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Metal-Free Methods in the Synthesis of Macrocyclic Schiff Bases

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Contents

1. Introduction

Schiff-base macrocycles have been of great importance in macrocyclic and supramolecular chemistry. In coordination chemistry the functionally substituted Schiff bases bearing additional donor groups represent the most important class of heteropolydentate ligands capable of forming mono-, bi-, and polynuclear complexes with transition and non-transition metals. They were among the first artificial metal macrocyclic complexes to be synthesized. Interest in exploring metal ion complexes with macrocyclic ligands has been continuously increasing owing to the recognition of the role played by these structures in metalloproteins. A broad variety of Schiff macrocycles can be utilized for metal biosites modeling. Expansion of our fundamental understanding of the macrocyclization processes allows diversity of ligands to be synthesized as artificial cationic, anionic, and neutral guest receptors. An overview of an approach toward the design and optimization of symmetrical and unsymmetrical macrocyclic Schiff bases is described in this paper. During the last two decades, considerable efforts have been made for developing metal-free methods for furnishing macrocycles starting from various dicarbonyl compounds and diamines in addition to standard metal-templated protocols. In this review we collected and analyzed for the first time data dealing with the synthesis of macrocyclic azomethines under metal-free conditions. It has been recently found that anions of appropriate size and geometry also can act as template agents in the synthesis of macrocycles containing pyrrole fragments and amide groups capable of forming strong hydrogen bonds. This effect provides new challenges in the synthesis of artificial anionic receptors. We summarize these anion template reactions into a special section. The literature in this review is covered until September 2006.

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2. Background

Condensation of carbonyl compounds with primary amines was discovered in 1864 by Hugo Schiff.[1] This acid-catalyzed reaction is universal and makes it possible to obtain a broad variety of azomethines. The classical Schiff condensation using monocarbonyl compounds and amines as the starting compounds occurs with high yields. Its mechanism is well understood (Scheme 1). All steps in this reaction sequence are reversible. Therefore, the Schiff condensation under thermodynamically controlled conditions can be used for generating dynamic combinatorial libraries if several different amines or carbonyl compounds are used as starting compounds simultaneously (see ref 2 and literature cited therein).

The reactions of dicarbonyl compounds with diamines are much more complicated and can produce a wide spectrum of products (Scheme 2). This reaction (1:1 molar ratio) initially gives acyclic product of [1+1]-condensation **I**. The latter can react with dicarbonyl compound or diamine to give [2+1]-condensation product **II** or [1+2]-condensation product **III**, respectively. Compounds **II** and **III** are capable of further reacting with diamine and dicarbonyl compound, respectively, to produce [2+2]-macrocycle **IV** as well as linear oligomers **V**. Therefore, dynamic combinatorial library can appear in this case as well.

In some cases formation of products with a larger macrocyclic core (e.g., [3+3], [4+4]-, [5+5]-, [6+6]-, and even [7+7]-condensation products) was also observed.[3]

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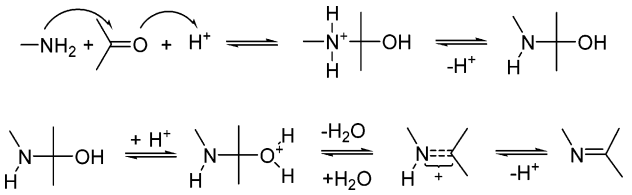
Nataliya E. Borisova was born in 1976 in Moscow. She graduated from the Chemistry Department of Moscow State University in 1999. She received her Ph.D. degree in Inorganic and Coordination Chemistry from the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences in 2004 for studies in the field of synthesis and structures elucidation of new polydentate macrocyclic Schiff bases and their complexes performed under the supervision of Professor I. L. Eremenko and Doctor M. D. Reshetova. Since 2004, she has been working in the group of Professor Yu. A. Ustynyuk. Her research interests lie in purpose-oriented construction of macrocycles and transition-metal complexes, NMR, as well as magnetochemistry, catalysis, enzyme modeling, and host–guest chemistry.

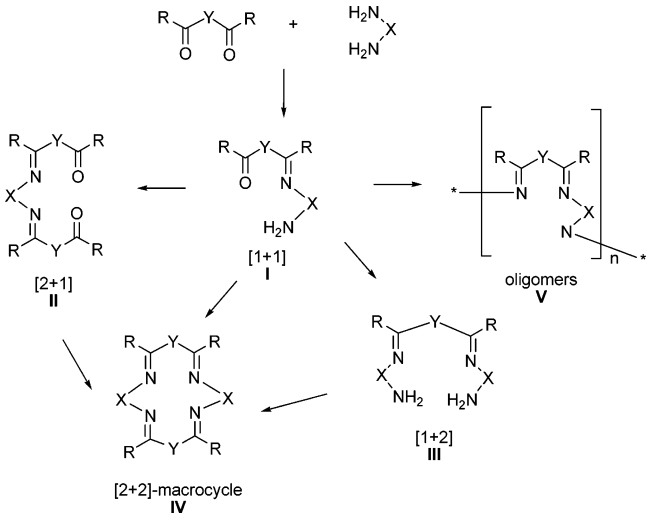
Marina D. Reshetova was born August 1939 in Moscow. She attended the Department of Chemistry of M. V. Lomonosov Moscow State University in 1961, where she studied ferrocene chemistry under the supervision of the late Professor Alexander N. Nesmeyanov and obtained her Ph.D. degree in Organometallic Chemistry in 1967. She spent several years working in the State Institute of Chemistry and Technology of Organoelement Compounds (Moscow) as a leading researcher working on industrial synthesis and application of different organometallics. She joined the group of Professor Yu. A. Ustynyuk at MSU in 1986, and now she is working in the field of organometallic and coordination chemistry, synthesizing pincers and macrocyclic ligands and their transition-metal complexes. She is author or coauthor of over 150 publications. She is actively working in chemical education, being involved in organization of the Russian National Chemistry Olympiads for high school children and the International Mendeleev Chemistry Olympiad. Her other interests are in Russian songs and romances and water traveling.

Born in Cherepovetz (northern part of Russia) in 1936, Yuri A. Ustynyuk began his university training at the Department of Chemistry of M. V. Lomonosov Moscow State University in 1953, where he obtained his Laurea degree in Chemistry in 1958 and Ph.D. degree in Organometallic Chemistry under the supervision of Professor Alexander N. Nesmeyanov in 1962. In 1965, he organized the NMR laboratory in the same department and still then has been working as a Head of this laboratory. In 1974, he obtained his Doctor of Science degree in Physical Chemistry and Organometallic Chemistry. He was promoted to full Professor of Organic Chemistry in 1976. His research interests include various aspects of organometallic and coordination chemistry, catalysis, spectroscopy, and quantum chemistry. He is author or coauthor of over 400 publications and has received several awards for his research. Since 1996 he has been Distinguished Professor of Moscow State University.

Scheme 1. Mechanism of Condensation of Carbonyl Compounds with Amines



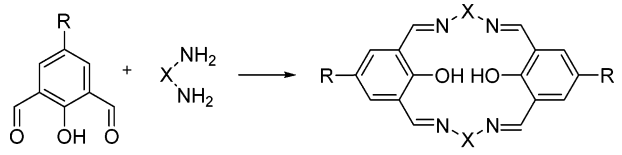
Scheme 2. Main Condensation Products of Dicarbonyl Compounds with Diamines

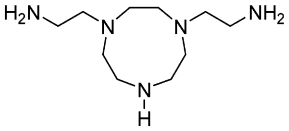


One of the products **I**−**IV** in the pure state can rarely be obtained selectively under standard reaction conditions. Usually a mixture of these compounds contains oligomeric products (oligomers **V**) of polycondensation. The key significance for achieving required chemoselectivity is to understand factors determining the position of equilibria in these complex systems.

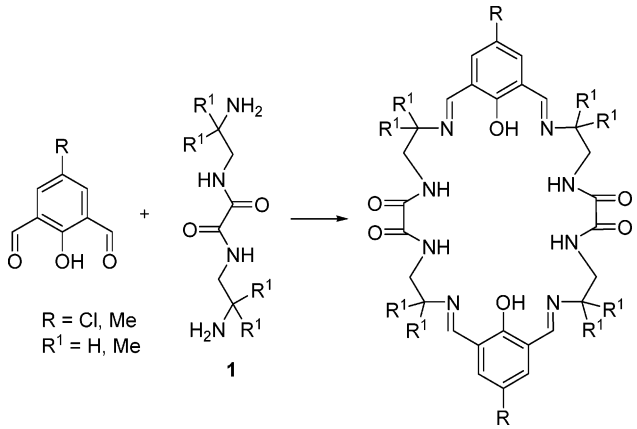
The target product is usually one of the compounds **I**−**IV**. Being polydentate ligands, they can bind into their cavities metal ions with large radii and high coordination numbers (e.g., lanthanides and actinides). When the molecule has additional donor groups, these ligands can form bi- and polynuclear complexes in which two or more metal atoms are placed in close proximity to each other. These complexes exhibit unusual magnetic properties[4] and catalytic activity.[5] Some azomethine complexes possess nonlinear optical

Scheme 3. Condensation of 2,6-Diformyl-4-R-phenols with Aliphatic Diamines

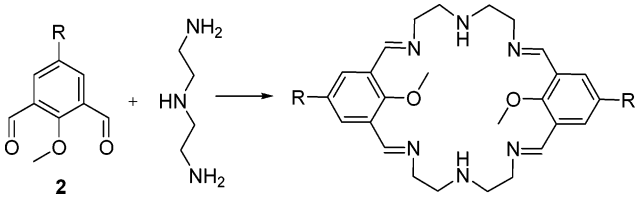


Diamine	Refs.
$H_2N(CH_2)_4NH_2$	28
$H_2N(CH_2)_2NH(CH_2)_2NH_2$	27, 31
$H_2N(CH_2)_2S(CH_2)_2NH_2$	31
$H_2N(CH_2)_2O(CH_2)_2NH_2$	29, 31
$H_2N(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$	29, 30
$H_2N(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$	30
	32

Scheme 4. [2+2]-Condensation of 2,6-Diformyl-4-R-phenols with *N,N′*-Bis(aminoethyl)oxamides



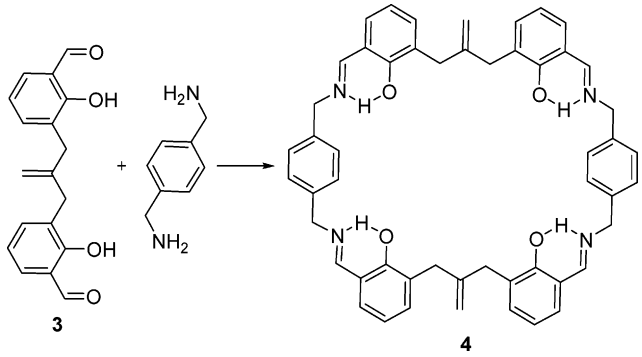
Scheme 5. Reaction of 2,6-Diformylanisoles with Diethylenetriamine



properties,[6] whereas macrocyclic azomethines themselves can form distotic liquid crystals (see ref 7 and references cited therein). A number of azomethines and their complexes possess high biological activity, including antineoplastic[8,9] and antiviral.[10] It has been recently shown that the macrocyclic Schiff bases can also recognize and selectively bind different anions acting as artificial anionic receptors.[11]

Introduction of a template agent is the most reliable method to prevent oligocondensation and switch a process toward forming macrocyclic Schiff bases **IV**. Preliminary coordination of the starting compounds into the metal cation, which acts as a template agent, fixes their mutual orientation favorable for C=N bond formation. As a result, macrocycle closure occurs in the coordination sphere of the ion and products with the rigidly controlled structure are formed. Use

Scheme 6. Synthesis of Macrocycle 4



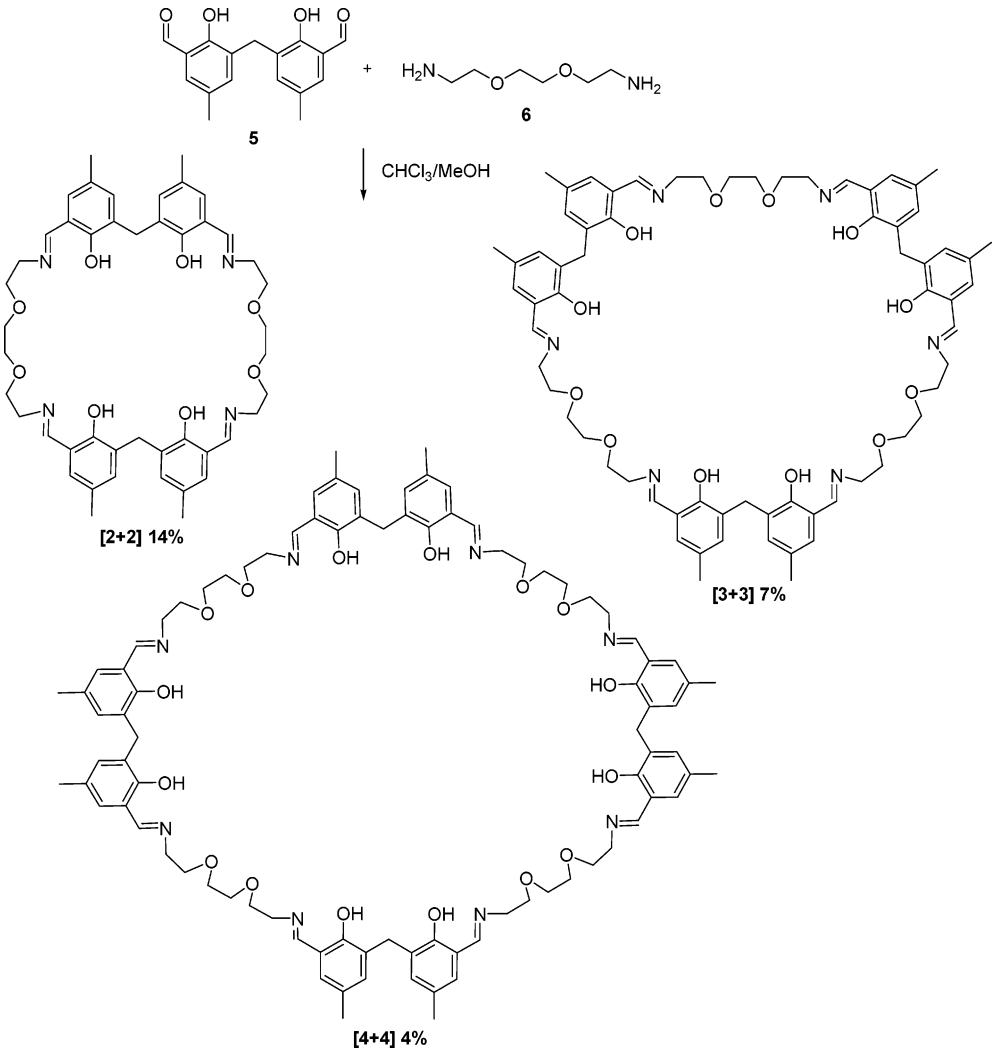
of metal ions with different ionic radii and coordination requirements makes it possible to control the structure of the macrocycle formed.[12] More than dozen books and reviews during the past decade have been devoted to template synthesis of the macrocyclic Schiff-base complexes and their properties.[13−19] Recently, template synthesis of the macrocyclic systems was thoroughly analyzed by Gerbeleu at al.[20] The reviews of Vigato and co-workers are the most comprehensive.[21,22] A review focused on the chemistry of pyrrole-containing macrocyclic Schiff bases was also published by Sessler.[23]

However, template synthesis of the macrocyclic Schiff bases on metal ions has two substantial disadvantages. First, rather often it does not allow one to synthesize metal-free macrocyclic Schiff bases. Usually the more complete and unambiguous the template condensation, the stronger the metal ion bound in the macrocyclic cavity. Therefore, in many cases it is rather difficult to isolate the free ligand, and then when performing demetalation of the complex the imino groups −C=N−R are reduced to the $-CH_2-NHR$ groups with simultaneous demetalation. Second, template synthesis from dicarbonyl compounds and diamines usually affords symmetric macrocyclic complexes. Other starting building blocks have to be used to obtain nonsymmetric macrocyclic Schiff bases.

3. Synthesis of Macrocyclic Schiff Bases of Symmetric Structure: [n+n]-Condensation, n = 2–4

The Schiff bases formed by carbonyl compounds of the aliphatic series have rather low hydrolytic stability. Macrocyclic ligands of this type are routinely synthesized via the template approach. Hydrolytically stable Schiff bases are formed from dicarbonyl derivatives of the aromatic and heteroaromatic series. The composition of the products formed in the reactions of the aromatic dicarbonyl compounds with diamines is determined by several factors, the nature of the starting diamine being the most important. All diamines used can be divided into three groups: the most nucleophilic and most flexible (aliphatic ones), nucleophilic and rigid (cycloaliphatic), and aromatic ones (slightly nucleophilic and rigid diamines). We will follow this classification in this section. Condensations of the dicarbonyl compounds with aliphatic α,ω-diamines have been studied most comprehensively since the vast majority of such reactions are stoichiometrically controlled.

Scheme 7. Library of Condensation Products of Bisphenol 5 with Linear Diamine 6



3.1. Cyclocondensation of Aliphatic Di- and Polyamines with Dicarbonyl Compounds

The main target products of the reactions of dicarbonyl derivatives of the aromatic or heteroaromatic series with aliphatic α,ω-diamines were the [2+2]-macrocyclic Schiff bases. Diamines of the aliphatic series are the most reactive in the Schiff condensation. If two amino groups are linked by flexible aliphatic spacer, they react independently and the process usually cannot be terminated at the step of generating noncyclic [1+1]-condensation product.

In the absence of metal salts, these reactions normally afford oligomeric products.[24,25] However, a proper choice of the solvent, ratio, and concentrations of reactants allows one to increase the regioselectivity of obtaining [2+2]-macrocycles.[26] To suppress intermolecular reactions leading to oligomers, high dilution conditions (concentration 10^{-2}–10^{-3} M and lower) are ordinary used along with the stoichiometric ratio of the starting compounds. The polarity of the solvent chosen should be high enough to dissolve the starting material, which is more polar than the target reaction product. That is why the solvents of choice are methanol, ethanol, and acetonitrile. The reaction is routinely carried out at ambient temperature for at least 12 h; refluxing decreased the reaction time to 0.5−4 h. The efficiency of the above approach in creating [2+2]-macrocycles from aromatic and heteroaromatic dicarbonyl compounds is well documented.

Reactions of dicarbonyl derivatives of phenols with α,ω-diamines have been studied in depth. Treatment of diluted (∼10^{-2} M) alcoholic solutions of 2,6-diformyl-4-R-phenols (R = Cl, Me) with aliphatic diamines which contain at least four carbon atoms in the chain leads to [2+2]-macrocyclic Schiff bases in nearly quantitative yield[27−32] (Scheme 3).

Under the same conditions 4-substituted 2,6-diformylphenols react with *N*,*N*′-bis(aminoethyl)oxamides **1** to form macrocyclic Schiff bases[33] in unspecified yields (Scheme 4).

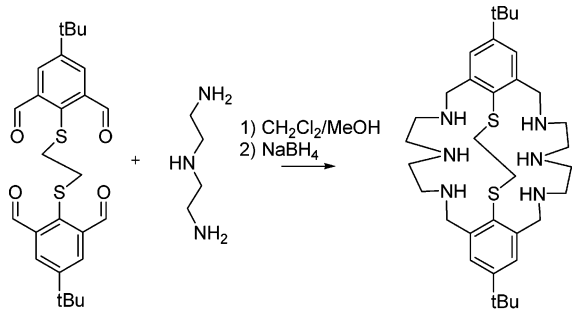
Treatment of 2,6-diformylanisole derivatives **2** (R = Br, Cl, Me, OMe) with diethylenetriamine gives [2+2]-macrocyclic Schiff bases in 65−80% yields[34] (Scheme 5).

Reaction of diformyl derivative **3** with 1,4-di(aminomethyl)benzene in THF for 30 h affords [2+2]-macrocyclic Schiff base **4** in 33% yield[35] (Scheme 6).

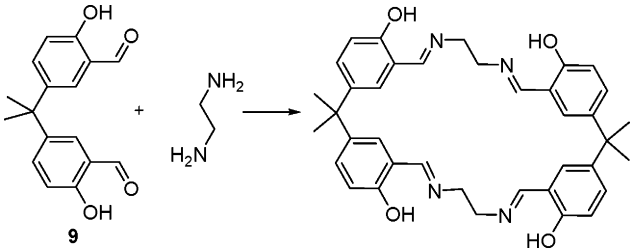
Treatment of bisphenol **5** with linear diamine **6** under high-dilution conditions generates the library of cyclooligomeric [2+2]-, [3+3]-, [4+4]-, [5+5]-, [6+6]-, and even [7+7]-condensation products with no eventual formation of [1+1]-macrocycles. Some of these products were isolated, and high-molecular-weight products were identified by MALDI-TOF mass spectrometry[36] (Scheme 7).

According to X-ray analysis the [2+2]-condensation product exhibits twisted to "figure eight"-conformation due

Scheme 8. Reaction of Tetracarbonyl Derivative 7 with Diethylenetriamine



Scheme 9. Condensation of Bisphenol 9 with Ethylenediamine



to π,π-stacking of two of the phenol fragments[36] (Figure 1).

Condensation proceeds with a greater degree of regioselectivity if both dicarbonyl fragments are bridged by a chain of appropriate length into one molecule. Diethylenetriamine reacts with bisthiophenol derivative **7** to give the respective bicyclic Schiff base, which was reduced to the corresponding polyamine **8** in nearly quantitative yield[37] (Scheme 8).

Recently, the Schiff bases obtained by reacting diformyl derivatives of different polyphenols or polythiophenols with diamines have attracted increasing interest as ligands. For example, bisphenol **9** reacts with ethylenediamine to give the macrocyclic Schiff base in unspecified yield[38] (Scheme 9).

By reacting equimolar amounts of ethylenediamine and dialdehyde **10** in a diluted solution (0.01 M) of acetonitrile upon 0.5-h reflux, the corresponding [2+2]-macrocyclic azomethine is obtained in 82% yield[39] (Scheme 10).

