho-20-crown-6 in $CDCl_3$.

Pyridyl Crown Ether Esters. Bradshaw and coworkers[21-25] have recently synthesized several series of crown ether esters. Compared with all but the simplest crown ethers, the preparation of crown ether esters is more facile.

Observed first-order rate constants for the thermal decomposition of **1** in the presence of 1 equiv of several pyridyl crown ether esters are recorded in Figure 3. Compared with the previously discussed crown ethers, the pyridyl crown ether esters have one ether oxygen replaced by pyridyl nitrogen and two ether oxygens substituted by ester oxygens. Comparison of the rate data for pyridyl crown ether **22** and dibenzo-18-crown-6, **11**, reveals that replacement of one crown ether oxygen by pyridyl nitrogen appears to involve a slight increase in the capacity for diazonium ion complexation.[26] On the other hand, comparison of the rate data for crown ether esters **23** and **24** with that for the analogous crown ethers **4** and **5**, respectively, shows a large decrease in diazonium ion complexation efficiency when two crown ether oxygens are replaced by two ester oxygens. Therefore, it seems reasonable to anticipate that pyridyl crown ether esters will, in general, be poorer arenediazonium ion complexing agents than crown ethers of the same ring size. This expectation is borne out by comparison of the rate data for pyridyl crown ether esters **25** and **26** with those for crown ethers **4** and **5**, respectively.

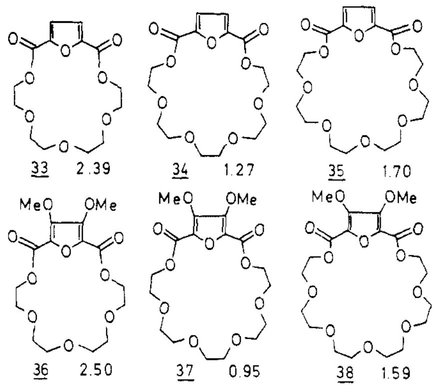

Figure 4. Observed first-order rate constants ($\times 10^4$ s^{-1}) for the thermolysis of 1 in 1,2-dichloroethane at 50.0 °C in the presence of 1 equiv of furanyl crown ether esters.

Examination of the relative complexing abilities of pyridyl crown ether esters **25**, **26**, and **27** shows the same ring size effect observed for crown ethers. Again the 21-membered-ring macrocycle is the best complexing agent of the series.

Convincing evidence that the pyridyl nitrogens are involved in diazonium ion complexation is provided by comparison of results for **25** and **26** with those for **28** and **30**, respectively. Replacement of the pyridine ring by a benzene ring produces macrocyclic compounds which, within experimental error, do not complex with **1**.

Effects of pyridyl ring substituents upon complexation efficiency are revealed by the results for macrocycles **26**, **31**, and **32**. Although the effects are small, the consistent pattern demonstrates that arenediazonium ion complexation is favored by electron-donating substituents, in agreement with the effect noted earlier for benzo-18-crown-6 compounds.

Replacement of an ethereal oxygen in pyridyl crown ether ester **25** by a sulfur as in **29** destroys the diazonium ion complexing capability of the ligand.

Furanyl Crown Ether Esters. Observed first-order rate constants for the thermal decomposition of **1** in the presence of six furanyl crown ether esters[25] are presented in Figure 4. Both the furanyl series **33**, **34**, and **35** and the 4,5-dimethoxyfuranyl series **36**, **37**, and **38** exhibit maximum arenediazonium complexation with the 21-membered-ring macrocycle. Little or no complexation is evident for the 18-membered-ring macrocycles **33** and **36**. For the larger ring macrocycles the presence of electron-donating methoxyl groups facilitates complexation.

Comparison between the 21-membered-ring furanyl crown ether esters **34** and **37** and pyridyl crown ether esters **26** and **31** shows that the latter class of multidentate macrocyclic compounds provides the stronger complexation of aryldiazonium ions.

Other Multidentate Macrocyclic Compounds. Effects of a number of other potential macrocyclic complexing agents upon the thermolysis rate of **1** were also determined. A variety of all thia crown ethers[27] with

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[18] J. M. Larson and L. R. Sousa, *J. Am. Chem. Soc.*, **100**, 1943 (1978).

[19] G. W. Gokel and D. J. Cram, *J. Chem. Soc., Chem. Commun.*, 481 (1973).

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[21] G. E. Maas, J. S. Bradshaw, R. M. Izatt, and J. J. Christensen, *J. Org. Chem.*, **42**, 3937 (1977).

[22] J. S. Bradshaw, R. E. Asay, G. E. Maas, R. M. Izatt, and J. J. Christensen, *J. Heterocycl. Chem.*, **15**, 825 (1978).

[23] J. S. Bradshaw and M. D. Thompson, *J. Org. Chem.*, **43**, 2456 (1978).

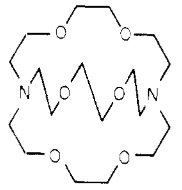
[24] J. S. Bradshaw, G. E. Maas, R. M. Izatt, J. D. Lamb, J. J. Christensen, *Tetrahedron Lett.*, 635 (1979).

[25] J. S. Bradshaw, S. L. Baxter, D. C. Scott, J. D. Lamb, R. M. Izatt, and J. J. Christensen, *Tetrahedron Lett.*, in press.