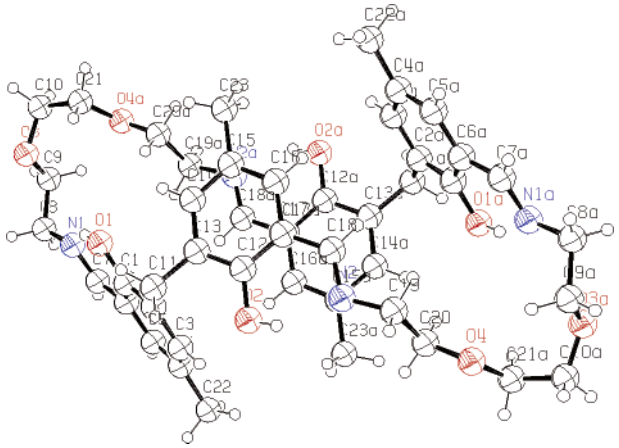
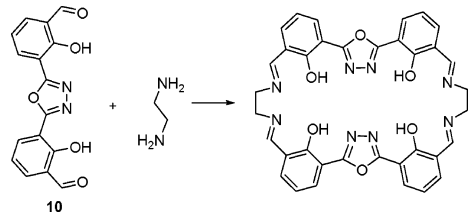
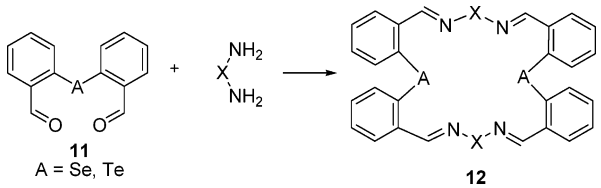


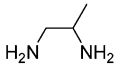
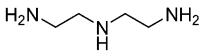
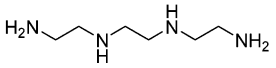
Figure 1. Structure of [2+2]-macrocycle according to X-ray analysis. This figure was generated using data downloaded from The Cambridge Crystallographic Data Centre (CCDC) and corresponds to a structure originally reported by Hisaeda et al.[36]

Scheme 10. Condensation of Dialdehyde 10 with Ethylenediamine

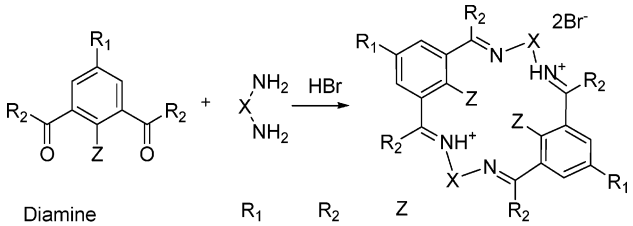


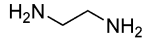
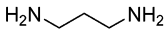
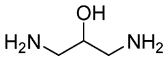
Scheme 11. Synthesis of Chalcogen-Containing [2+2]-Macrocyclic Schiff Bases



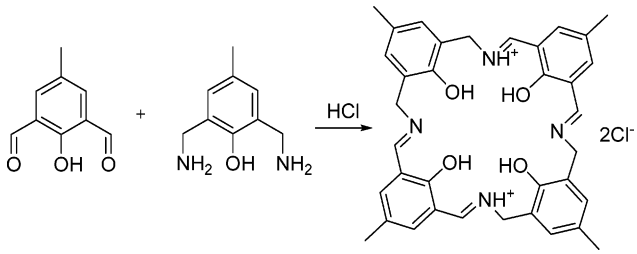
Diamine	Yield
$H_2N(CH_2)nNH_2$ n = 3, 6	61%
	71%
	32%
	60%

Scheme 12. Condensation of 2,6-Dicarbonyl Derivatives of Phenols and Thiophenols with Diamines in the Presence of Acid



Diamine	R_1	R_2	Z
	Me tBu	H Me	OH
	Me	H Me	OH SH
	Me	H	SH

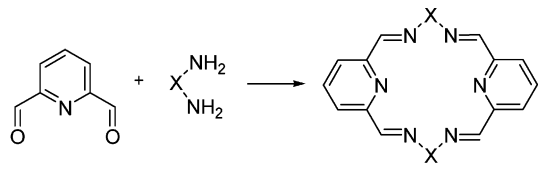
Scheme 13. Condensation of 2,6-Diformyl-4-methylphenol and 2,6-Di(aminomethyl)-4-methylphenol

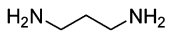
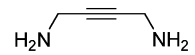
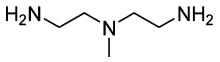
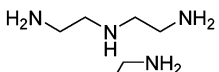
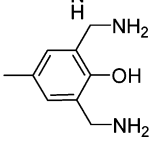


Treatment of bis(2-formylphenyl)chalcogenides **11** (A = Se, Te) with aliphatic diamines in boiling acetonitrile gives macrocyclic Schiff bases **12**[40,41] (Scheme 11).

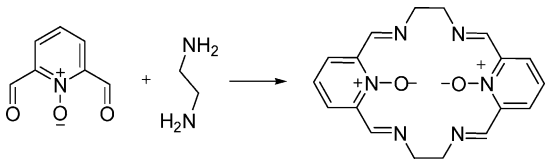
In contrast to the above-presented examples, 2,6-dicarbonyl derivatives of 4-alkylphenols produce no macrocyclic Schiff bases upon treatment with ethylene- and propylenediamines under standard conditions.[42,43] However, these macrocycles can be obtained in diluted methanol solutions

Scheme 14. Reaction of 2,6-Diformylpyridine with Aliphatic Diamines

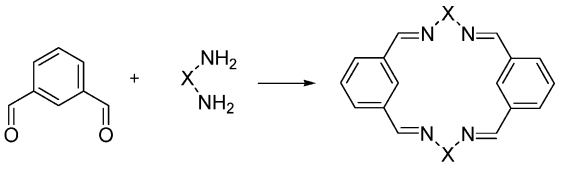


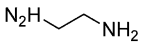
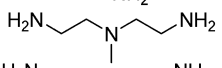
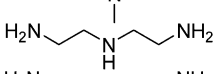
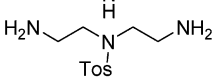
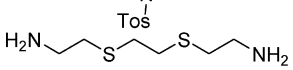
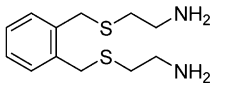
Diamine	Solvent	Yield	Refs.
	MeCN	62%	49
	MeOH	86%	45
	MeCN	60%	46
	MeCN	60-70%	26, 47
	MeOH	45%	48

Scheme 15. Condensation of 2,6-Diformylpyridine N-Oxide with Ethylenediamine



Scheme 16. Reaction of Aliphatic Diamines with Isophthalic Dialdehyde



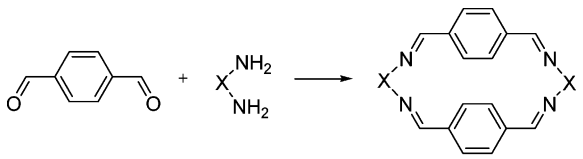
Diamine	Yield	Refs.
	88%	51
	10%	46
	60-70%	26
	87%	46
	71%	51
	86%	53

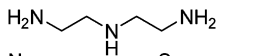
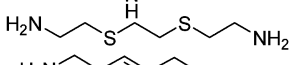
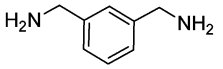
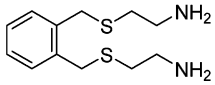
($\sim 10^{-2}$ M) in the presence of two or more equivalents of strong protonic acid (HBr). In this case, the [2+2]-macrocyclic Schiff bases are isolated as salts[42,43] (Scheme 12).

Acidic catalysis is also useful for constructing [2+2]-macrocycle from 2,6-di(aminomethyl)-4-methylphenol and 2,6-diformyl-4-methylphenol[44] (Scheme 13).

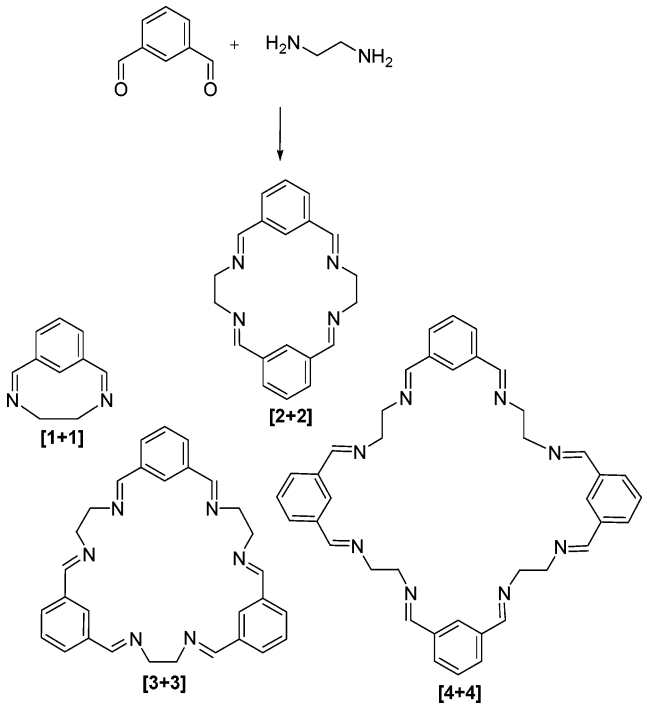
[2+2]-Macrocycles can be obtained from dicarbonyl derivatives of pyridine or benzene both at room temperature in acetonitrile and upon reflux in alcohols. Contrary to the 2,6-dicarbonyl derivatives of phenols, the length of the aliphatic chain of the diamine does not affect the product nature if pyridine derivatives are used[26,45−49] (Scheme 14).

Scheme 17. Reaction of Aliphatic Diamines with Terephthalic Dialdehyde



Diamine	Yield	Refs.
		47
	48%	52
		47
	96%	53

Scheme 18. Condensation Products of Isophthalic Dialdehyde with Ethylenediamine According to the Mass-Spectrometric Data



The reaction leads to macrocycles even if short aliphatic amine (1,2-diaminoethane or 1,3-diaminopropane) was used.

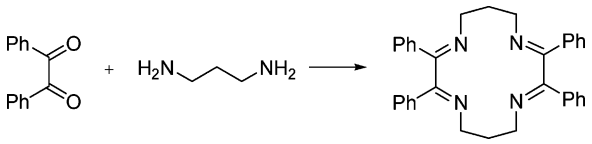
Macrocyclic Schiff base was obtained in a similar manner by condensing 2,6-diformylpyridine N-oxide with 1,2-ethylenediamine upon reflux in methanol[50] (Scheme 15).

Isophthalic and terephthalic dialdehydes react with aliphatic diamines similar to 2,6-diformylpyridine. [2+2]-Macrocyclic Schiff bases are formed by condensing dialdehydes with various diamines under high dilution conditions ($\sim 10^{-2}-10^{-3}$ M)[26,46,47,51−53] (Schemes 16 and 17).

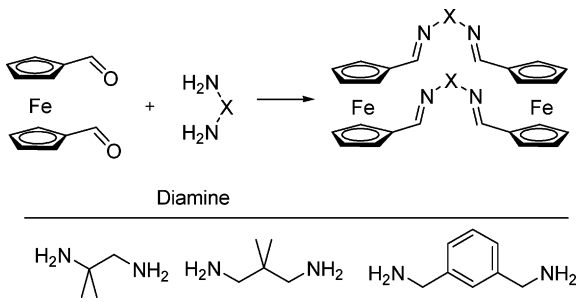
According to FD-MS mass spectrometry it was found that treatment of isophthalic dialdehyde with ethylenediamine in methanol generates a combinatorial library of [1+1]-, [2+2]-, [3+3]-, and even [4+4]-condensation products[54] (Scheme 18).

Aromatic diketones react with aliphatic diamines under acid catalysis to form [2+2]-condensation products. For

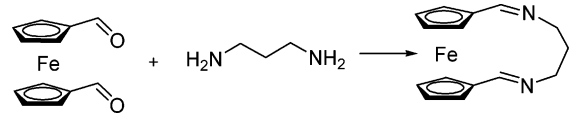
Scheme 19. Reaction of Benzyl with 1,3-Diaminopropane



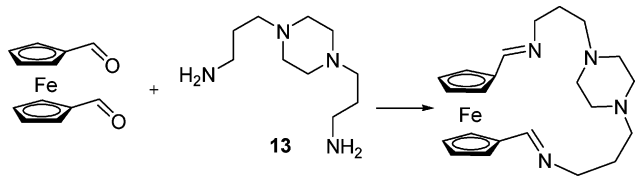
Scheme 20. Reaction of Aliphatic Dialdehydes with 1,1′-Diformylferrocene



Scheme 21. Reaction of 1,1′-Diformylferrocene with Propylenediamine in Methanol



Scheme 22. [1+1]-Condensation of 1,1′-Diformylferrocene with Diamine 13



example, benzyl reacts with 1,3-diaminopropane to give macrocyclic Schiff base in 84% yield[55] (Scheme 19).

Reactions of 1,1′-diformylferrocene with various diamines in acetonitrile or chloroform at concentrations lower than 0.1 M afford [2+2]-macrocyclic Schiff bases. Diamine nature plays a crucial role in macrocyclization (Scheme 20). Thus, aliphatic diamines and 1,3-di(aminomethyl)benzene solely give [2+2]-cyclocondensation products, whereas 1,4-di-(aminomethyl)benzene leads to oligomeric products.[56]

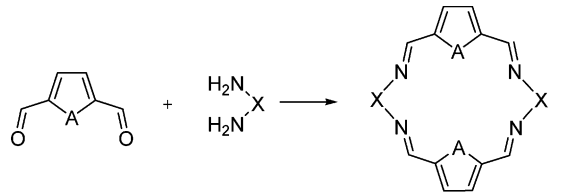
By replacing acetonitrile with methanol, the reaction path dramatically changed: [1+1]-macrocycle became the only product[57] (Scheme 21).

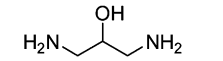
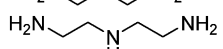
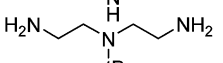
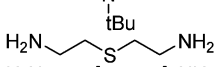
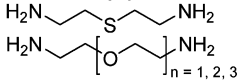
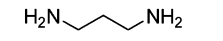
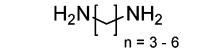
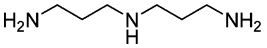
When flexible diamine with a long distance between the amino groups is used, formation of [1+1]-macrocycles becomes the main direction of the reaction. Thus, reaction of 1,1′-diformylferrocene with diamine **13** in ethanol/chloroform mixture under high dilution conditions provides [1+1]-macrocycle[56] (Scheme 22; also see section 4).

Reaction of diformyl derivatives of five-membered heterocycles with aliphatic diamines proceeds smoothly to give [2+2]-macrocyclic Schiff bases under high dilution conditions if a spacer containing at least three atoms connects terminal amino groups[26,47,48,58−63] (Schemes 23 and 24).

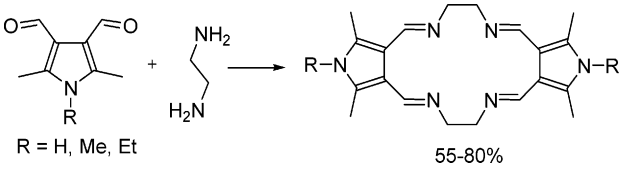
An unusual result is obtained when 3,4-dialkoxy-2,5-diformylpyrroles is treated with hydrazine (formally the simplest diamine) in the presence of HCl. Thus, [4+4]-cyclocondensation products **14** are formed in moderate yields[64] (Scheme 25).

Scheme 23. Reaction of 2,5-Diformyl Derivatives of Five-Membered Heterocycles with Aliphatic Diamines

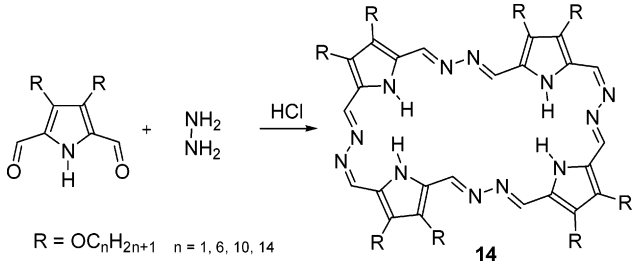


Diamine	A	Yield	Refs.
	NH, S	50-55%	58
	O, NH, S		47, 59
	S	48%	60, 62
	S	70%	59, 61
	O, S	60-70%	26, 59
	NH	66%	48
	S	50-90%	59
	S	50-90%	59

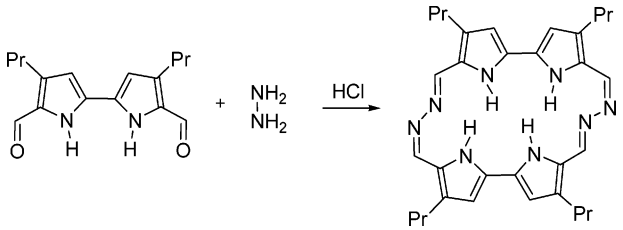
Scheme 24. Reaction of 2,5-Dimethyl-4,5-diformylpyrroles with Ethylenediamine[63]



Scheme 25. Reaction of 3,4-Dialkoxy-2,5-diformylpyrroles with Hydrazine



Scheme 26. Reaction of Hydrazine with 4,4′-Dipropyl-5,5′-diformyl-2,2′-bipyrrole

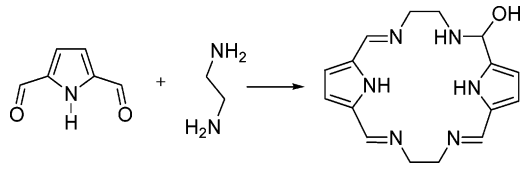


Contrary to previous condensation, treatment of 4,4′-dipropyl-5,5′-diformyl-2,2′-bipyrrole with hydrazine provides [2+2]-condensation product[65] (Scheme 26).

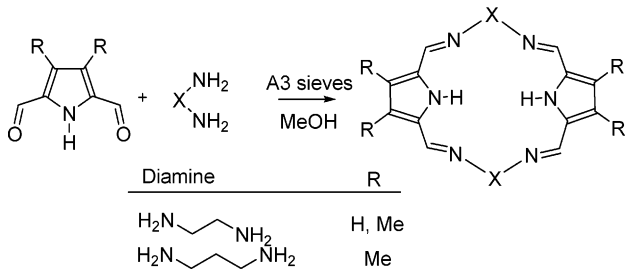
Reaction of ethylenediamine with 2,5-diformylpyrrole gives aminol due to the addition of water to the double bond of the initially formed macrocyclic Schiff base[24] (Scheme 27).

Similarly to 2,6-dicarbonyl phenol derivatives, 2,5-diformylpyrroles produce oligomers with ethylenediamine or

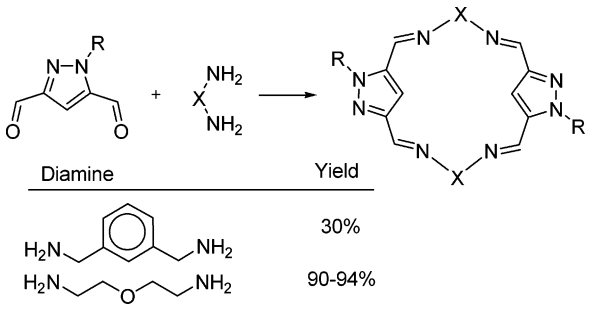
Scheme 27. Condensation of 2,5-Diformylpyrrole with Ethylenediamine



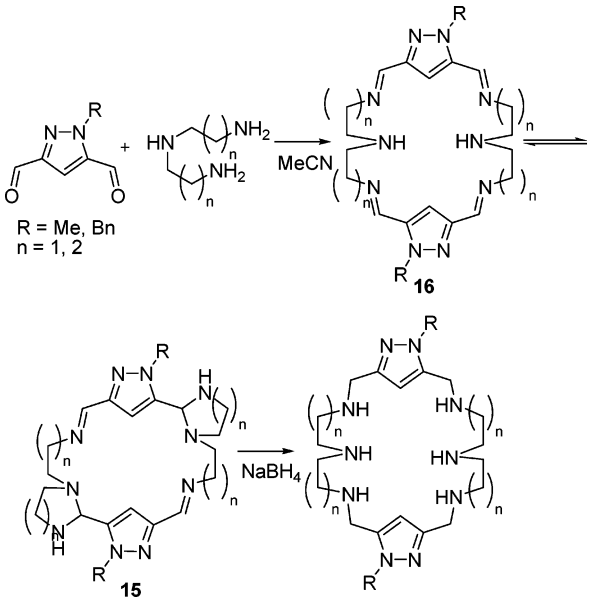
Scheme 28. Condensation of 2,5-Diformylpyrroles with Diamines in the Presence of Molecular Sieves



Scheme 29. Reaction of 3,5-Diformylpyrazoles with Diamines



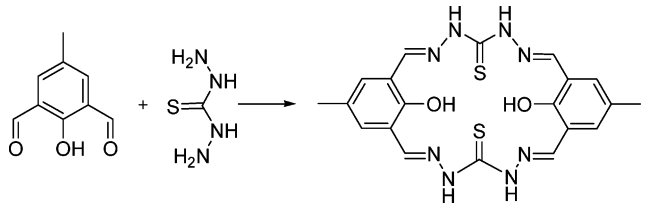
Scheme 30. Condensation of 1-R-3,5-Diformylpyrazoles with Diamines and Intramolecular Amination of the C═N Bond



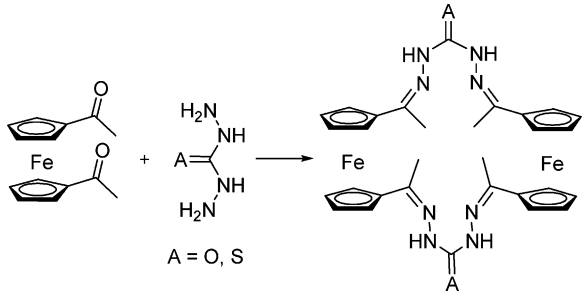
propylenediamine. Selective macrocyclization can be achieved by adding molecular sieves to the reaction mixture[66] (Scheme 28).

Reactions of 1-R-3,5-diformylpyrazoles (R = H, Me, Bn) with diamines in acetonitrile under ambient temperature produced macrocyclic Schiff bases[67,68] (Scheme 29).

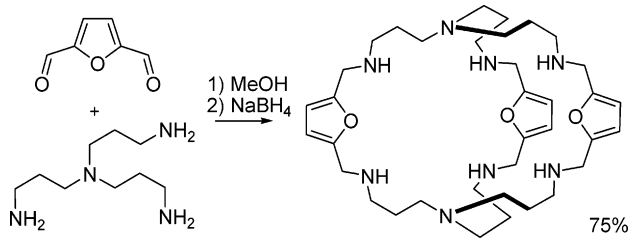
Scheme 31. Reaction of 2,6-Diformyl-4-methylphenol with Thiocarbohydrazide



Scheme 32. Reaction of 1,1′-Diacetylferrocene with Carbohydrazide and Thiocarbohydrazide



Scheme 33. Reaction of 2,5-Diformylfuran with Tris(3-aminopropyl)amine[77]



Under the same conditions, treatment of 1-R-3,5-diformylpyrazoles (R = Me, Bn) with diethylenetriamine or dipropylenetriamine leads to pentacyclic products **15** in 80% yield.[67] Mechanistically, macrocycle **16** is initially generated followed by intramolecular ring closure through nucleophilic addition of the secondary amino group to the C═N bond[67,68] (Scheme 30). This process seems to be reversible since both imidazolidines undergo ring opening upon reducing Schiff bases **15.**[67−69]

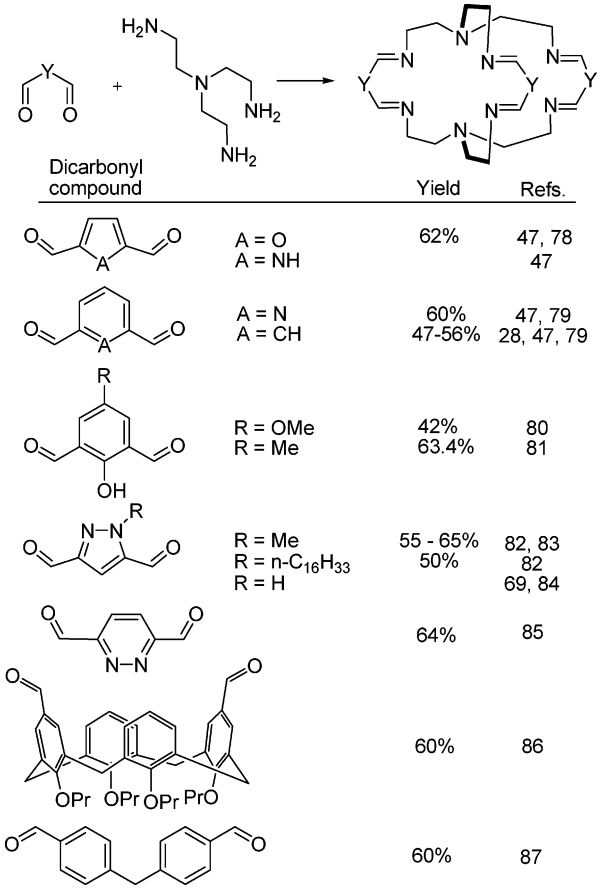
Intramolecular nucleophilic addition to the C═N bond was also observed for the template condensation of diformyl compounds with functionally substituted diamines[70−73] (2-hydroxy-1,3-diaminopropane, diethylenetriamine, etc.). This reaction is actually reversible, and equilibrium can be controlled by metal ion radius.

Thiocarbohydrazide was also used in the synthesis of macrocyclic Schiff bases. Although thiocarbohydrazide is a polytopic compound bearing multiple coordinating centers, it behaves similarly to aliphatic diamines in obtaining macrocyclic Schiff bases. Thus, [2+2]-macrocycles are formed in 70% yield by condensing thiocarbohydrazide with equimolar amounts of 2,6-diformyl-4-methylphenol[74] (Scheme 31).

The same protocol was extended to [2+2]-macrocyclic azomethines by reacting 1,1′-diacetylferrocene with carbohydrazide and thiocarbohydrazide[75] (Scheme 32).

Reactions of dicarbonyl compounds with polyamines provide a useful tool toward obtaining a broad variety of cryptands.[76] A series of papers provides strong evidence of the flexibility of this methodology.[28,48,70,77−87] This condensa-

Scheme 34. Condensation of Dicarbonyl Compounds with Tris(2-aminoethyl)amine



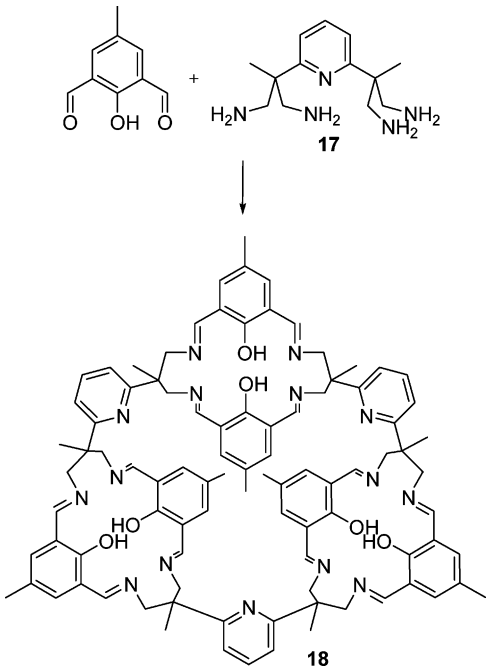
tion is a remarkable example of creating various [3+2]-macrocycles under high dilution conditions ($\sim 2 \times 10^{-2}$ M) (Schemes 33 and 34).

The same methodology was successfully expanded to assembling polycyclic systems via directly condensing dicarbonyls with polyamines. Treatment of 2,6-diformyl-4-methylphenol with tetraamine **17** in the presence of HBr affords [6+3]-polycycle **18** in nearly quantitative yield[88,89] (Scheme 35).

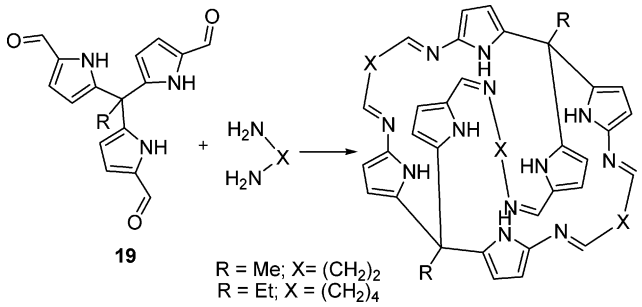
To the best of our knowledge, the only example of creating a cryptand by condensing tricarbonyl compound with diamine was reported in 2001.[90] Thus, treatment of tricarbonyl tripyrromethane derivative **19** with ethylenediamine or butylenediamine in THF affords the corresponding cryptands[90] (Scheme 36).

Summarizing the results presented in this section we can state that two procedures for obtaining macrocyclic Schiff bases from dicarbonyl compounds and aliphatic diamines are most frequently used: (a) condensation of equimolar amounts of the starting compounds ($\sim 10^{-2}$ M) in acetonitrile at room temperature and (b) condensation of diluted solutions ($\sim 10^{-3}$ M) in alcohols upon reflux. The result of the reaction is mainly governed by the ratio of the starting compounds. Detailed studies of the reaction by mass spectrometry show that the condensation provides a library of products, thus complicating isolation of individual components in a pure state. When amino groups are linked by a long aliphatic chain, both amino groups react independently. Treatment of any dicarbonyl compounds with diamines of the above type leads to [2+2]-macrocycles. If amino groups are located in

Scheme 35. Synthesis of [6+3]-Polycycle 18



Scheme 36. Condensation of Tricarbonyl Derivative 19 with Aliphatic Diamines



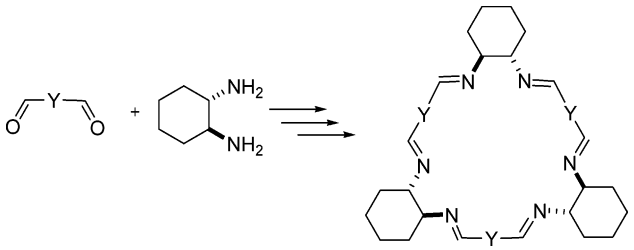
close proximity to each other (e.g., α,β- and α,γ-diamines), the respective diamines react with acidic dicarbonyl compounds (e.g., 2,6-diformylphenols or 2,5-diformylpyrroles) to give oligomers. Excess of strong acids (HCl, HBr) directs the reaction to [2+2]-macrocycles.

3.2. Reactions of Dicarbonyl Compounds with Diaminocyclohexanes and Other Aliphatic Diamines with Rigid Spatial Arrangement of Amino Groups

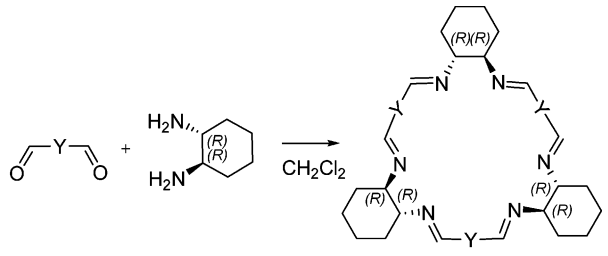
Contrary to most aliphatic diamines, diaminocyclohexanes exist in rigidly fixed conformations. In particular, amino groups in *trans*-1,2-diaminocyclohexanes occupy the equatorial positions and the dihedral angle between two C−NH_2 bonds is about 60°. Therefore, in the reaction of dicarbonyl compounds with a 180° dihedral angle between the CHO groups with *trans*-1,2-diaminocyclohexanes behave as almost planar building blocks prone to formation of trianglimine [3+3]-macrocycles (Scheme 37).

Thus, treatment of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with terephthalic dialdehydes leads to [3+3]-condensation products **20** when ~0.1 M solutions in methylene chloride are refluxed or stirred at ambient temperature[91−94] (Scheme 38). The isolated yields of trianglimines are usually moderate because of the need for repeated recrystallization of crude

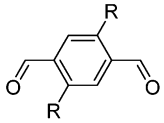
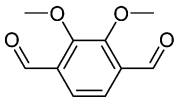
Scheme 37. Formation of [3+3]-Macrocycles by Condensing Dialdehydes with *trans*-1,2-Diaminocyclohexanes



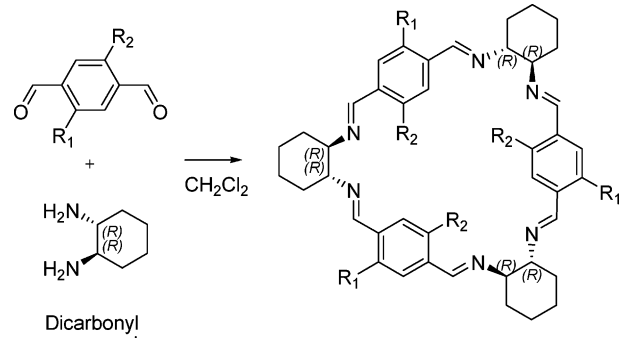
Scheme 38. Reaction of Terephthalic Aldehydes with *trans*-(*R*,*R*)-1,2-Diaminocyclohexane



20

Dicarbonyl compound		Yield	Refs.
	R = H	90%	92
	R = Me	97%	94
	R = OMe	90%	93, 94
	R = OEt	18%	91
	R = OPr	17%	91
	R = OBu	32%	91
	R = OBn	23%	91
	R = O(p-FBn)	29%	91
		25%	94

Scheme 39. Diastereoselective Trianglimines Formation



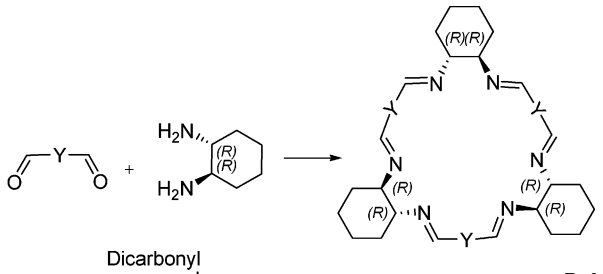
Dicarbonyl compound	Yield
R_1 = Et; R_2 = OMe	8%
R = Bu; R_2 = OMe	13%
R = Bn; R_2 = OMe	15%
R = $(CH_2)_2$OMe; R_2 = OMe	5%
R = Me; R_2 = H	46%

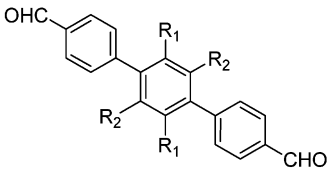
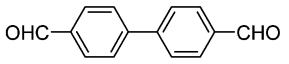
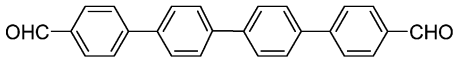
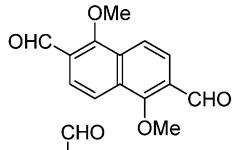
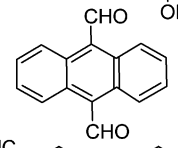
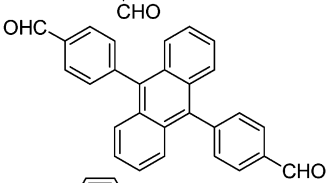
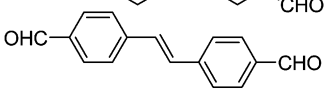
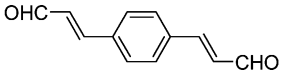
macrocycles, although the yields of crude substances are satisfactory (60−80%).[91]

Detailed investigation of the reaction shows that using C_{2v}-symmetric dialdehydes caused formation of only one C_3-symmetric trianglimine[91] (Scheme 39). The yields of crude macrocycles are about 80%. Thus, it is clear that reactions of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with dialdehydes proceed with a high degree of diastereocontrol.[91]

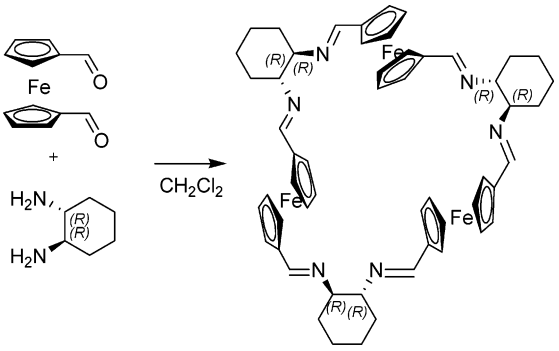
This approach was expanded to related diformyls. A broad variety of linear rigid diformyls lead to [3+3]-triangleimines

Scheme 40. Synthesis of [3+3]-Condensation Products from Various Dicarbonyl Compounds



Dicarbonyl compound		Yield	Refs.
	R_1 = H, R_2 = Me	18%	96
	R_1 = R_2 = F	55%	97
	R_1 = R_2 = H	99%	98
		32-67%	95, 98
		57%	96
		14%	96
		80%	95
		99%	98
		68%	98
		58%	98

Scheme 41. Reaction of 1,1′-Diformylferrocene with *trans*-(*R*,*R*)-1,2-Diaminocyclohexane

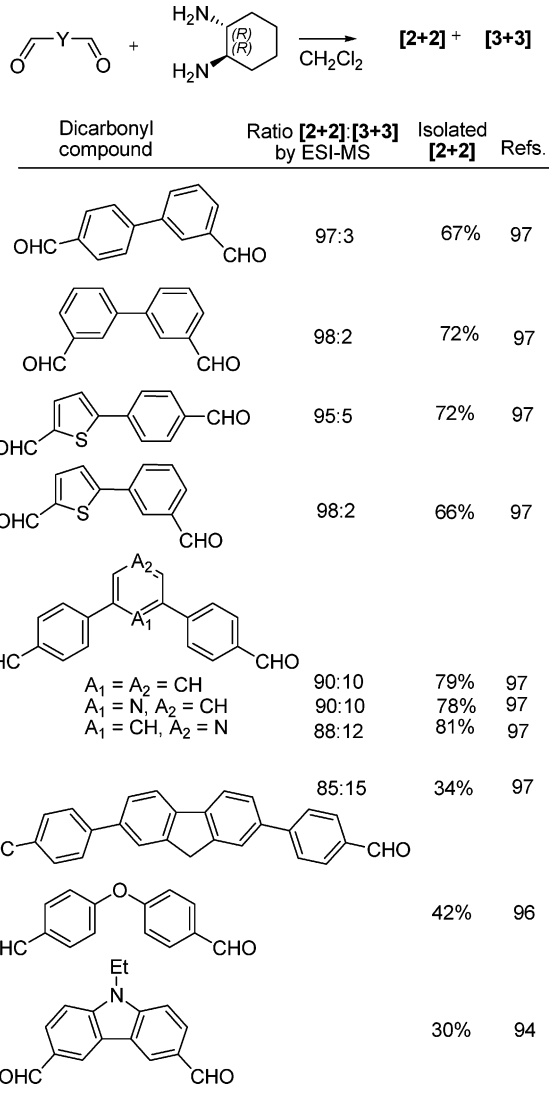


21

when ∼0.1 M solutions in methylene chloride are refluxed[92−98] (Scheme 40).

According to molecular mechanics simulation,[92,95,96] the reaction is apparently driven by the structural predisposition

Scheme 42. Macrocycles Formation in Reaction of Various Dialdehydes with *trans*-(*R,R*)-1,2-Diaminocyclohexane



of the intermediate imines as well as by the thermodynamic stability of the final trianglimines.

The carbonyl groups in 1,1′-diformylferrocene lie in different planes, thus allowing this dialdehyde to form [3+3]-azomethine **21** upon treatment with *trans*-(*R,R*)-1,2-diaminocyclohexane[96] (Scheme 41).

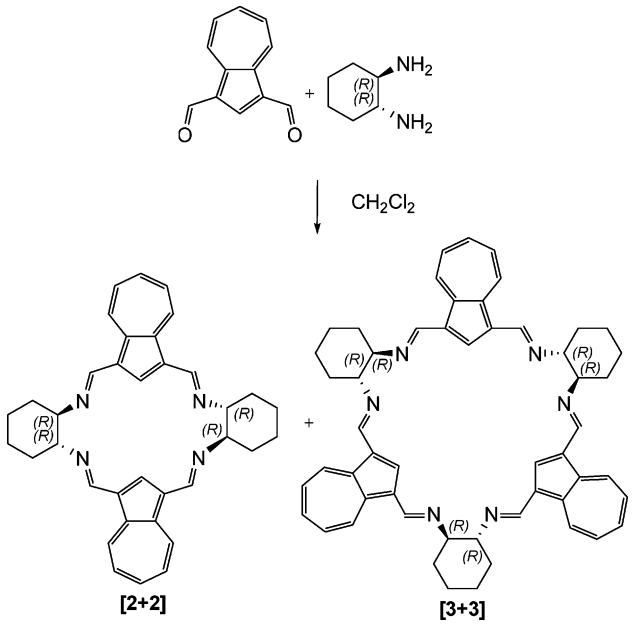
According to NMR NOE experiments data, imino groups form a dihedral angle of 180° to each other in solution since cyclopentadienyl rings in each ferrocene cycle are unfolded.[96]

Generally when the angle between the CHO groups is less than 180°, mixtures of [2+2]- and [3+3]-condensation products are formed. Detailed investigation of the reaction of various dicarbonyl compounds with *trans*-(*R,R*)-1,2-diaminocyclohexane in methylenechloride shows that the ratio of [2+2]- and [3+3]-condensation products depends on the geometry of the dicarbonyls (Scheme 42). The major products were [2+2]-macrocycles, but [3+3]-trianglimines formed as well.

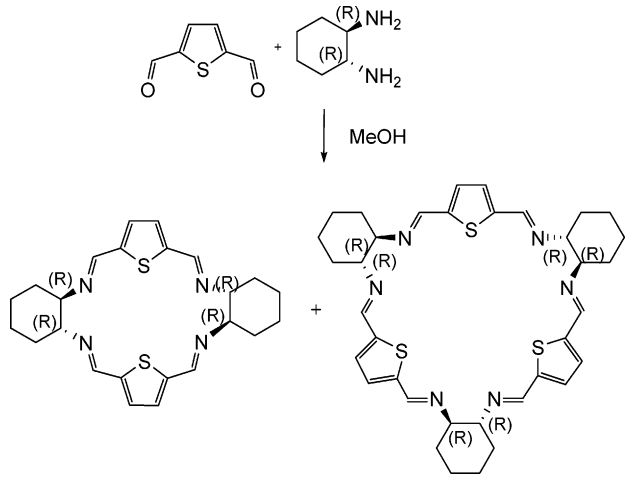
1,3-Diformylazulene reacts with *trans*-(*R,R*)-1,2-diaminocyclohexane in methylene chloride at room temperature to produce [3+3]- and [2+2]-condensation products in a 4:1 ratio[94] (Scheme 43).

[2+2]- and [3+3]-Macrocycles are also formed by treating 2,5-diformylthiophene with *trans*-(*R,R*)-1,2-diaminocyclo-

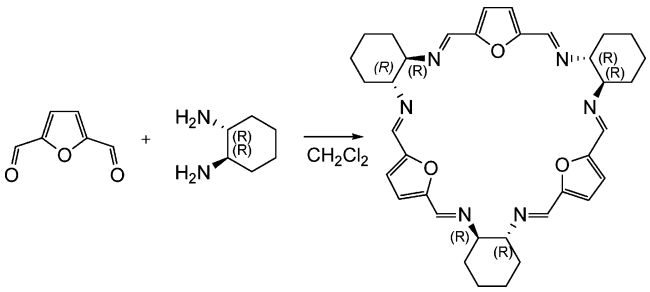
Scheme 43. Condensation of 1,3-Diformylazulene with *trans*-(*R,R*)-1,2-Diaminocyclohexane



Scheme 44. Reaction of 2,5-Diformylthiophene with *trans*-(*R,R*)-1,2-Diaminocyclohexane



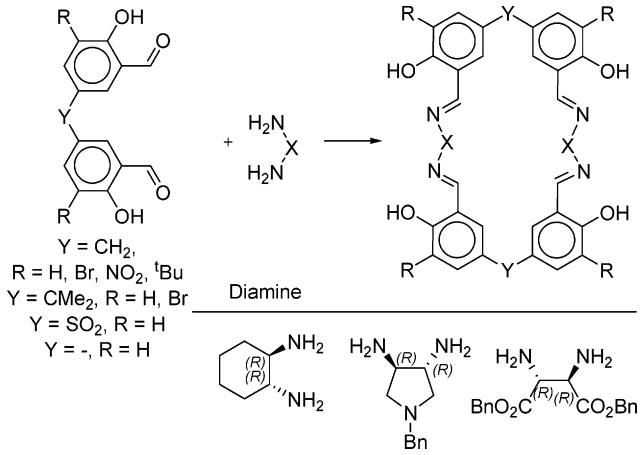
Scheme 45. Reaction of 2,5-Diformylfuran with *trans*-(*R,R*)-1,2-Diaminocyclohexane



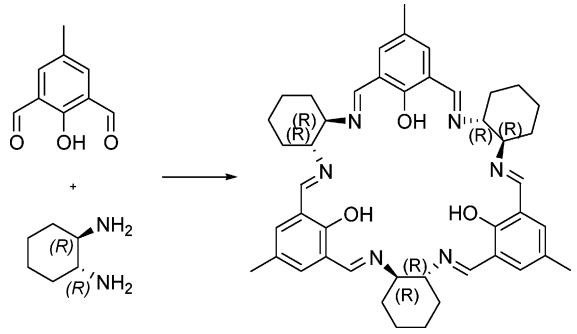
hexane in methanol at ambient temperature. Judging by the mass-spectrometry data the above mixture contains products in equal amounts[99] (Scheme 44). If dichloromethane is used as a solvent, the reaction solely gives [3+3]-macrocycle.[94]

Treatment of 2,5-diformylfuran with *trans*-(*R,R*)-1,2-diaminocyclohexane in dichloromethane at ambient temperature affords [3+3]-azomethine in quantitative yield[96] (Scheme 45).

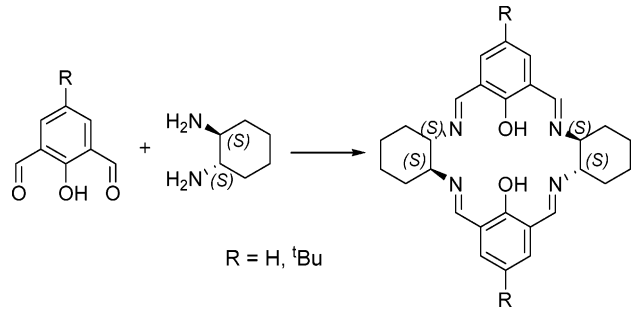
Scheme 46. Selective Generation of [2+2]-Macrocycles under Microwave Irradiation



Scheme 47. Formation of [3+3]-Macrocyclic Azomethine from 2,6-Diformyl-4-methylphenol



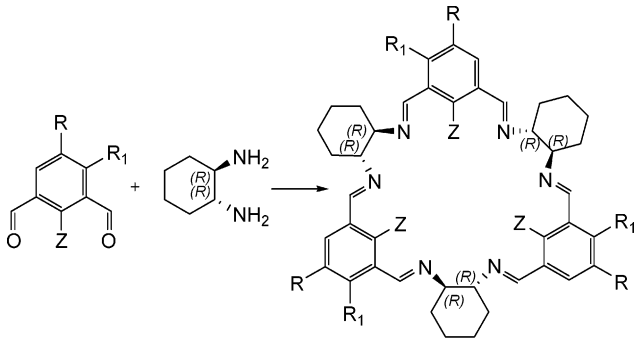
Scheme 48. Reaction of 2,6-Diformyl-4-alkylphenols with *trans*-(*S*,*S*)-1,2-Diaminocyclohexane



Summarizing the data above, one can conclude that relatively nonpolar solvent (methylene chloride) favored formation of the [3+3]-condensation products, while a mixture of products is observed in more polar media (methanol). It is likely that the stability of large macrocycles is enhanced in aprotic solvents. In support of this assumption, the results of Gawronski's group indicate that even in the case of reaction of terephthalic aldehyde with *trans*-(*R*,*R*)-1,2-diaminocyclohexane trianglimine formed without a noticeable amount of the [2+2]-condensation products if benzene, dichloromethane, THF, or acetonitrile was used as solvent. On the other hand, a small amount of the [2+2]-product was detected in the crude reaction mixture obtained in methanol.[100]

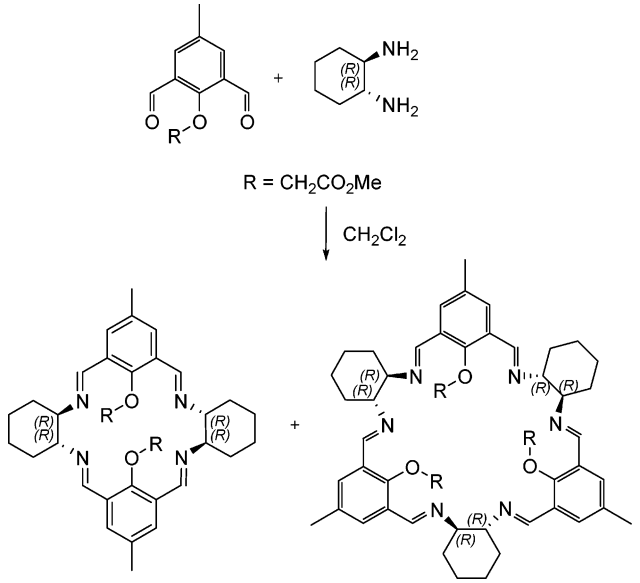
Another way to produce [2+2]-macrocycles is treating dicarbonyl compounds with salts of chiral diamines in ethanol−water mixture in the presence of potassium carbonate under microwave irradiation[101,102] (Scheme 46). Formation of [3+3]-macrocycles was not reported.