[26] If the lone pair of electrons on the pyridyl nitrogen is not directed into the macrocyclic cavity as in **22**, the pyridyl nitrogen apparently attacks the β nitrogen atom of **1**, forming a diazopyridinium ion which decomposes by a free-radical mechanism.

varying ring sizes, numbers of sulfur atoms, and numbers of carbon atoms bridging the sulfurs exhibited no complexation with 1.

In the presence of cryptand **39** the thermolysis of **1** proceeded somewhat faster than in the absence of complexing agent. Apparently the diazonium group of **1** is unable to penetrate the cryptand cavity, and **39** acts as an amine in promoting the decomposition of 1 via nucleophilic attack on the β nitrogen.



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Conclusions

The results of this investigation allow several conclusions regarding the influence of multidentate macrocyclic compound structure upon the strength of complexation with aryldiazonium ions in chlorocarbon solvent to be reached. First, stronger complexation is observed with 21-membered-ring macrocyclic compounds than with corresponding 18- or 24-membered-ring macrocycles. Second, electron-donating substituents on aromatic rings of the macrocyclic ligands promote stronger complexation. Third, replacement of a crown ether oxygen with a pyridyl nitrogen enhances association, whereas substitution by an ester oxygen or sulfur diminishes complexation. Thus, the qualitative results of this investigation provide important insight into structural features of the ligand which provide the most efficient complexation of arenediazonium ions by multidentate macrocyclic compounds.

Experimental Section

Materials. The 1,2-dichloroethane (Aldrich Chemical Co., Gold Label) was used directly. The diazonium tetrafluoroborate 1 was prepared by the procedure of Swain and Rogers.[28]

A number of the multidentate macrocyclic compounds were obtained from other researchers and were used as received. Except as indicated, these compounds have been reported, and the melting points of the macrocyclic compounds agreed with the literature values. The multidentate macrocyclic compounds include the following: **23**,[21] **24**,[21] **25–27**,[22] **28**,[23] **29**,[22] **30**,[23] **31**,[24] **32**,[24] **33–38**[25] (J. S. Bradshaw, Brigham Young University), **21** (mp 191–192 °C, M. W. Davis, University of South Carolina), **13**[29] (G. W. Gokel, University of Maryland), **9** (mp 103–105 °C) and **10** (mp 183–186 °C) (A. E. Merz, University of Regensburg), **16**[30] and **17**[30] (J. Smid, University of Syracuse), **18–20**[18] (L. R. Sousa, Bowling Green State University), **22**[31] (F. Vögtle, University of Bonn). Macrocycles **2**, **3**, **4**, **6**, and **11** were obtained from Aldrich Chemical Co. and used directly. Crown ethers **8**, **14**, and **15** and cryptand **39** were obtained from Parish Chemical Co. and used directly.

Crown ether **5** was prepared by the procedure of Dale and Kristiansen[32] and purified via its complex with acetonitrile. Crown ethers **7** and **12** were prepared by the method of Pederson.[29] Thin-layer chromatography of the prepared **7** showed it to be a mixture of at least two isomers. The isomeric mixture was used in the kinetic study.

Kinetic Measurements. A solution containing 5.84×10^{-5} M 1 and an equimolar amount of macrocyclic compound in 1,2-dichloroethane was prepared in a 100-mL volumetric flask. The flask was immersed to the neck in a 50.0 °C water bath. Samples (3.5–4 mL) were removed with a pipet at desired time intervals and transferred to screw-top vials partially immersed in ice–water. After this quenching of the reaction, the vials were kept in a refrigerator until analyzed. Ultraviolet spectra of the samples in the region 400–250 nm were recorded with a Cary 17 ultraviolet–visible spectrophotometer. The disappearance of the absorption maximum for 1 at 285–270 nm was followed. Plots of ln $(A_t - A_\infty)$ vs. time were strictly linear for 2 half-lives with the slope k_{obsd}.

Acknowledgment. This investigation was supported by Grant No. CA 21421, awarded by the National Cancer Institute, DHEW. The authors wish to express their appreciation to the researchers who donated several of the macrocyclic compounds used in this investigation: J. S. Bradshaw, M. W. Davis, G. W. Gokel, A. E. Merz, G. R. Newkome, L. A. Ochrymowycz, J. Smid, L. R. Sousa, and F. Vögtle. Parish Chemical Co. is thanked for performing the high-pressure catalytic hydrogenation of **12** to **7**.

Registry No. **1**, 52436-75-6; **2**, 294-93-9; **3**, 33100-27-5; **4**, 17455-13-9; **5**, 33089-36-0; **6**, 16069-36-6; **7**, 17455-21-9; **8**, 17455-23-1; **9**, 72638-74-5; **10**, 72690-79-0; **11**, 14262-61-4; **12**, 14098-41-0; **13**, 14174-09-5; **14**, 29471-17-8; **15**, 14098-24-9; **16**, 32702-28-6; **17**, 60835-74-7; **18**, 61899-30-7; **19**, 61899-31-8; **20**, 66393-66-6; **21**, 14098-27-2; **22**, 59945-37-8; **23**, 62796-84-3; **24**, 63689-61-2; **25**, 64379-58-4; **26**, 68436-52-2; **27**, 68436-53-3; **28**, 65745-83-7; **29**, 68436-50-0; **30**, 65930-71-4; **31**, 71045-39-1; **32**, 71022-78-1; **33**, 72638-75-6; **34**, 72638-76-7; **35**, 72638-77-8; **36**, 72638-78-9; **37**, 72638-79-0; **38**, 72638-80-3.

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