Scheme 49. Reaction of Dicarbonyl Compounds with *trans*-(*R*,*R*)-1,2-Diaminocyclohexane



	R	Yield	Refs.
22	R = R1 = Z = H	90%	92
23	R = Me, R1 =Z = H	75%	93, 94
24	R = R1 = H, Z = Me	67%	94
25	R = R1 = Z = OMe	70%	94
26	R = Me, R1 = OH, Z = H	78%	105
27	R = Me, R1 = H, Z = OTs	59%	91

Scheme 50. Reaction of the Methoxycarbonylmethyl Ether of 5-Methyl-2-hydroxyisophthalaldehyde with *trans*-(*R*,*R*)-1,2-Diaminocyclohexane



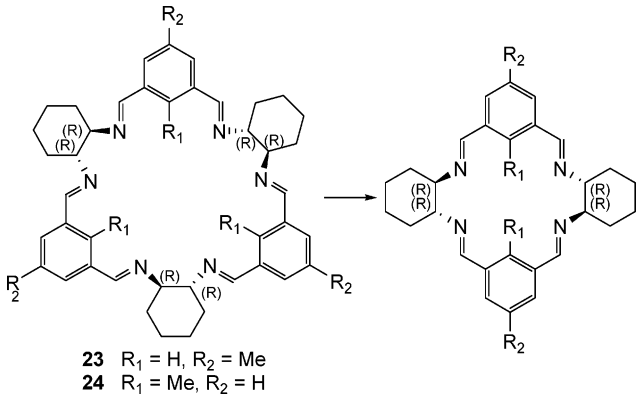
When the angle between the CHO groups is about 120°, the ring size selectivity changes and [2+2]-, [3+3]-, and [4+4]-condensation products can be generated. Thus, reaction of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with 2,6-diformyl-4-methylphenol in concentrated (0.1 M) methanol solution at ambient temperature provides [3+3]-macrocyclic azomethine in quantitative yield[3,99,103−105] (Scheme 47).

In spite of the above condensations, treatment of *trans*-(*S*,*S*)-1,2-diaminocyclohexane with 2,6-diformyl-4-R-phenols leads to [2+2]-macrocycles upon reflux in ethanol for 5 h[106] (Scheme 48).

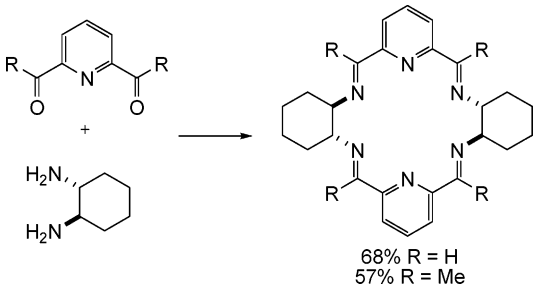
Condensation of isophthalic dialdehydes with *trans*-(*R*,*R*)-1,2-diaminocyclohexane in concentrated (0.1 M) dichloromethane solution at ambient temperature gives [3+3]-macrocyclic azomethines **22**−**27**[91−94,105] (Scheme 49).

On the other hand, treatment of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with methoxycarbonylmethyl ether of 5-methyl-

Scheme 51. Thermal Cycle Contraction in [3+3]-Macrocycles 23 and 24



Scheme 52. Reaction of Dicarbonyl Derivatives of Pyridine Derivatives with Racemic *trans*-1,2-Diaminocyclohexane



2-hydroxyisophthalaldehyde leads to a mixture of [2+2]- and [3+3]-condensation products; the former was isolated in 6% yield[91] (Scheme 50).

[2+2]-Schiff bases were detected by ESI-MS during synthesis of compounds **23** and **24**.[94] In addition, [3+3]-condensation products were found to undergo cycle contraction to give the corresponding [2+2]-macrocycles in ~100% yield upon prolonged (12−72 h) reflux in dichloromethane[94] (Scheme 51). This suggests that [3+3]-macrocycles are kinetically controlled products, whereas thermodynamically controlled processes generate [2+2]-Schiff bases.

Similar results were obtained by condensing racemic *trans*-1,2-diaminocyclohexane with 2,6-diformyl- or 2,6-diacetylpyridine upon reflux (3 h) in methanol. [2+2]-Macrocyclic Schiff bases were isolated from both diluted and concentrated solutions[107] (Scheme 52).

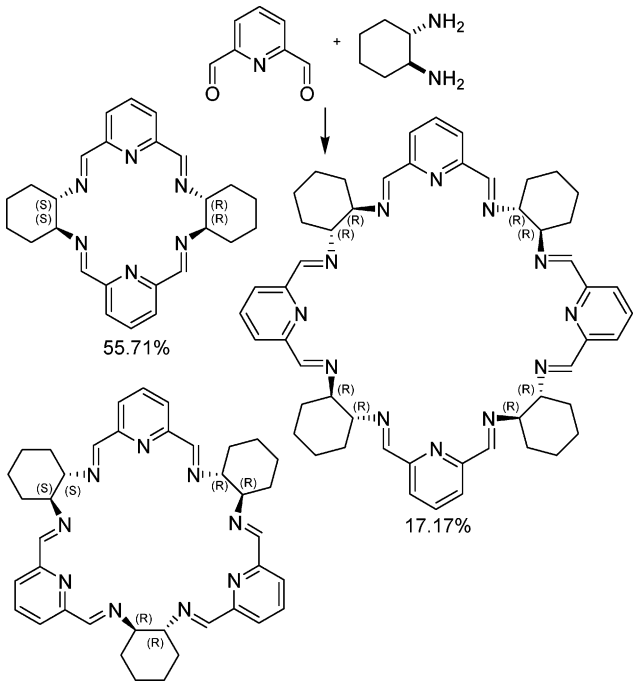
Detailed studies have demonstrated that reflux of 2,6-diformylpyridine with racemic *trans*-1,2-diaminocyclohexane in methanol gave a library of [2+2]-, [3+3]-, and [4+4]-condensation products[108] (Scheme 53).

Reaction of 2,6-diformylpyridine with optically pure *trans*-(*R*,*R*)-1,2-diaminocyclohexane produced a library of [2+2]-, [3+3]-, and [4+4]-condensation products[108] as well.

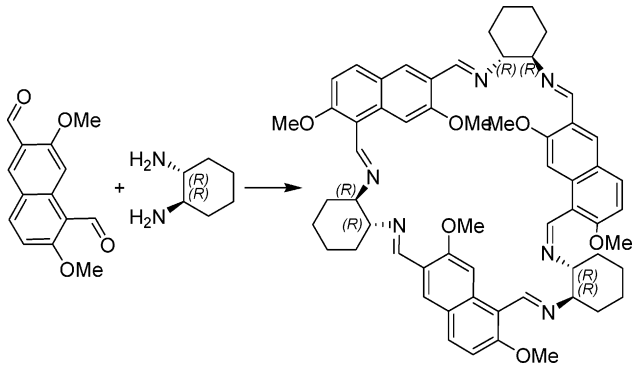
Reactions of polycyclic aromatic dicarbonyl compounds with *trans*-(*R*,*R*)-1,2-diaminocyclohexane in methylene chloride produce both [3+3]- and [2+2]-condensation products. The result of the reaction is determined by both the angle between carbonyl groups and mutual complementarity of the reagents. For example, treatment of 1,6-diformyl-2,7-dimethoxynaphthalene with *trans*-(*R*,*R*)-1,2-diaminocyclohexane leads to [3+3]-condensation product[96] (Scheme 54).

Two bulky phenyl groups capable of serving as "conformational anchors" fix the conformation in (*R*,*R*)- or (*S*,*S*)-1,2-diamino-1,2-diphenylethanes, providing dihedral angle

Scheme 53. Reaction Products of 2,6-Diformylpyridine with Racemic *trans*-1,2-Diaminocyclohexane



Scheme 54. Cyclization of 1,6-Diformyl-2,7-dimethoxynaphthalene with *trans*-(*R*,*R*)-1,2-Diaminocyclohexane



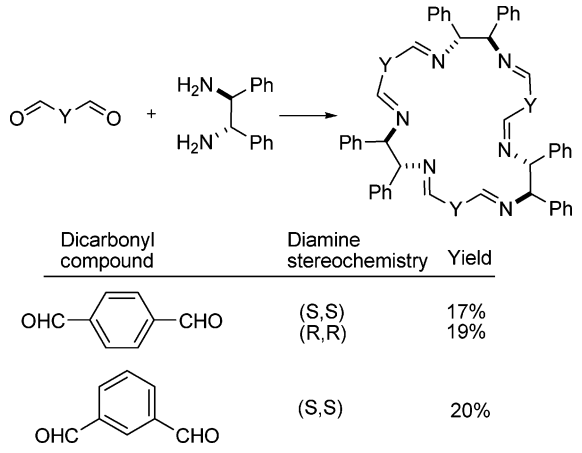
between C−NH_2 bonds of approximately 60°. Consequently, their reactions with dicarbonyl compounds proceed similarly to those of *trans*-1,2-diaminocyclohexanes. For instance, they react with isophthalic and terephthalic dialdehydes in dichloromethane at room temperature to form the [3+3]-macrocycles[93] (Scheme 55). Chloroform solutions of [3+3]-macrocycles were found to decompose irreversibly to give oligomeric condensation products, suggesting that trianglimine is the kinetically controlled product.[93] It cannot be also excluded that thermodynamic stability is determined by solvation effects (see Schemes 44 and 45).

Reaction of 2,6-diformyl-4-methylphenol with (*R*,*R*)-1,2-diamino-1,2-diphenylethane in methylene chloride at −5 °C gives trianglimine isolated in quantitative yield[104] (Scheme 56).

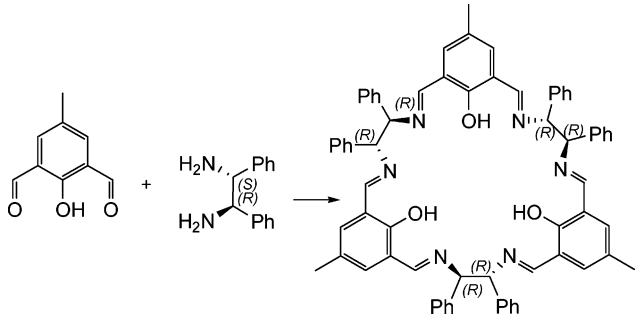
Reactions of 2,6-diformyl-4-R-phenols with (*S*,*S*)-1,2-diamino-1,2-diphenylethane in ethanol upon reflux for 5 h lead to the [2+2]-macrocycles[106] (Scheme 57).

Similarly to *trans*-1,2-diaminocyclohexanes, one can conclude that trianglimines might be generated from (*R*,*R*)- or (*S*,*S*)-1,2-diphenylethylenediamines by kinetically controlled

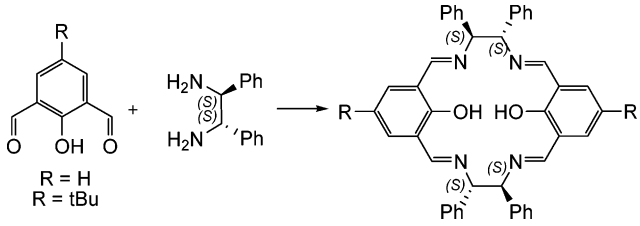
Scheme 55. Reaction of Phthalic Dialdehydes with 1,2-Diamino-1,2-diphenylethanes



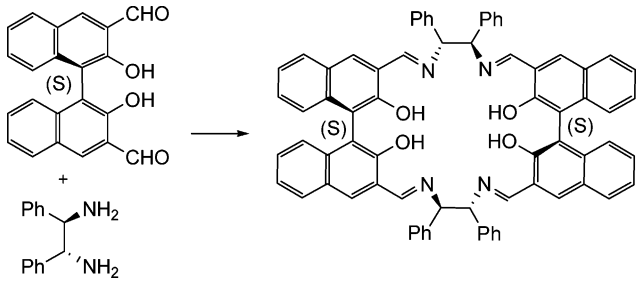
Scheme 56. Reaction of 2,6-Diformyl-4-methylphenol with (*R*,*R*)-1,2-Diamino-1,2-diphenylethane



Scheme 57. Reactions of 2,6-Diformyl-4-R-phenols with (*S*,*S*)-1,2-Diamino-1,2-diphenylethane



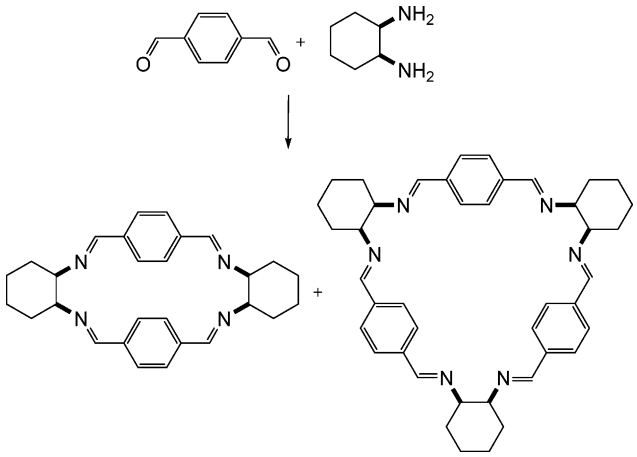
Scheme 58. Reaction of (*S*)-2,2′-Dihydroxy-3,3′-diformylbinaphthyl with (*R*,*R*)-1,2-Diamino-1,2-diphenylethane



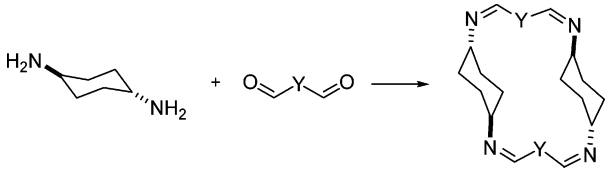
reactions, while thermodynamic control directs the process toward creating [2+2]-macrocycles.

Reaction of 2,2′-dihydroxy-3,3′-diformylbinaphthyl with (*R*,*R*)-1,2-diamino-1,2-diphenylethane provides only oligomers in the case of the (*R*)-isomer,[109,110] whereas (*S*)-isomer forms [2+2]-macrocycle[111] (Scheme 58). Stereoselectivity of this reaction made it possible to successfully separate the

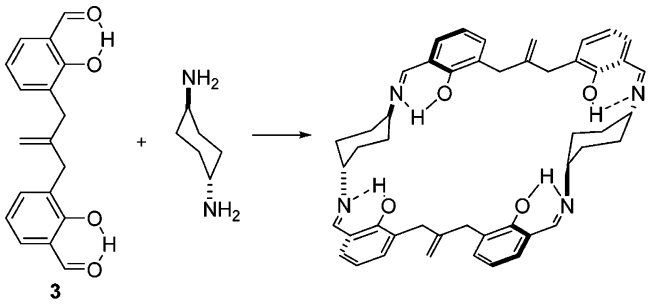
Scheme 59. Reaction of Terephthalic Dialdehyde with Racemic *cis*-1,2-Diaminocyclohexane



Scheme 60. Reactions of *trans*-1,4-Diaminocyclohexane with Dialdehydes



Scheme 61. Reaction of Dialdehyde 3 with Racemic *trans*-1,4-Diaminocyclohexane



racemic carbonyl compound into enantiomers with an efficiency of 50−60%.[111]

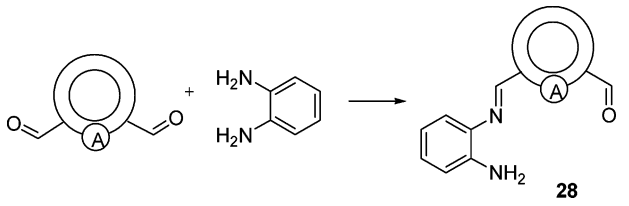
Treatment of terephthalic dialdehyde with racemic *cis*-1,2-diaminocyclohexane provides a mixture of [2+2]- and [3+3]-macrocycles, the latter being the major product as indicated by ESI-MS data[112] (Scheme 59).

trans-1,4-Diaminocyclohexane, whose amino groups occupy equatorial positions, is a useful building block for formation of [2+2]-structures by condensing with dicarbonyl compounds of complementary geometry (the angle between the CHO fragments should be about 120°) (Scheme 60).

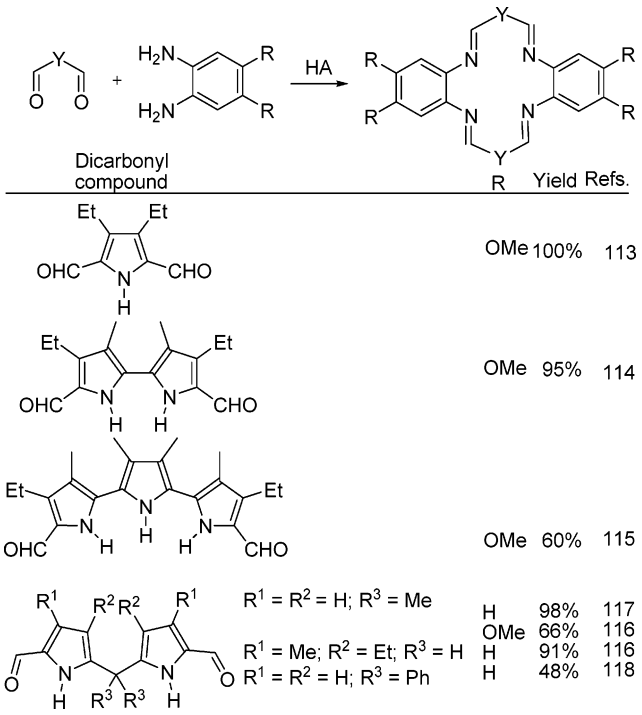
For example, reaction of racemic *trans*-1,4-diaminocyclohexane with dicarbonyl bisphenol derivative **3**, in which the position of the carbonyl groups is fixed by strong hydrogen bonding, leads to [2+2]-macrocyclic Schiff base in 57−79% yields[35] (Scheme 61).

The data collected in this section shows that proper choice of reaction conditions and utilization of starting materials with proper geometries makes it possible to obtain individual macrocyclic Schiff bases or their libraries without using metal ions as template agents. The flexible nature of triangl compounds (trianglimines and trianglamines) allows ready accommodation of a variety of guest molecules to form

Scheme 62. [1+1]-Condensation Products in the Reaction of Dicarbonyl Compounds with *o*-Phenylenediamine



Scheme 63. Reaction of Dicarbonyl Pyrrole Derivatives with *o*-Phenylenediamine under Acidic Conditions



inclusion complexes.[100] Undoubtedly, further development of this approach will extend possibilities of designing of polytopic macrocyclic systems possessing required predictable structural and coordination properties.

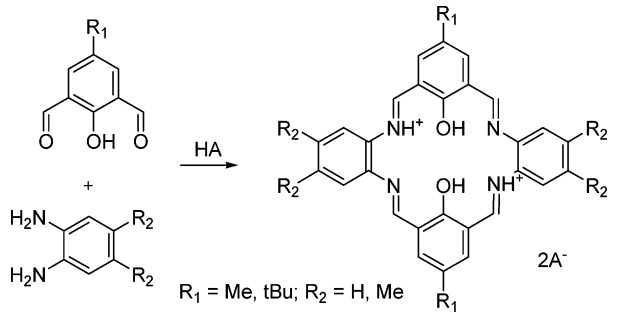
3.3. Reactions of Dicarbonyl Compounds with Aromatic Diamines

Aromatic diamines and unsaturated diamines which exist in the enamine form possess lower nucleophilicity compared with aliphatic ones. Reactions of *o*-phenylenediamine and its derivatives with aromatic dicarbonyl compounds have been most investigated. Since both amino groups of *o*-phenylenediamine are involved in direct conjugation, the reactivity of the second amino group after the end of condensation of the first one dramatically drops (Scheme 62). As a result, [1+1]-Schiff base **28** participates in further condensation only through a template path or acidic catalysis.

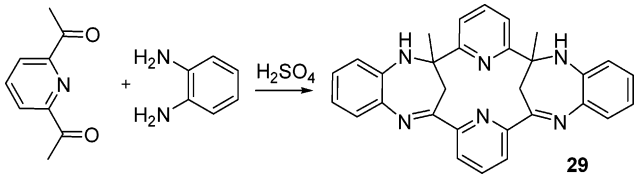
Thus, reactions of *o*-phenylenediamine and its derivatives with diformyl derivatives of phenols, pyrroles, or polypyrroles proceed smoothly only in the presence of acids to give salts of [2+2]-macrocycles (Schemes 63 and 64). In the case of pyrrole derivatives (Scheme 63), free macrocyclic bases were isolated by treating with triethylamine.

When dicarbonyl pyridine derivatives were used macrocycles were formed in the presence of sulfuric acid. The structure of the condensation product of 2,6-diacetylpyridine

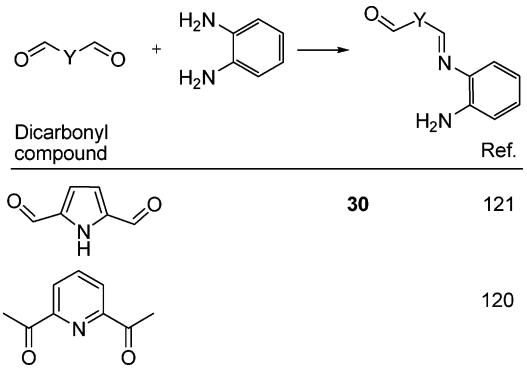
Scheme 64. Reaction of 2,6-Diformyl-4-alkylphenols with *o*-Phenylenediamine in the Presence of Acids[24]



Scheme 65. Synthesis of Macrocycle 29



Scheme 66. Reaction of Dicarbonyl Compounds with *o*-Phenylenediamine



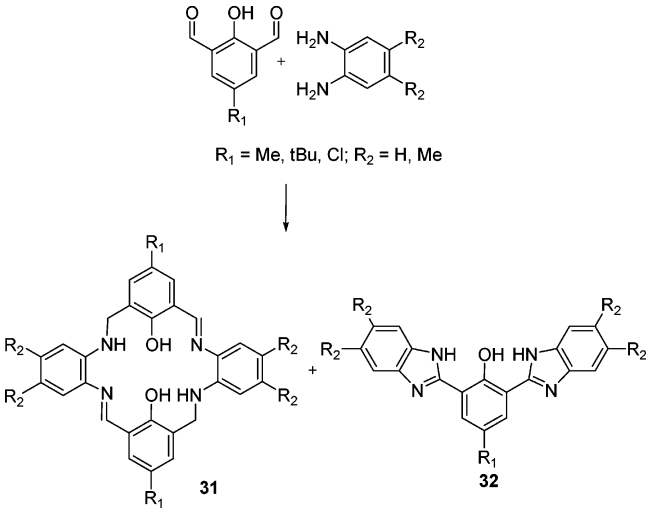
with *o*-phenylenediamine was initially assigned as [2+2]-macrocycle.[119] A more detailed examination of the reaction has shown that tricyclic product **29** was formed through intramolecular alkylation of the C=N bond after macrocycle closure[120] (Scheme 65).

Under acid-free conditions 2,5-diformylpyrrole and 2,6-diacetylpyridine react with *o*-phenylenediamine in ethanol to solely give [1+1]-condensation products (Scheme 66), which are not capable of reacting with dicarbonyl compound and diamine without additional activation.[120,121]

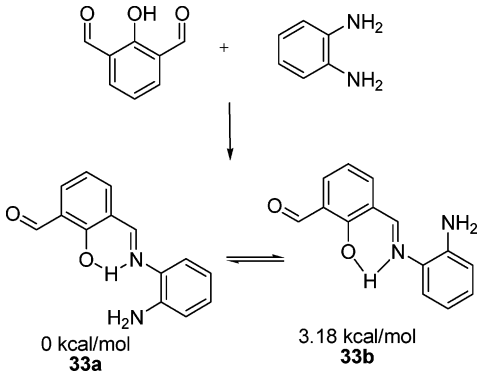
Since the carbonyl function of [1+1]-Schiff bases is involved in a delocalization path with the amino group, the reactivity of both groups decreases dramatically. According to X-ray analysis, two molecules of azomethine **30** give a stable dimer linked to each other by four hydrogen bonds. According to DFT calculations, the energy of formation of this dimer is 15.4 kcal/mol.[121] Since this energy is sufficient enough to stabilize this dimer in solutions, the ability of **30** to enter into further condensation proved problematic without adding template ion. The binuclear complex of a [2+2]-macrocycle is formed in 53% yield in the presence of nickel pivalate.[121]

Condensation of 2,6-diformylphenols with *o*-phenylenediamine in the absence of acid gives [2+2]-macrocyclic Schiff bases **31** and 2,6-bis(benzimidazol-2-yl)phenols **32**[27,122−124] (Scheme 67). It was indicated that macrocycle **31** (R^1 = Me; R^2 = H) can be also obtained by carrying out

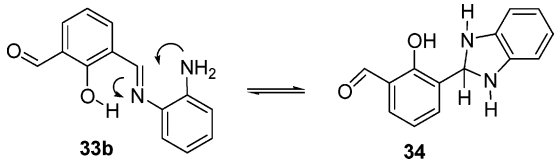
Scheme 67. Reaction of 2,6-Diformyl-4-alkylphenols with *o*-Phenylenediamines



Scheme 68. First Step of Condensation of 2,6-Diformylphenols with *o*-Phenylenediamines



Scheme 69. Formation of Benzimidazoline 34



condensation in the presence of a catalytic amount of hydrochloric acid .[25]

Similar to condensation of 2,5-diformylpyrrole or 2,6-diacetylpyridine, [1+1]-condensation product **33** is formed at the initial step of the above reaction[123] (Scheme 68).

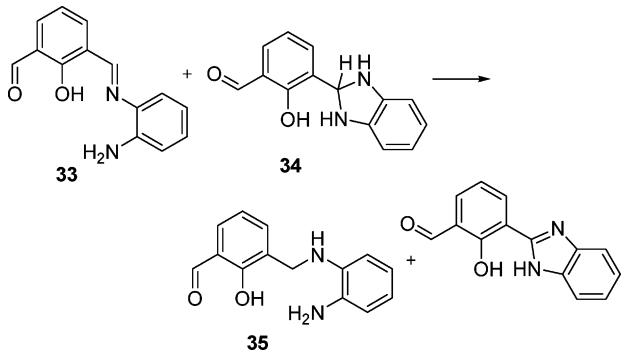
According to quantum-chemical DFT data, conformer **33b** coexists in equilibrium with **33a** and differs by 3.18 kcal/mol in energy, although **33a** is the most stable. In conformer **33b**, the distance between the nitrogen atom of the amino group and the carbon atom of the imino group is about 3.5 Å favorable to intramolecular ring closure (Scheme 69).

Benzimidazoline **34** in this process is a strong reducing agent. Its interaction with [1+1]-Schiff base results in reducing the latter to diamine **35** (Scheme 70).

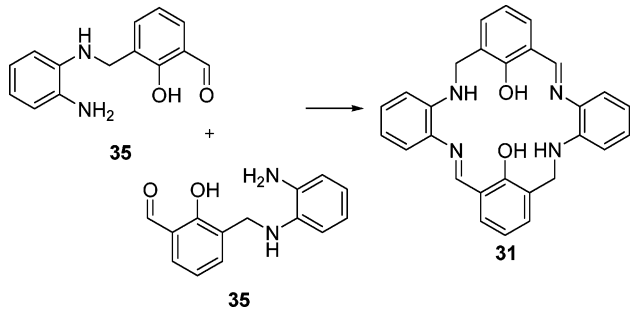
Two molecules of diamine **35**, in which the carbonyl and amino groups are separated by an aliphatic spacer, readily enter into subsequent condensation to form **31** (Scheme 71). This reaction is exothermic ($\Delta H° = -0.12$ kcal/mol, $\Delta G° = -9.15$ kcal/mol).

3,6-Diformylpyrocatechol reacts with *o*-phenylenediamines in acetonitrile under catalyst-free conditions to give [3+3]-

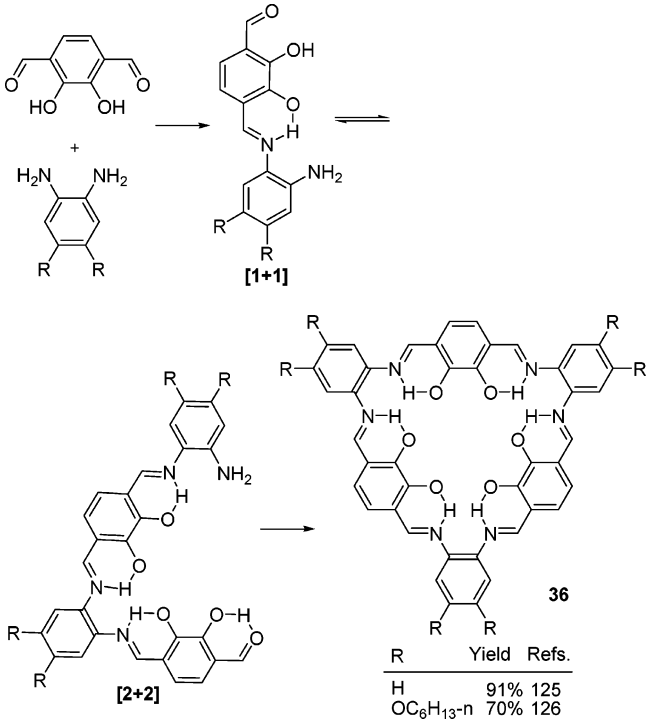
Scheme 70. Reduction of Azomethine 33 by Benzimidazoline 34



Scheme 71. Furnishing of Macrocycle 31



Scheme 72. Formation of [3+3]-Macrocycle 36

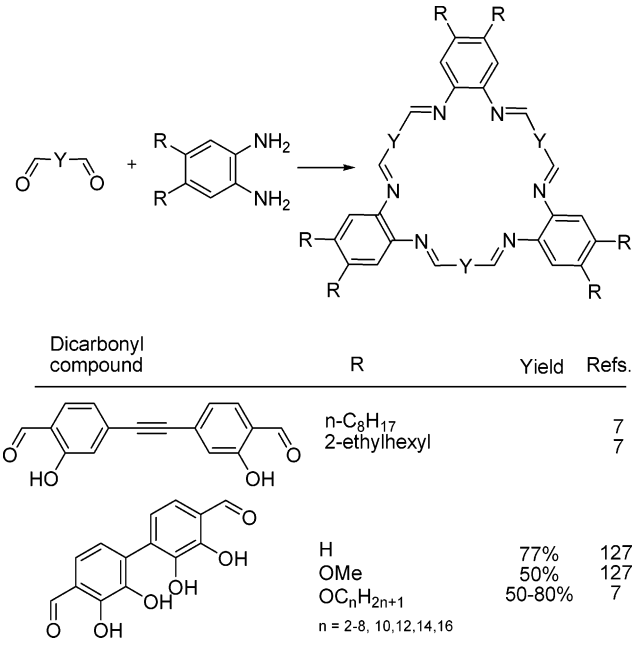


condensation product (trianglimines, Scheme 72). The reaction proceeds through the acyclic [1+1]- and [2+2]-condensation products, which are stabilized by a system of hydrogen bonds.[125,126] Thermodynamically the most stable [3+3]-macrocycle **36** precipitates from the reaction mixture, thus driving the process toward completion.

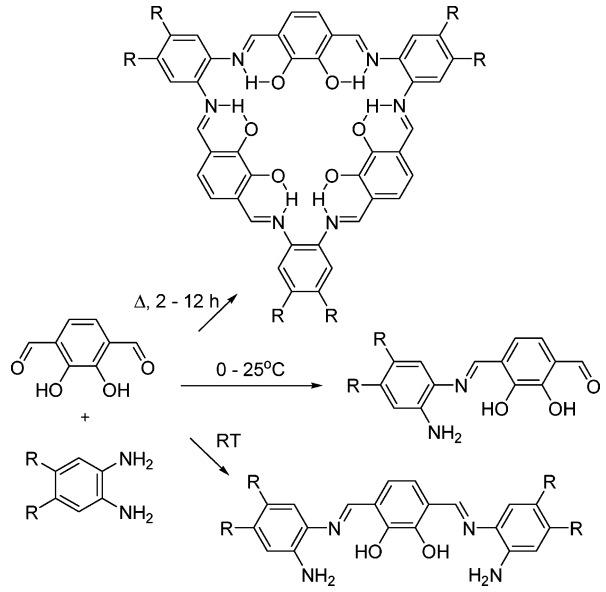
The above reaction was successfully applied to a broad variety of starting compounds[7,127] (Scheme 73).

According to the X-ray analysis, these antiaromatic 48 π-electron macrocycles are nonplanar.[7,125,127,128]

Scheme 73. Formation of [3+3]-Macrocycles from *o*-Phenylenediamines

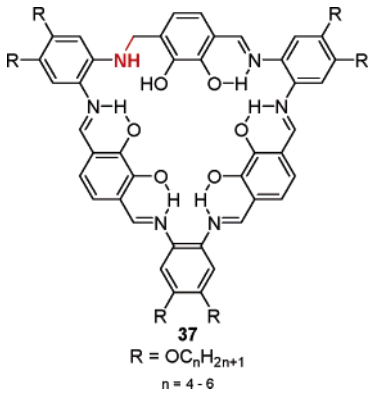


Scheme 74. Condensation of 3,6-Diformylpyrocatechol with Diamines



[3+3]-Macrocycles can be also produced when the reaction is carried out in a chloroform−acetonitrile mixture under reflux. When amines bearing longer side chains are loaded, prolonged heating is required to achieve reasonable yields.[7] The reaction mixture contains the whole set of [1+1]-, [1+2]-, and [2+1]-condensation products together with [3+3]-macrocycle. The contents of a dynamic combinatorial library are controlled by the reaction conditions (Scheme 74). Since the macrocycle is a thermodynamically controlled product, its yield can be optimized by prolonged reflux. When the reaction is kinetically controlled (low temperature and short reaction time), the [1+1]-condensation product is mainly formed, while the [1+2]-condensation product is obtained at ambient temperature. It should be noted that [1+2]- and [2+1]-compounds were shown to be intermediates in generating [3+3]-macrocycle, which is formed under thermodynamically controlled conditions.[7]

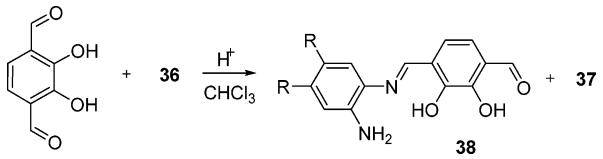
In addition to [3+3]-macrocycles, their reduced analogs **37** are always formed simultaneously during the course of



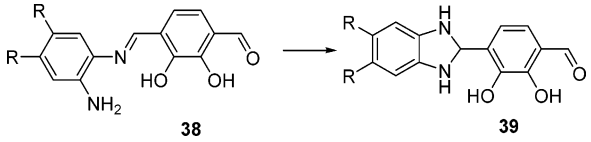
the reaction if commercial chloroform is used. When acid-free chloroform was utilized, no reduction products were detected.[7,129]

The mechanism of generating **37** is presented in Schemes 75−77. Reaction of macrocycle **36** with the starting dialde-

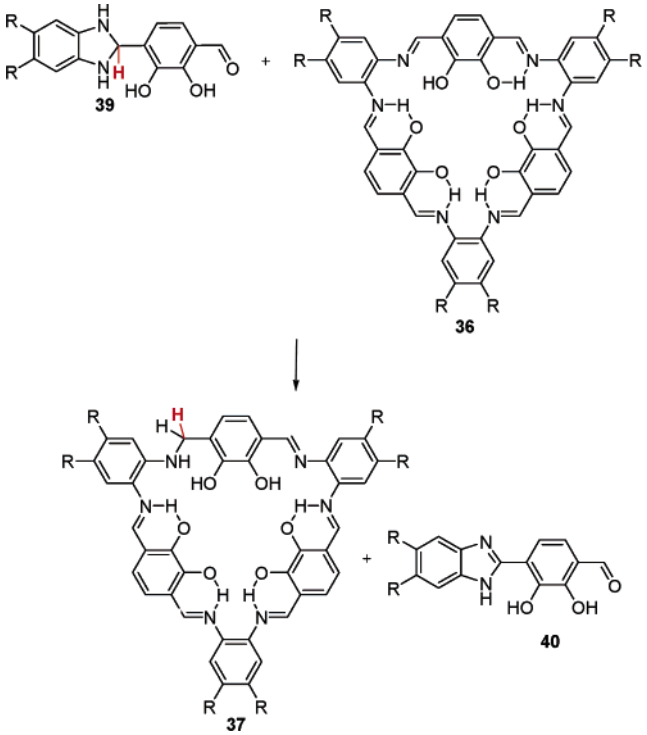
Scheme 75. Degradation of Macrocycle 36 in the Presence of Acid



Scheme 76. Intramolecular Cyclization of 38

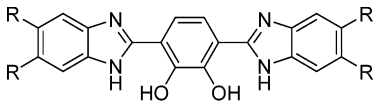


Scheme 77. Transformations of [3+3]-Macrocycle 36 toward Compound 37

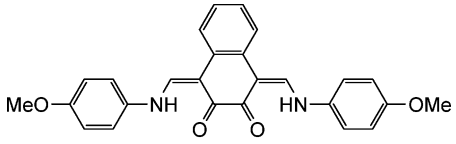


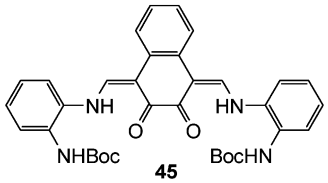
hyde in commercial chloroform containing trace amounts of acid affords products of macrocycle opening (e.g., [1+1]-condensation product **38**) (Scheme 75). The latter can form benzimidazoline derivative **39** (Scheme 76) through intramolecular cyclization similar to that described for acyclic azomethine **33b** (Scheme 69).[123] According to experiments with isotope labeling, upon reduction of [3+3]-macrocycle **36** the hydrogen atom located at position 2 of benzimidazoline is transferred to the carbon one of the imino group to give compound **37** (Scheme 77).[126]

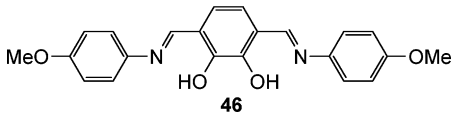
Disproportionation of **36** gives rise to reduced macrocycle **37** and benzimidazole derivative **40**. Bis(benzimidazol) derivative **41** was also found to be produced during the reaction.[7,129]



The methodology of [3+3]-condensing *o*-phenylenediamines with aromatic 1,4-dialdehydes was successfully applied to naphthalene derivatives as well as allowing creation of macrocycle **42**. The latter was found to exist only in keto-enamine tautomeric form with no azomethine **43** being detected[130] (Scheme 78). Strong hydrogen bonding between the phenolic hydroxyl group and the nitrogen atom of the imino group observed for related trianglimines governs full shift of the proton to the nitrogen in the case of naphthalene derivatives. Formation of suitable keto-enamine is a sufficient driving force to overcome aromatic stabiliza-

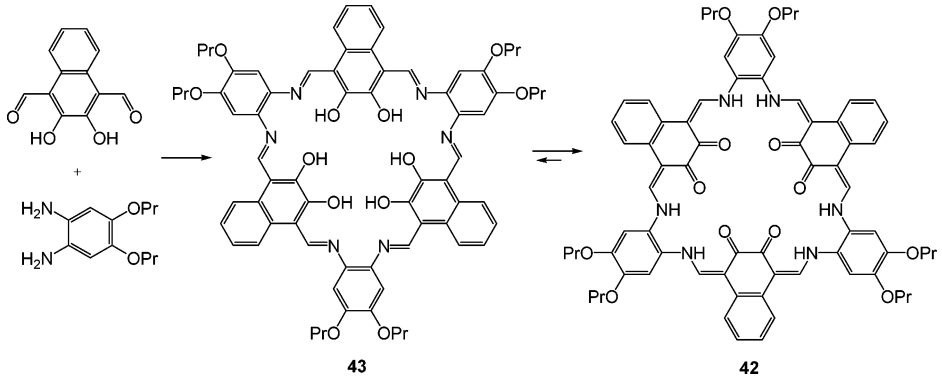




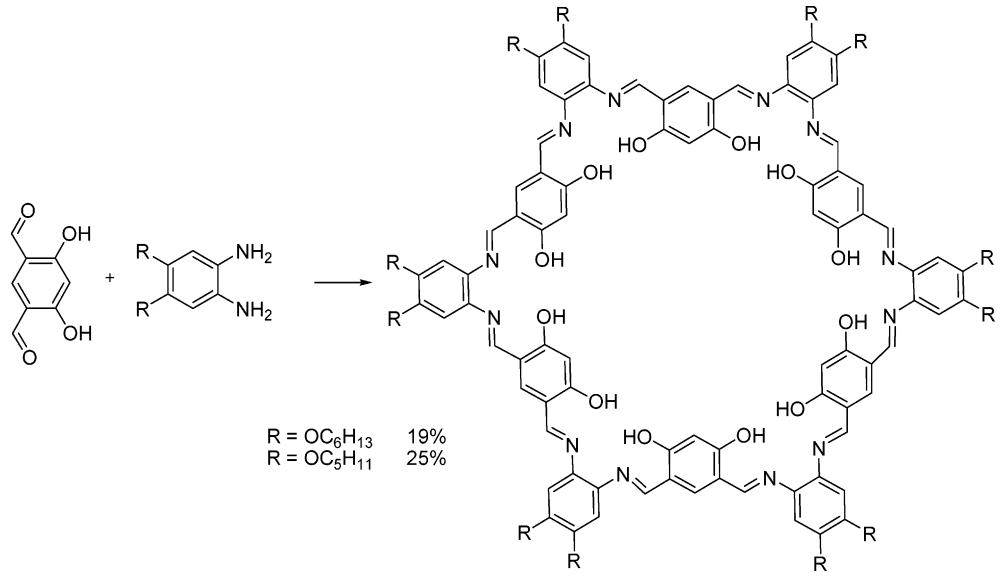


tion of the second ring in naphthalene.[130] According to quantum-chemical calculations and X-ray analysis, model azomethines of 1,4-diformyl-2,3-dihydroxynaphthalene derivatives **44** and **45**, unlike their monocyclic analogs **46**, exist only in keto-enamine form.

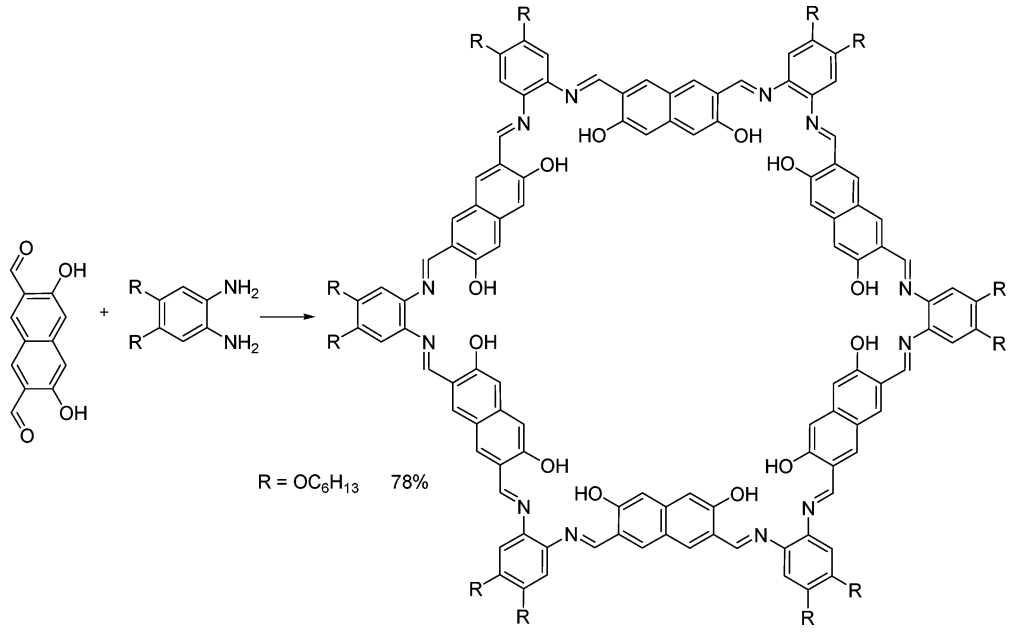
Scheme 78. Condensation of 3,4-Dipropoxy-1,2-phenylenediamine with 1,4-Diformyl-2,3-dihydroxynaphthalene



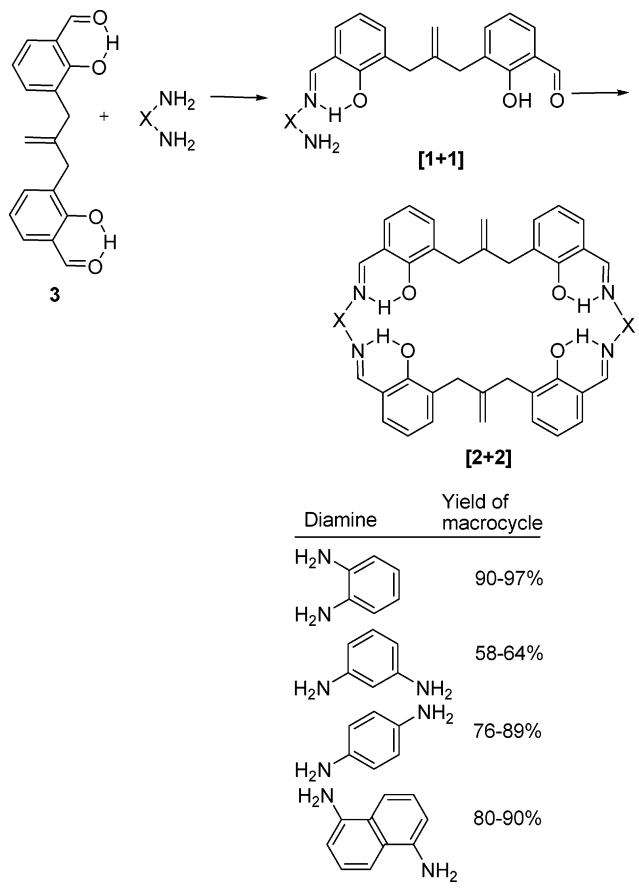
Scheme 79. [6+6]-Macrocyclization of *o*-Phenylenediamines and 4,6-Diformylresorcine



Scheme 80. [6+6]-Macrocycle Formation from Naphthalene Dicarbonyl Precursor



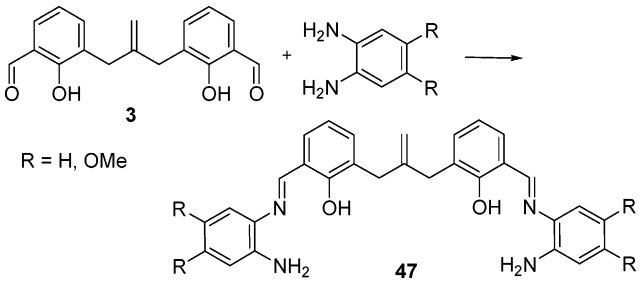
Scheme 81. Reaction of Dialdehyde 3 with Aromatic Diamines



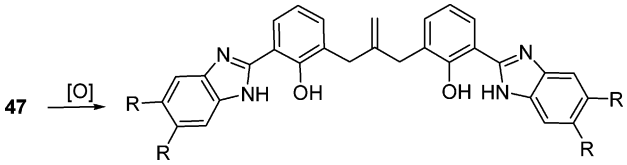
Formation of multiple hydrogen bonds is also a powerful driving force for macrocyclization. If two hydroxyl groups in an aromatic ring are in a meta position to each other, the [6+6]-macrocycle could be prepared[131] (Scheme 79).

Utilizing a rigid precursor that is predisposed to a particular geometry, [6+6]-macrocycle could be synthesized as well[131] (Scheme 80).

Scheme 82. Synthesis of [1+2]-Condensation Product 47



Scheme 83. Oxidation of Compound 47



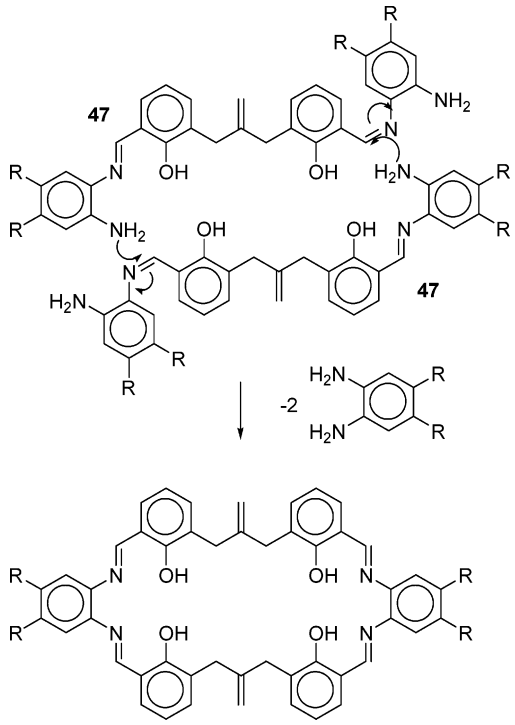
If the delocalization path between the carbonyl groups in polycyclic dicarbonyl compounds is absent, the reactivity of dicarbonyl compounds with respect to aromatic diamines is considerably enhanced. Treatment of 0.1 M solutions of dialdehyde **3** with aromatic diamines (1:1 molar ratio) in THF or DMF for 30 h at room temperature affords the corresponding [2+2]-macrocycles[35] (Scheme 81). According to the ^{1}H NMR data, both [1+1]-condensation products were initially formed and final [2+2]-macrocycles were stabilized by strong hydrogen bonds between the phenol hydroxyls and azomethine nitrogen atoms.[35]

Treatment of dilute (0.04 M) methanol solutions of dialdehyde **3** with *o*-phenylenediamine (1:6 molar ratio) at room temperature leads to [1+2]-condensation product **47** in 85% yield[132] (Scheme 82).

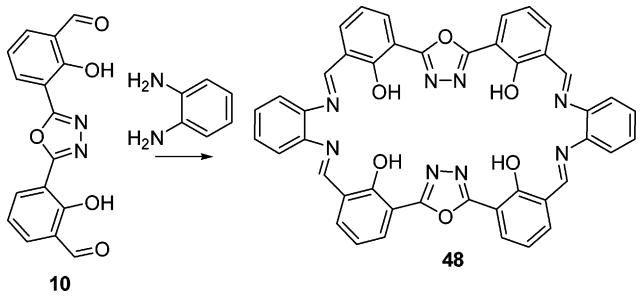
Schiff bases **47** are very sensitive to air oxygen and oxidized to the corresponding benzimidazole derivatives (~13%)[132] (Scheme 83).

According to X-ray analysis, molecules of **47** in the unit cell form a dimer structure in which the nitrogen atoms of the amino groups are in close vicinity with the carbon atoms

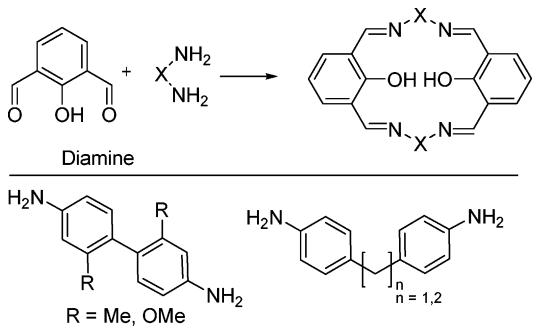
Scheme 84. Cyclization of Compound 47



Scheme 85. Synthesis of [2+2]-Macrocycle 48



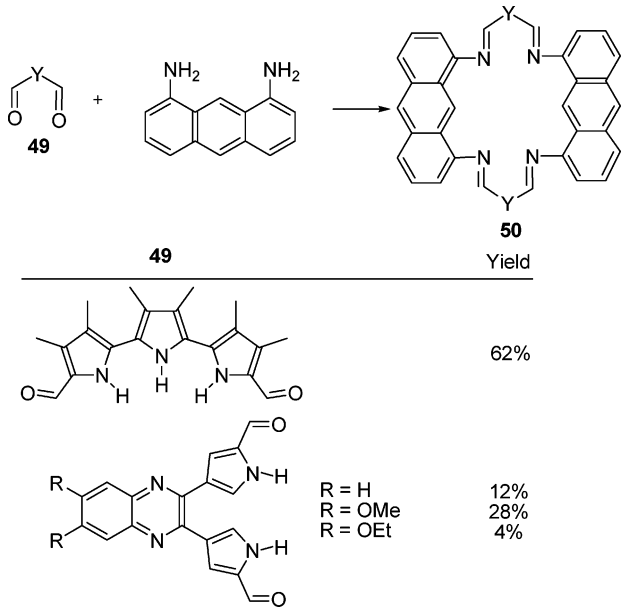
Scheme 86. Reaction of 2,6-Diformylphenol with Some Aromatic Diamines



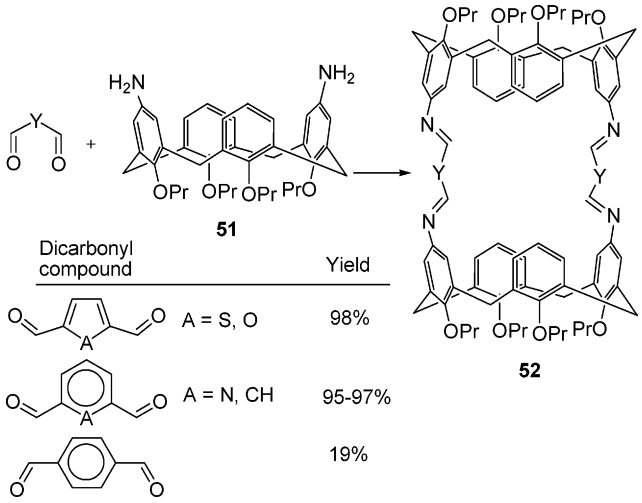
of the azomethine fragments of the neighboring molecule. It is supposed that the dimeric structure of **47** exists in solution. On the basis of this assumption, dimerization of **47** to [2+2]-macrocyclic Schiff base can be explained[132] (Scheme 84).

An illustrative example of the stoichiometrically controlled condensation of the polycyclic dicarbonyl compound with *o*-phenylenediamine is given in Scheme 85.[39] Thus, treatment of dicarbonyl compound **10** with *o*-phenylenediamine in a 0.01 M acetonitrile solution gives [2+2]-macrocycle **48** in 74% yield.

Scheme 87. Synthesis of [2+2]-Macrocycles 50



Scheme 88. Reaction of Dicarbonyl Compounds with Diaminocalixarene 51



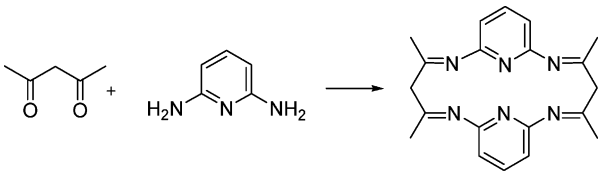
When polycyclic aromatic diamines containing amino groups in different aromatic rings are treated with dicarbonyl compounds, they act similar to aliphatic α,ω-diamines. Thus, condensation of equimolar amounts of 2,6-diformylphenol with diamines bearing amino functions in different phenyl rings affords the expected [2+2]-macrocycles[133] (Scheme 86).

Reaction of 1,8-diaminoanthracene with diformylpyrroles **49** under acid-catalyzed conditions also leads to [2+2]-macrocyclic Schiff bases **50**[115,134] (Scheme 87).

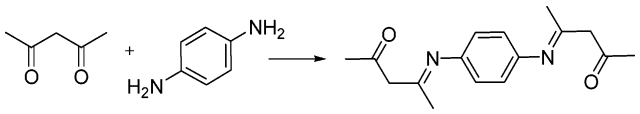
Treatment of diaminocalix[4]arene **51** with various diformyls (1:1 molar ratio) gives [2+2]-macrocycles **52** in high yields[135,136] (Scheme 88).

Azomethines obtained from aromatic diamines and aliphatic dicarbonyl compounds are stable enough to be isolated as free ligands, whereas azomethines derived from aliphatic diamines exist only as metal complexes. Thus, condensation of acetylacetone with 2,6-diaminopyridine in methanol in the presence of acidic catalyst affords the corresponding [2+2]-macrocycle in 71% yield[137] (Scheme 89).

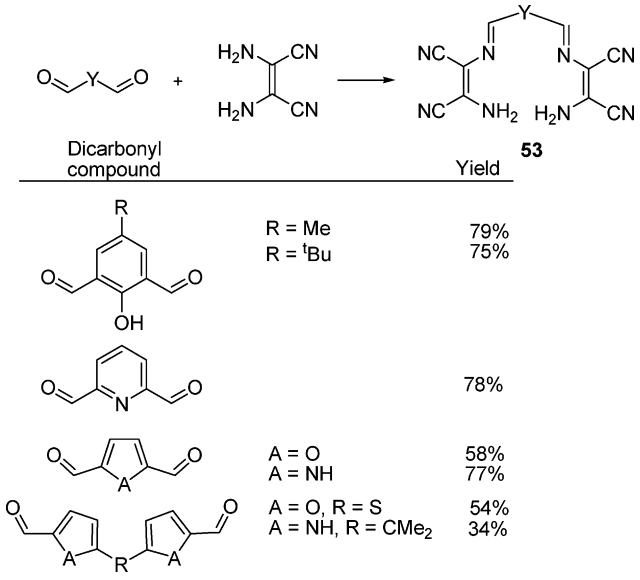
Scheme 89. Condensation of Acetylacetone with 2,6-Diaminopyridine



Scheme 90. [2+1]-Condensation of Acetylacetone with *p*-Phenylenediamine



Scheme 91. Reaction of 2,3-Diaminomaleodinitrile with Dicarbonyl Compounds



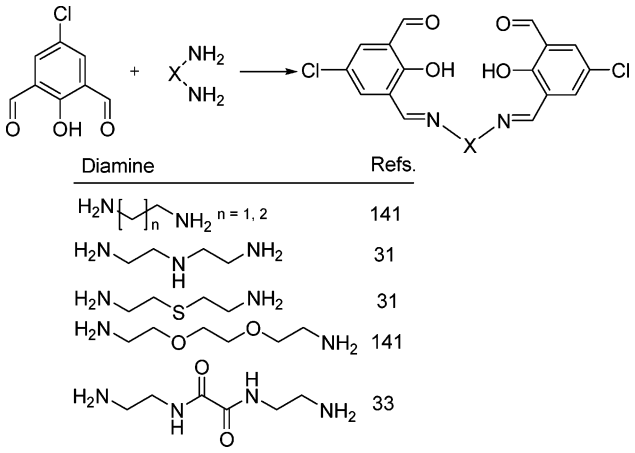
Treatment of acetylacetone with of *p*-phenylenediamine (1:1 molar ratio) solely gives [2+1]-condensation product in 82−96% yield[138] (Scheme 90).

3.4. Reactions of Dicarbonyl Compounds with 2,3-Diaminomaleodinitrile

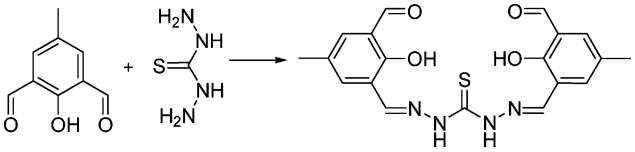
Formally, 2,3-diaminomaleodinitrile existing in the enamine form as well as *o*-phenylenediamine comprises reduced basicity and nucleophilicity due to the strong acceptor influence of the two nitrile groups conjugated with amino functions. As a result, reactions of this diamine with dicarbonyl compounds lead to [1+2]-condensation products **53** (Scheme 91). The latter represent a new class of polydentate Schiff bases with open structure.[139,140]

When condensation of the first group is completed, the nucleophilicity of the second group decreases dramatically, thus excluding the very possibility of further condensation. As a result, diamines **53** are the only products. DFT calculations have demonstrated that acyclic azomethines **53** are capable of incorporating one or two transition-metal cations into the inner cavity.[139,140] A broad variety of supramolecular structures can be created using addition coordination capacity provided by the four nitrile groups available.

Scheme 92. [2+1]-Condensation of 2,6-Diformyl-4-chlorophenol with Aliphatic Diamines



Scheme 93. Reaction of Thiocarbohydrazide with 2,6-Diformyl-4-methylphenol



4. Synthesis of Macrocyclic Schiff Bases of Nonsymmetric Structure: Strategy for Fragment-to-Fragment Assembling from Enlarged Building Blocks

4.1. Acyclic Condensation Products from Dicarbonyl Compounds and Diamines

[2+1]-Condensation products, readily available by reacting dicarbonyl compounds with diamines in a 2:1 molar ratio, provide a promising class of building blocks useful for assembling nonsymmetric macrocycles. The versatility of this method was demonstrated by efficient synthesis of [2+1]-dicarbonyl blocks from 2,6-diformylphenols and aliphatic diamines in a 2:1 molar ratio (Scheme 92). The ratio of the starting compounds plays a crucial role in providing selectivity of the above reaction, whereas the degree of dilution does not affect the process.

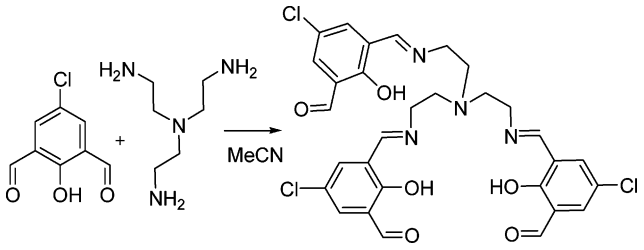
When 2,6-diacetyl-4-methylphenol and ethylenediamine are used the yield of the [2+1]-condensation product is 88%.[142] Reaction of thiocarbohydrazide with dicarbonyl phenol in a 1:2 molar ratio provides [2+1]-condensation product in 75% yield[74] (Scheme 93).

[3+1]-Condensation product can be obtained if 2,6-diformylphenols and tris(2-aminoethyl)amine react in a 3:1 molar ratio in anhydrous acetonitrile[81,141,143,144] (Scheme 94). Acyclic condensation product is formed only if a stoichiometric ratio of reactants is used; otherwise, cryptands formation occurs (see section 3.1).

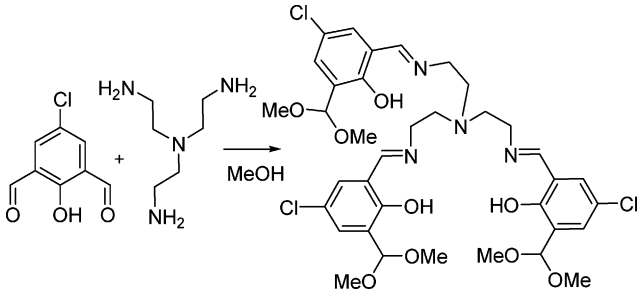
When the reaction is carried out in methanol, the corresponding acetal is formed instead of the triformyl derivative[145] (Scheme 95).

Attempts to perform the stoichiometrically controlled [1+2]-condensation of a dicarbonyl compound with two equivalents of aliphatic diamine were unsuccessful. [1+2]-Condensation products are only formed when 50−100-fold excess of diamine is used, but they cannot be isolated as

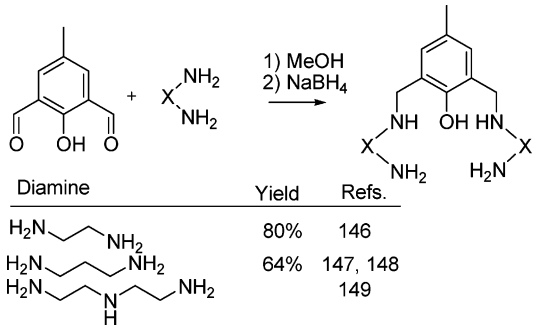
Scheme 94. [3+1]-Condensation of 2,6-Diformyl-4-chlorophenol with Tris(2-aminoethyl)amine



Scheme 95. Reaction of 2,6-Diformyl-4-chlorophenol with Tris(2-aminoethyl)amine in Methanol



Scheme 96. [1+2]-Condensation of 2,6-Diformyl-4-methylphenol with Aliphatic Diamines



Diamine	Yield	Refs.
H_2N–(CH$_2$)$_2$–NH_2	80%	146
H_2N–(CH$_2$)$_3$–NH_2	64%	147, 148
H_2N–(CH$_2$)$_2$–NH–(CH$_2$)$_2$–NH_2		149

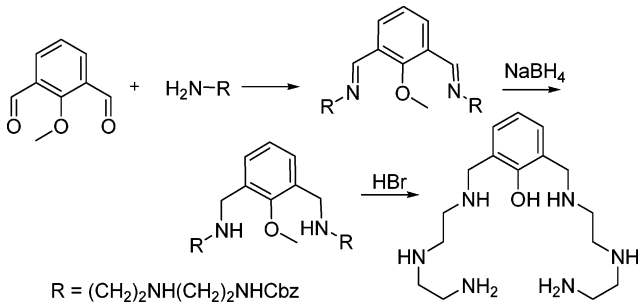
single substances. The corresponding amines can be only obtained after reduction of Schiff bases with sodium borohydride (Scheme 96).

With the aim of obtaining pure [1+2]-diamine blocks, special methods for their controlled synthesis were developed. The first step implies selected protection of only one amino group of the diamine followed by deprotection after further condensation and reduction of the amino group. Thus, treatment of monoacetyl[150] and monobenzyloxycarbonyl[151] derivatives of 1,3-diaminopropane or diethylenetriamine with diformylpyridines or diformylanisoles gives [1+2]-condensation products without the necessity of using excess amounts of reactants. The resulting Schiff bases were reduced in situ to the corresponding amines, and then protective groups were removed to furnish the target blocks[150,151] (Schemes 97 and 98).

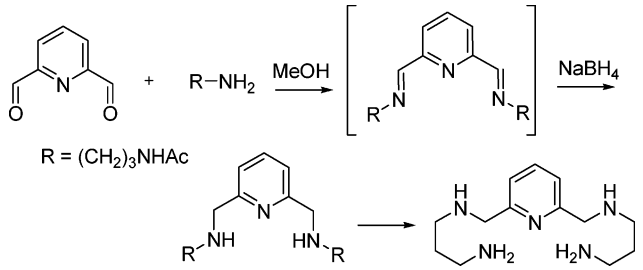
Reactions of 2,6-diformyl-4-R-phenols (R = H, Cl) with a twofold excess of the diaminocalixarene **51** in methanol afford the stoichiometrically controlled [1+2]-condensation product in 56% yield[86] (Scheme 99). Here, aromatic diamine gives [1+2]-condensation products without eventual macrocyclization.

Similar to aliphatic diamines, one amino group in the starting diamine is protected to provide selective [1+2]-condensation between dicarbonyl compounds and *o*-phenylenediamine. Thus, *N*-acetyl-*o*-phenylenediamine reacts

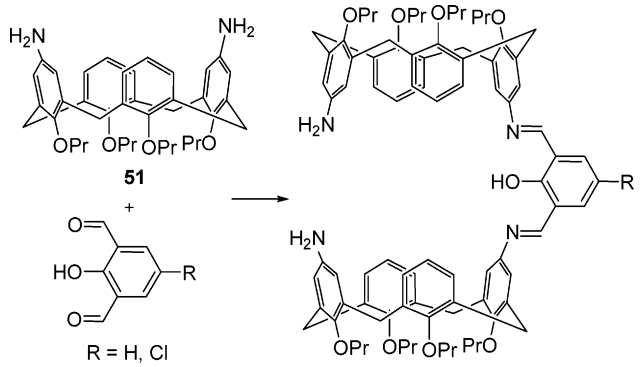
Scheme 97. Directed Synthesis of [1+2]-Condensation Products from 2,6-Diformylphenol



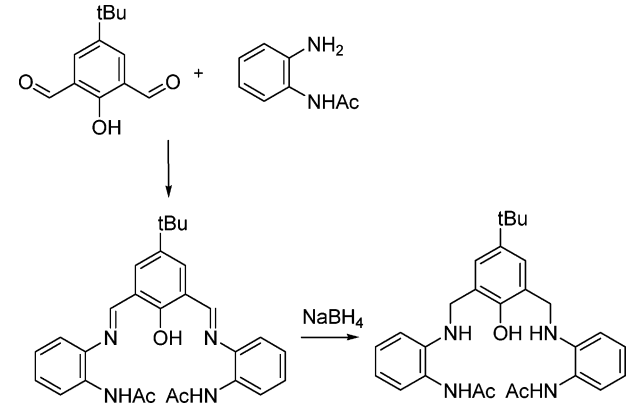
Scheme 98. Directed Synthesis of [1+2]-Condensation Products from 2,6-Diformylpyridine



Scheme 99. [1+2]-Condensation of 2,6-Diformylphenols with Diaminocalixarene 51



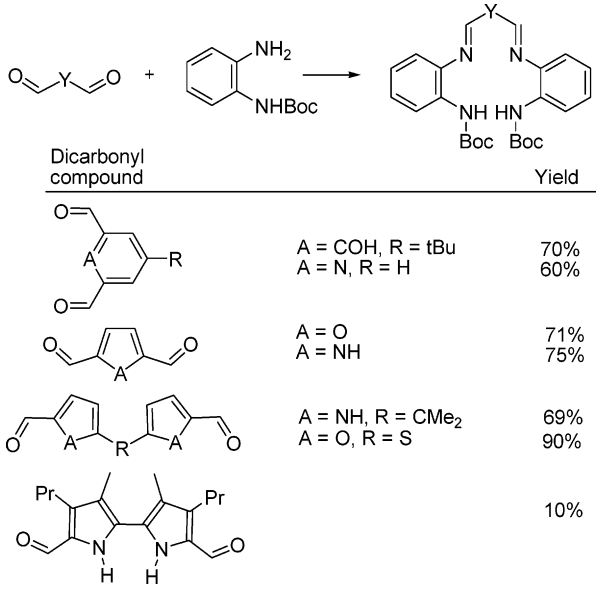
Scheme 100. Directed Synthesis of [1+2]-Condensation Products from 2,6-Diformyl-4-methylphenol and *N*-Acetyl-*o*-phenylenediamine



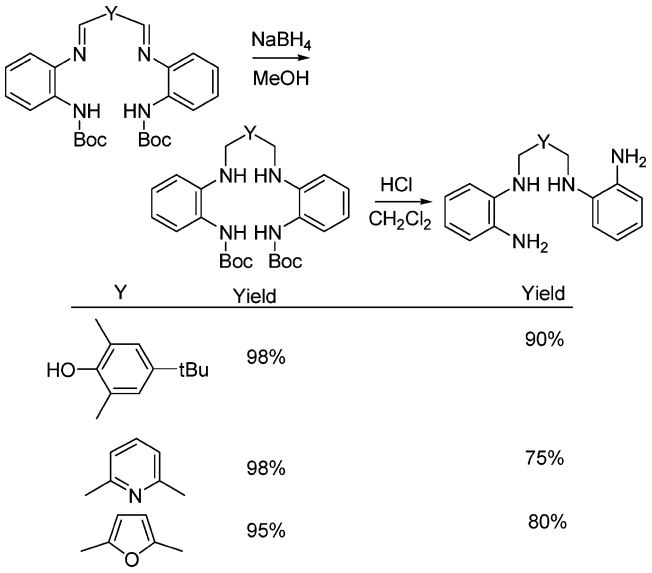
with 2,6-diformyl-4-*tert*-butylphenol in methanol at ambient temperature to give [1+2]-condensation product in 98% yield; further reduction with $NaBH_4$ allows obtaining tetraamine[152,153] (Scheme 100).

When the same protocol is applied, *N*-*tert*-butoxycarbonyl-*o*-phenylenediamine affords [1+2]-Schiff bases (Scheme

Scheme 101. Directed Synthesis of [1+2]-Condensation Product from *N*-*tert*-Butoxycarbonyl-*o*-phenylenediamine



Scheme 102. Reduction and Deprotection of [1+2]-Condensation Product from *N*-*tert*-Butoxycarbonyl-*o*-phenylenediamine



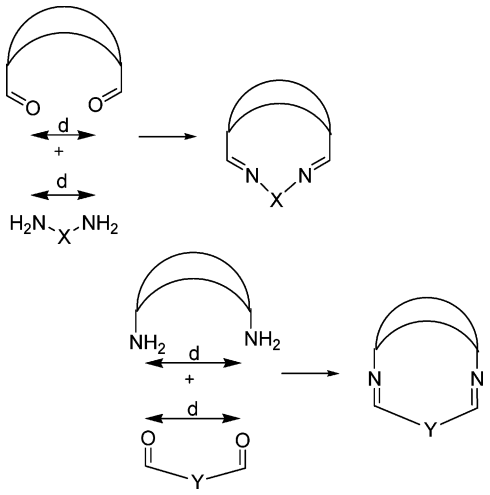
101). Further reduction and deprotection by gaseous HCl in methylene chloride give acyclic diamines[153] (Scheme 102).

Judging by the well-documented flexibility of the above approach, one can prepare a broad variety of diamines and dicarbonyl derivatives comprising additional functional groups amenable for further synthetic manipulations. They can be used as building blocks to create macrocycles with a more complicated structure, which are of interest as polydentate ligands.

4.2. Strategy for Assembling of Macrocyclic Schiff Bases from Enlarged Building Blocks

Extensive literature analysis allows one to assume that condensation of dicarbonyl compounds with diamines provides a powerful synthetic tool toward creating numerous polydentate Schiff bases. Special attention was focused on nonsymmetric macrocycles containing at least two non-

Scheme 103. Fragment-to-Fragment Assembling of Macrocyclic Schiff Bases



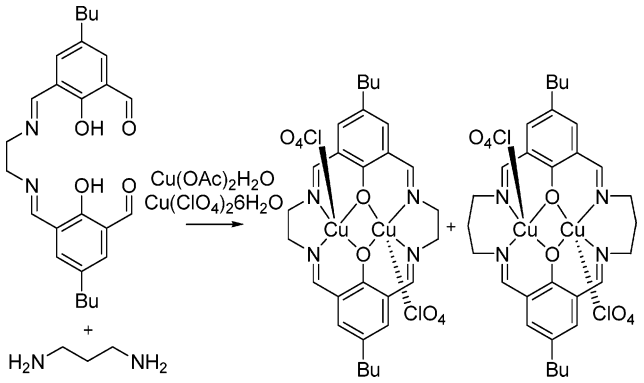
equivalent coordination environments inside the cavity. Soft donor functionality is optimal for bonding late transition-metal ion, whereas a hard site allows fixing earlier transition-metal ions. This type of complexes (the so-called heterobinuclear early−late complexes) is of extreme interest as catalysts. On the basis of quantum-chemical calculations, this family of complexes is capable of bonding and activating various low reactive substrates (alkenes, carbon oxide and monoxide, nitrogen, and even alkanes) through concerted push−pull interaction of guest molecule with two catalytic centers.[154] Several reviews have been devoted to the synthesis, structure, and properties of heterobinuclear complexes.[20−22,155]

In previous sections, we described some illustrative examples of obtaining nonsymmetric macrocyclic Schiff bases. The most promising strategy for fragment-to-fragment assembling of macrocyclic Schiff bases is convergent and implies [1+1]-condensation of preliminary produced difunctional blocks. According to this strategy, diamine and dicarbonyl components are most frequently used, although blocks containing two different functional groups are also utilized. The above-mentioned blocks are synthesized through [1+2]- and [2+1]-condensations (section 4.1). The most studied case is one that implies use of building blocks containing one coordinated metal ion.

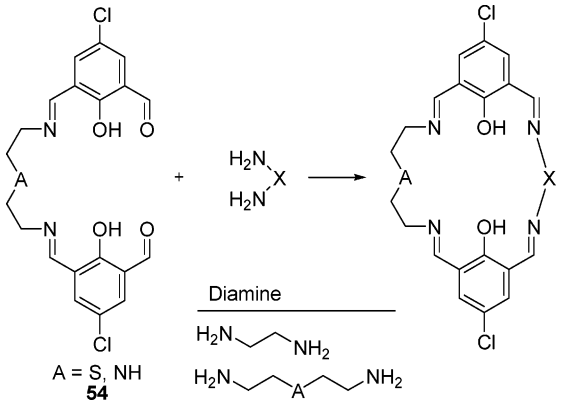
Complementarity of reagents is the main structural requirement for successful macrocycle closure (Scheme 103); the ability of reagents to adopt a conformation favorable for cyclization should be also considered.

The choice of appropriate solvent capable of stabilizing these conformations is of special importance. The reactions can be performed both under acidic catalysis conditions and in the absence of acid. In some cases, the anion nature exerts a substantial effect on the reaction in the presence of acids, which indicates that anions can act as template agents (see below). Many [1+1]-condensations of large difunctional blocks using metal ions as template agents have been described.[21,22,155] In these type of reactions the metal ion provides preliminary coordination of the polydentate fragment by fixing the conformation favorable for cyclization. In addition, the metal coordination number and ionic radii determine the size of the ring formed. Very frequently at the first step metal ions are inserted into preliminarily prepared dicarbonyl blocks to fix them in a rigid geometry

Scheme 104. Unexpected Formation of Symmetric Complexes during Fragment-to-Fragment Assembling



Scheme 105. Macrocyclization of Dicarbonyl Precursors Based on Substituted Phenols



suitable for template assembling of the macrocyclic Schiff bases in the reaction with diamines. Template assembling of macrocycles from diamine blocks is not popular since starting blocks are scarce.

This approach of assembling mono- and binuclear complexes is of particular usefulness for dicarbonyl precursors derived from substituted phenols. Due to the reversibility of Schiff condensation, a dynamic combinatorial library of products is usually observed, thus complicating the procedure of obtaining target macrocycles. As a result, a mixture of symmetric complexes can be formed instead of the expected products of nonsymmetric structure[156] (Scheme 104). It is probably caused by the higher thermodynamic stability of homobinuclear complexes of symmetric structure.

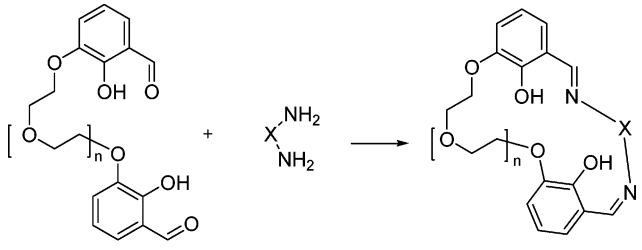
The next section is focused on metal-free reactions of dicarbonyl and diamine blocks to give unsymmetrical macrocycles.

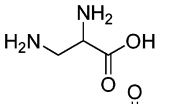
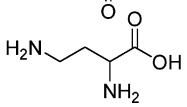
4.3. Metal-Free Assembling in the Absence of Acidic Catalyst

Usually macrocycles are assembled from enlarged blocks in aprotic solvents (acetonitrile, chloroform, dioxane), which rather poorly solvate polar carbonyl and amine groups of the starting compounds but do not prevent formation of hydrogen bonds between them. This bonding provides the required orientation of molecules during the reaction, allowing macrocyclization to become the predominant direction.

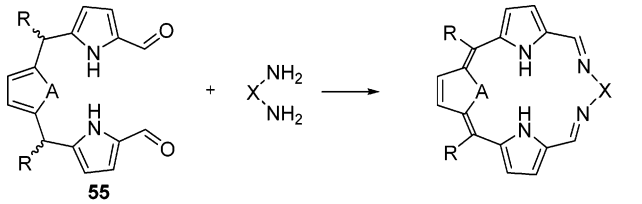
Thus, dicarbonyl blocks **54** react with diamines in chloroform at ambient temperature under kinetically controlled conditions to form nonsymmetric macrocycles without any oligomerization[31] (Scheme 105).

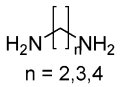
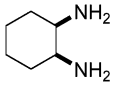
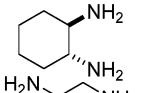
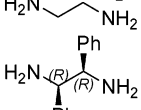
Scheme 106. Macrocyclization of Dicarbonyl Precursors Containing the Oxaethylene Chains



Diamine	Yield	Ref.
$H_2N(CH_2)_2NH_2$	62-65%	157, 158
$H_2N(CH_2)_3NH_2$	42%	159
$H_2N(CH_2)_2N(CH_2)_2NH_2$	55-60%	160, 157
$H_2N(CH_2)_2NH(CH_2)_2NH_2$	60-70%	157
$H_2N(CH_2)_2N(C_{11}H_{23})(CH_2)_2NH_2$	54-59%	158
$H_2N(CH_2)_3NH(CH_2)_3NH_2$	54-59%	158
	69-70%	158
	69-70%	158

Scheme 107. Condensation of 55 with Diamines

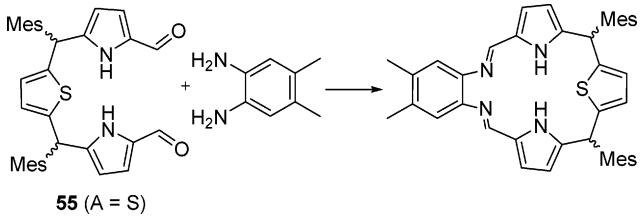


Diamine		Yield	Refs.
 n = 2,3,4	A=S; R=Mes		161
	A=S; R=Mes		161
	A=S; R=Mes		161
	A=S; R=Ph	20%	162
	A=S; R=Ph A=S; R=Mes	40% 50%	162 162
$H_2N{-}NH_2$	A=O; R=Mes	43%	163

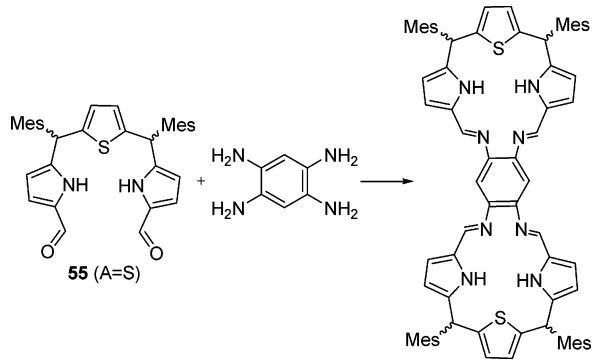
[1+1]-Macrocycles are the major condensation products when polar aprotic solvents (chloroform, acetonitrile) are used. Separation of carbonyl groups by a long flexible oxaethylene chain is also desirable if dicarbonyl phenol derivatives react with aliphatic α,ω-diamines[157−160] (Scheme 106).

High dilution is also required when obtaining [1+1]-condensation products. Thus, reactions of dicarbonyl building

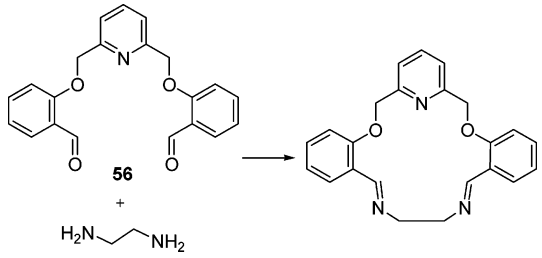
Scheme 108. Condensation of 55 (A = S) with *o*-Phenylenediamine



Scheme 109. Condensation of 55 (A = S) with 1,2,4,5-Tetraaminobenzene



Scheme 110. Reaction of 56 with Ethylenediamine



blocks **55** with 1,2-diamines afford [1+1]-condensation products in moderate yields only at concentrations of 2×10^{-3} M in the presence of molecular sieves[161−163] (Scheme 107). Under these conditions, oxidation of the polycyclic system occurs together with condensation. The reactivity of blocks **55** is determined by the spatial orientation of the carbonyl groups.

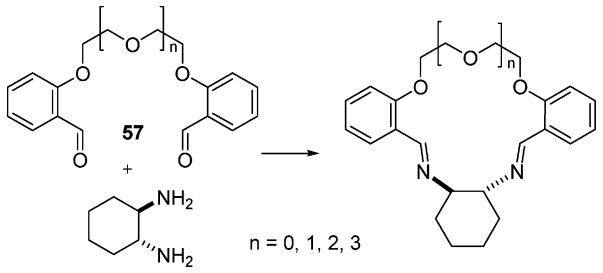
Reactions of the above dicarbonyl compounds with *o*-phenylenediamine also afford [1+1]-macrocycles. Treatment of dicarbonyl derivative **55** (A = S) with *o*-phenylenediamine leads to the expected [1+1]-macrocycle[161] (Scheme 108). Contrary to macrocycles bearing aliphatic diamine fragments, no dehydrogenation leading to a conjugated macrocyclic system was observed in the case of the above reaction. This fact is possibly due to the antiaromaticity of the fully conjugated macrocycle which could be formed.

Similar condensation of **55** (A = S) with 1,2,4,5-tetraaminobenzene gives unusual bicyclic Schiff base[161] (Scheme 109).

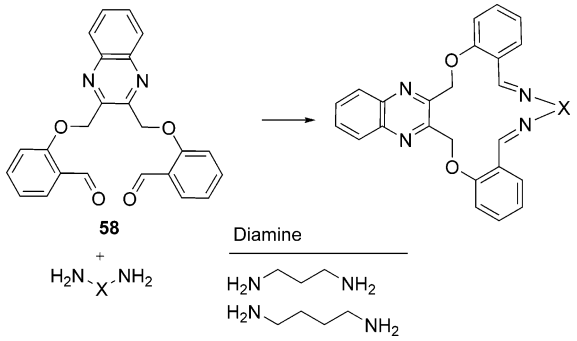
Macrocyclic Schiff bases can also be furnished in methanol under thermodynamically controlled conditions. Thus, treatment of dicarbonyl compound **56** with ethylenediamine in boiling methanol affords macrocyclic [1+1]-condensation product in 68% yield[164] (Scheme 110).

Similarly, treatment of dicarbonyl compounds **57** with racemic *trans*-1,2-diaminocyclohexane leads to [1+1]-macrocycles in 89−95% yields[165] (Scheme 111).

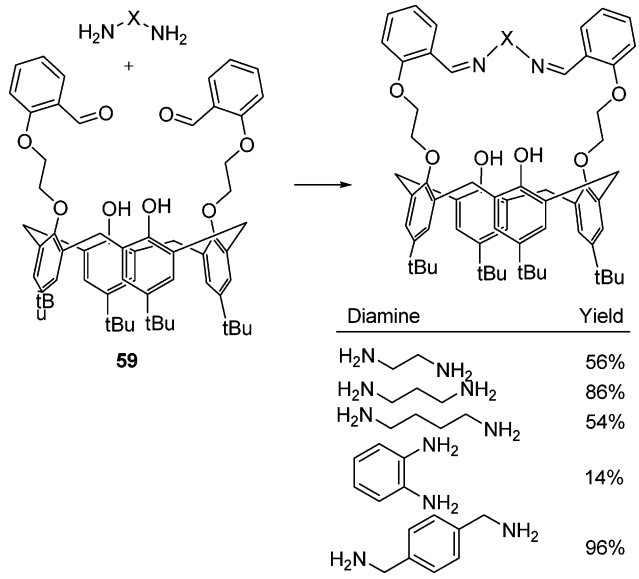
Scheme 111. Condensation of 57 with Racemic *trans*-1,2-Diaminocyclohexane



Scheme 112. Condensation of Dialdehyde 58 with Aliphatic Diamines



Scheme 113. Reaction of Dicarbonyl Block 59 with Diamines

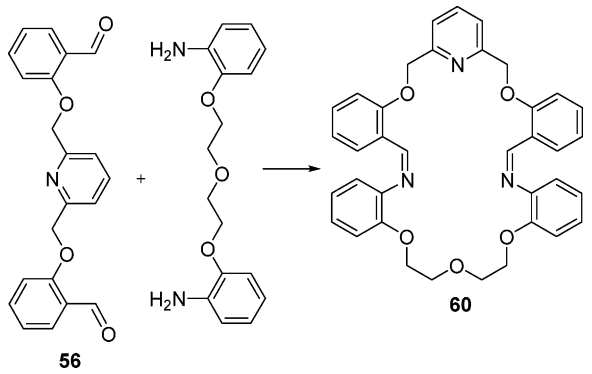


If structures of the dicarbonyl block and diamine are not complementary, a mixture of products is usually formed. For instance, dicarbonyl derivative **58** reacts with ethylenediamine to give mixture of the [1+1]- and [2+2]-condensation products which could not be separated into individual components. By treating the above block with 1,3-diaminopropane or 1,4-diaminobutane, only [1+1]-condensation products were obtained[166] (Scheme 112).

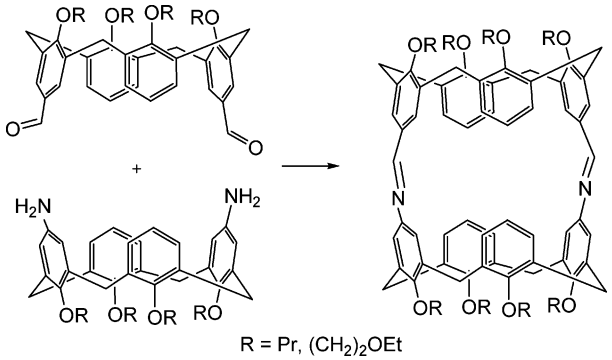
When calixarene **59** was used, [1+1]-macrocycles were obtained upon prolonged (21 h) reflux in methanol−acetonitrile mixture[167] (Scheme 113).

The enlarged precursor blocks can react with each other to form a huge macrocycle. Thus, dialdehyde **56** reacts in boiling methanol not only with 1,2-diaminoethane (Scheme 110) but also with more expanded diamines containing the polyoxaethylene chain, causing macrocycle **60** to form in

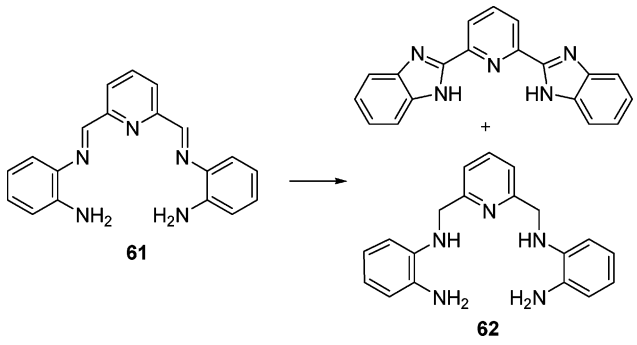
Scheme 114. Synthesis of Macrocycle 60



Scheme 115. [1+1]-Condensation of Precursors of the Calixarene Type



Scheme 116. Redox Disproportionation of 61



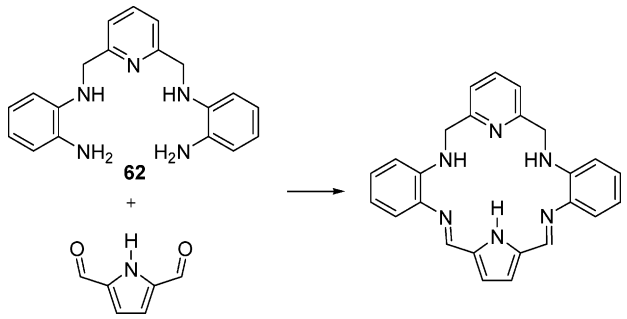
31−75% yield[168,169] (Scheme 114).

Diformylcalixarenes react with the complementary diamine blocks to form [1+1]-macrocycles in high (74−92%) yields[170] (Scheme 115).

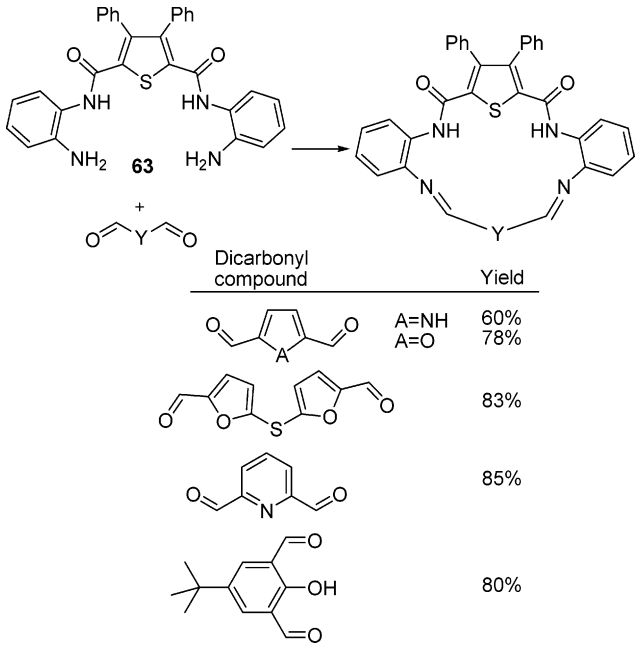
Application of diamine blocks in fragment-to-fragment assembling is limited by their low synthetic availability. Diamine **61**, obtained by demetalation of template [1+2]-condensation product of 2,6-diformylpyridine with *o*-phenylenediamine,[49] does not react with dicarbonyl compounds due to the electron-acceptor effect of the azomethine groups conjugated with the amino ones (see sections 3.3 and 3.4). Reduction product **62**, formed by disproportionation of **61** (Schemes 116) under reflux in toluene, gives nonsymmetric macrocycle by treating with dicarbonyl compound[171] (Scheme 117).

Contrary to *o*-phenylenediamines (see section 3.2), monoacylated analogs react readily to give macrocycles. Diamine **63** reacts with various dicarbonyl compounds in 1,4-dioxane to produce [1+1]-macrocycles[172] (Scheme 118). Diamine **63** is planar, and in its macrocycle closure reactions the most

Scheme 117. Condensation of 62 with 2,5-Diformylpyrrole



Scheme 118. Condensation of 63 with Dicarbonyl Compounds



efficient are the dicarbonyl compounds that can take planar conformations.

4.4. Fragment-to-Fragment Assembling in the Presence of Proton Acids

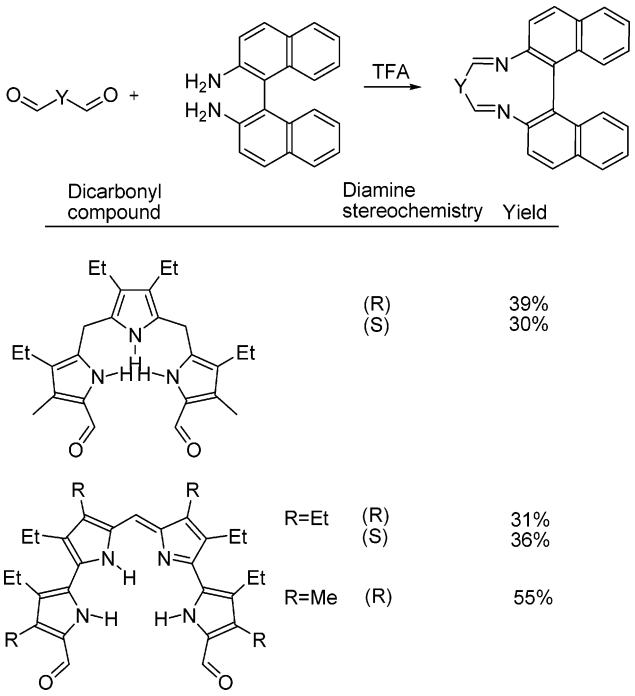
Reactions of diamines with dicarbonyl blocks have been studied in detail with pyrrolic and polypyrrolic compounds under acid-catalyzed conditions. When polar proton solvents capable of solvating amino groups (e.g., methanol) are used, diformylpyrroles act as the dicarbonyl component only in the presence of strong proton acids. Under these conditions, diformylpyrroles are normally condensed with optically active 2,2′-diaminobinaphthyls to produce macrocycles[173−175] (Schemes 119).

Acid catalysis allows preparing a broad variety of macrocycles from weak nucleophilic diamines as *o*-phenylenediamines or even 2,3-diaminomaleodinitrile (Scheme 120).

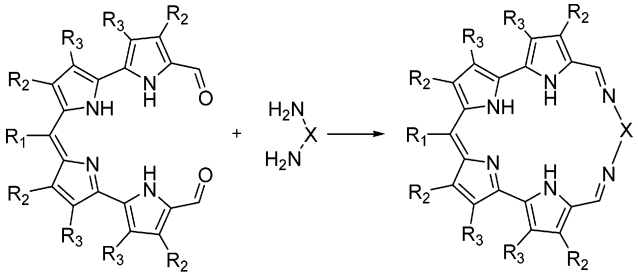
Polypyrrole dialdehyde **64** reacts with both hydrazine and 1,3-diaminoguanidine in the presence of hydrochloric acid to give the corresponding macrocycles in 50% yield[175] (Scheme 121).

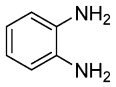
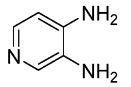
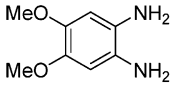
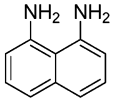
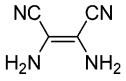
Highly conjugated polymacrocycles could be created by reaction of pyrrolic blocks with tetraamines. Thus, treating dialdehyde **64** with 3,3′,4,4′-tetraaminobiphenyl leads to formation of expanded porphyrine dimer[175] (Scheme 122).

Scheme 119. Condensation of Polypyrrole Dialdehydes with 2,2′-Diaminobinaphthyls[173]



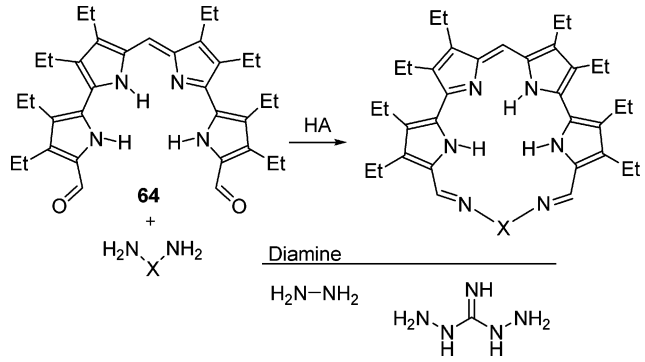
Scheme 120. Condensation of Polypyrrole Dialdehydes with Weak Nucleophilic Diamines



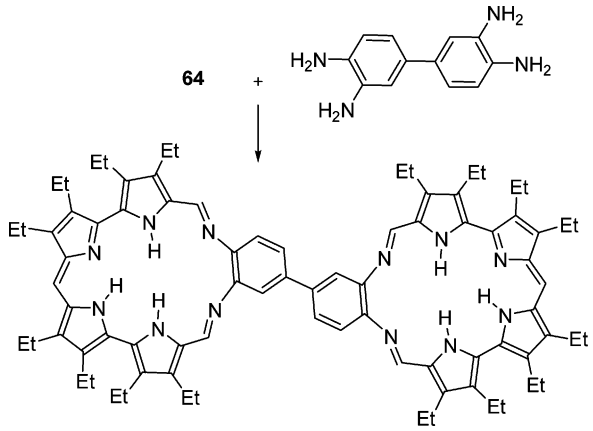
Diamine	R_1, R_2, R_3	Yield	Ref.
	R_1 = p-$NO_2C_6H_4$; R_2 = Me; R_3 = Et	95%	177
	R_1 = p-$NO_2C_6H_4$; R_2 = R_3 = Me	98%	177
	R_1 = R_3 = H, R_2 = Pr	83%	174
	R_1 = R_3 = H, R_2 = Pr	80%	174
	R_1 = H; R_2 = Et; R_3 = Me		176
	R_1 = Ph; R_2 = R_3 = Me	70%	177
	R_1 = p-$NO_2C_6H_4$; R_2 = R_3 = Me	52%	177
	R_1 = R_3 = H, R_2 = Pr	8.6%	175
	R_1 = H, R_2 = R_3 = Et	86%	175

Application of diamine blocks in fragment-to-fragment assembling is limited by their low synthetic availability. Sseveral examples of acid-catalyzed condensations have been studied. Reaction of diamine blocks with dicarbonyl compounds proceeds in glacial acetic acid or in methanol−acid mixtures. Treating aminotriazine-blocks **65** with dialdehydes

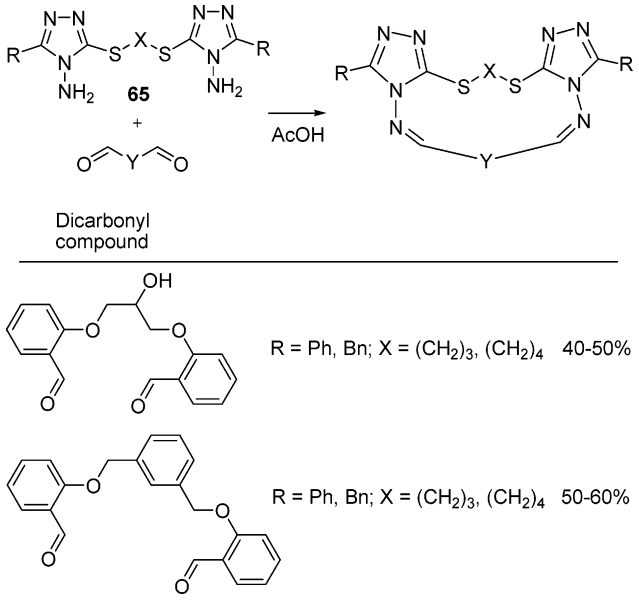
Scheme 121. Condensation of Dialdehyde 64 with Hydrazine and Guanidine



Scheme 122. Condensation of Dialdehyde 64 with 3,3′,4,4′-Tetraaminobiphenyl



Scheme 123. Synthesis of Triazole-Based Macrocycles via Acid-Catalyzed Condensations

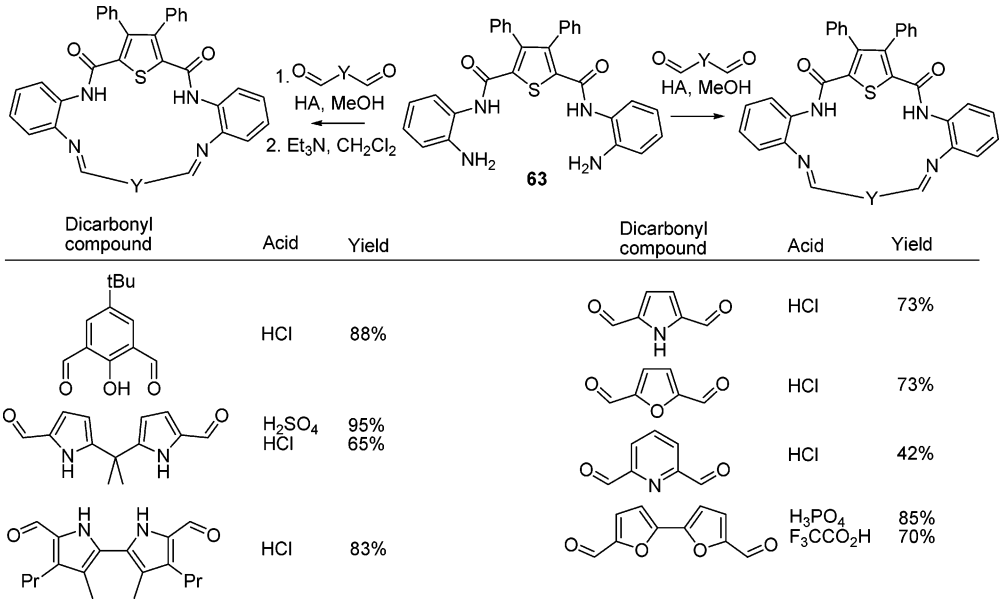


in glacial acetic acid under reflux leads to the corresponding macrocycles[178,179] (Scheme 123).

Compound **63** reacts with several dicarbonyls in methanol only in the presence of protonic acids to give free Schiff bases or their salts[172,180] (Scheme 124).

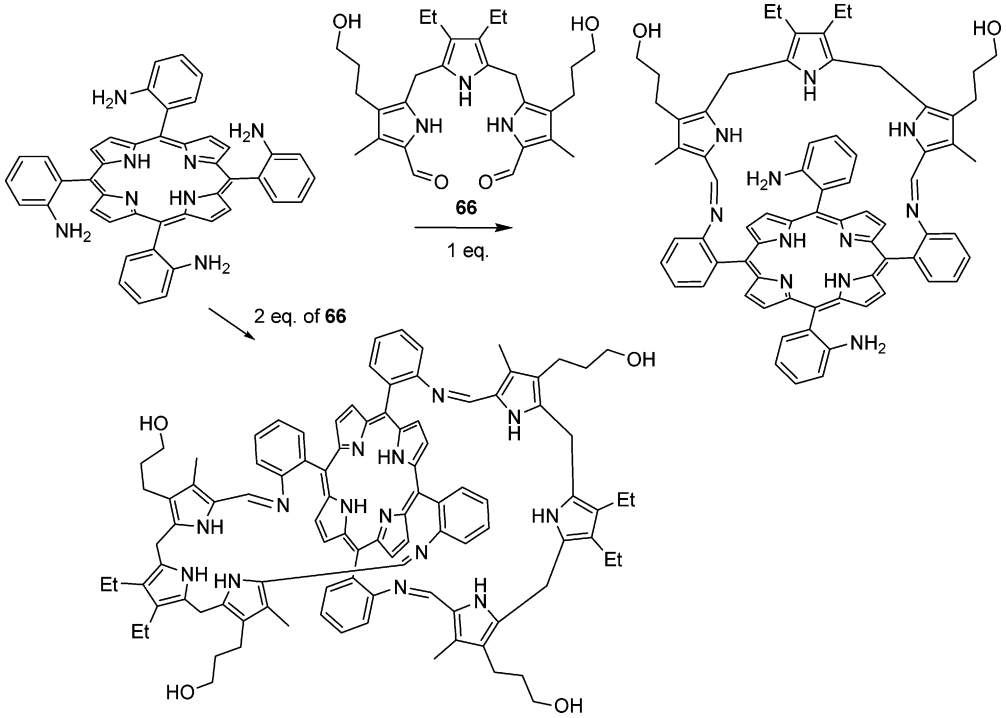
Synthesis of three-dimensional structures can also be achieved using a strategy of fragment-to-fragment assembling. Condensation of *meso*-(2-aminophenyl)porphyrin

Scheme 124. Condensation of 63 with Dialdehydes in the Presence of Acids



Dicarbonyl compound	Acid	Yield	Dicarbonyl compound	Acid	Yield
	HCl	88%		HCl	73%
	H_2SO_4 HCl	95% 65%		HCl	73%
				HCl	42%
	HCl	83%		H_3PO_4 F_3CCO_2H	85% 70%

Scheme 125. Reaction of *meso*-(2-Aminophenyl)porphyrin with Dialdehyde 64



with one or two equivalents of tripyrrolemethane dialdehyde **66** in the presence of trifluoroacetic acid gives the corresponding three-dimensional tri- and tetracyclic systems in moderate yields[181] (30−45%) (Scheme 125).

5. Anionic Template Effect in Formation of Macrocyclic Ligand Schiff Bases

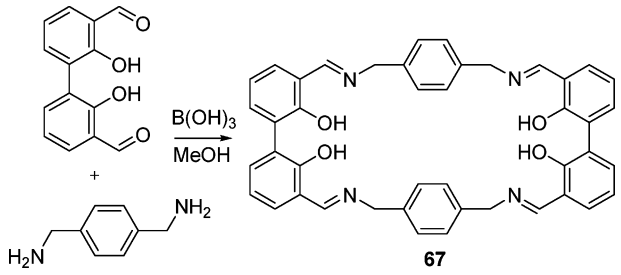
In most cases the nature of the Bronsted acid's anion does not affect the Schiff condensation, neither its structure of the products formed nor their yields. However, in 1982 Corey found that cyclocondensation during synthesis of boron-containing antibiotic Aplasmomycin occurred efficiently only in the presence of weak boric acid.[182] Corey suggested that borate anion acts in the above reaction as an efficient template agent. In support, Pierre et al. found that boric acid was capable of acting as an excellent catalyst of [2+2]-condensation between 2,2′-dihydroxy-3,3′-diformylbiphenyl and 1,4-diaminomethylbenzene to give macrocycle **67** in 80% yield[183] (Scheme 126).

Following the same protocol, macrocycles **68** were obtained in 88−90% yields[184] (Scheme 127).

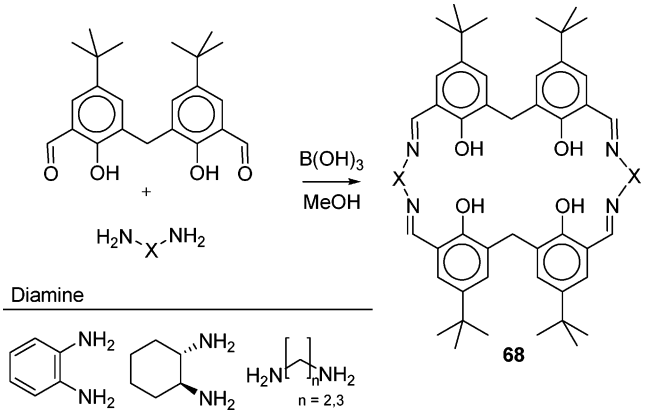
Mechanistically, tetrahedral borate ester can fix two molecules of diformylbisphenols to give an intermediate in which the relative arrangement of the carbonyl fragments is favorable for macrocycle closure.

Using up the phenylboronic acids in this reaction leads to preparation of boron-containing macrocycles. Thus, treating 2-salicylidenaldiminoethanols with phenylboronic acids affords macrocycles **69** in moderate to high yields via boron-

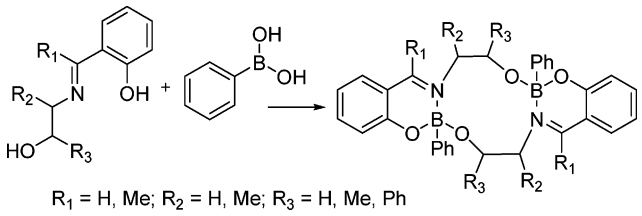
Scheme 126. Borate-Template Synthesis of 67



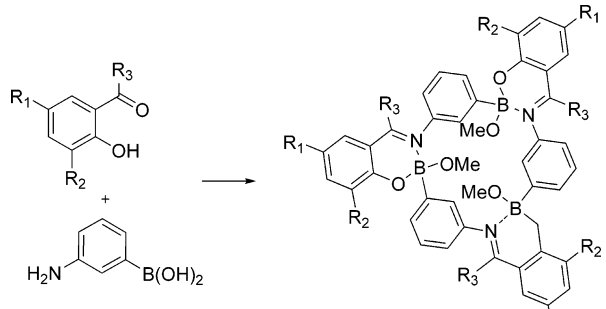
Scheme 127. Borate-Template Synthesis of Macrocycles 68



Scheme 128. Reaction of Hydroxysalene Derivatives with Phenylboronic Acid



Scheme 129. [3+3]-Macrocyclization of Salicylaldehydes with 3-Aminophenylboronic Acid

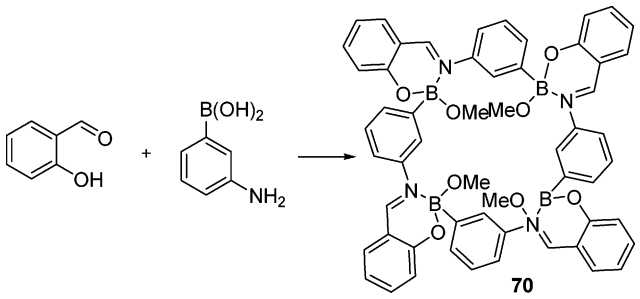


R_1, R_2	Yield	Ref.
$R_1 = R_2 = tBu$; $R_3 = H$	92%	187
$R_1 = R_2 = I$; $R_3 = H$	56%	188
$R_1 = OH$; $R_2 = R_3 = H$	57%	188
$R_1 = R_2 = H$; $R_3 = Me$	48%	189
$R_1 = R_2 = H$; $R_3 = Ph$	65%	189

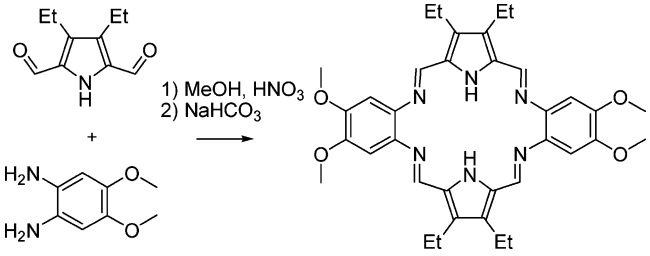
template [1+1]-macrocyclization reactions[185,186] (Scheme 128).

Insertion of an amino group into the molecule of phenylboronic acid leads to [3+3]-macrocycles in high yields via a similar autotemplate reaction with salicylaldehydes.[187−189] Thus, treatment of 3-aminophenylboronic acid with salicylaldehydes in methanol results in trimeric macrocyclic Schiff bases **69** in high yields (Scheme 129).

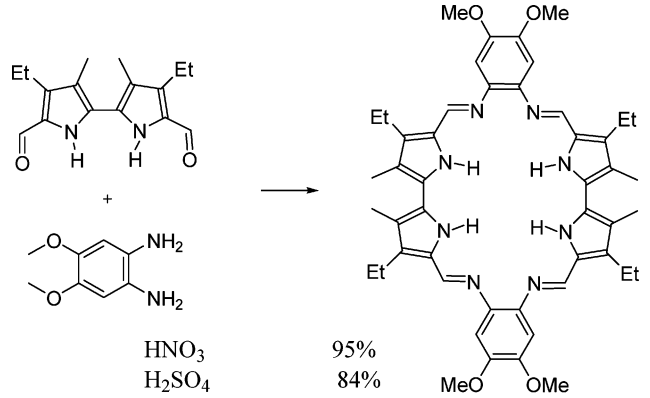
Scheme 130. Unusual Formation of [4+4]-Macrocycle from Salicylaldehyde and 3-Aminophenylboronic Acid



Scheme 131. Nitric-Acid-Templated Condensation of 2,5-Diformyl-3,4-diethylpyrrole with 4,5-Dimethoxy-*o*-phenylenediamine



Scheme 132. Reaction of Bipyrroledialdehyde with 4,5-Dimethoxy-1,2-phenylenediamine in the Presence of Different Acids



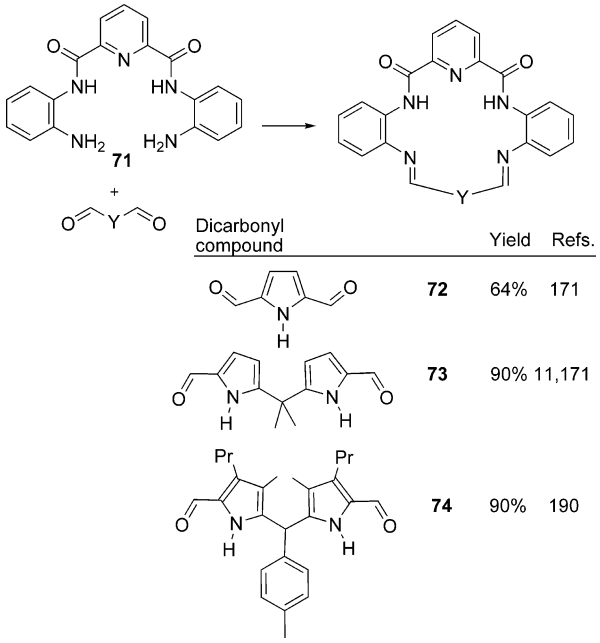
HNO_3	95%
H_2SO_4	84%
$HClO_4$	81%
TFA	74%
HCl	47%
HI	37%
$HCl+(Bu_4NNO_3)$	>80%

In contrast to the previous condensations, treatment of unsubstituted salicylaldehyde with 3-aminophenylboronic acid leads to tetrameric macrocycle **70** in 64% yield[189] (Scheme 130).

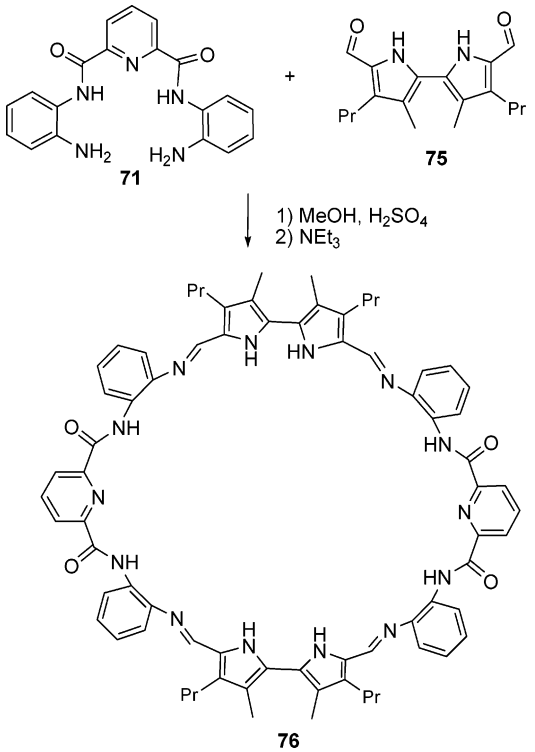
The influence of anions of other acids, which cannot form a covalent bond with dicarbonyl compound or diamines, remained unclear for a long time. Sessler's group was the first to shed light on this problem. It was found out that [2+2]-cyclization of pyrroledialdehyde with *o*-phenylenediamine occurs in quantitative yield only in the presence of nitric acid[113] (see section 3.3, Schemes 63 and 131).

Detailed study of condensing of bipyrroledialdehyde with *o*-phenylenediamine (see section 3.3, Scheme 63) and various acids showed that reaction proceeds in the presence of nitric acid in 95% yield, whereas lower yields were obtained when using another acids[114] (Scheme 132).

Scheme 133. Condensation of 71 with Dialdehydes in the Presence of Acids



Scheme 134. Formation of the [2+2]-Condensation Product by Reacting Diamine 71 with Bipyrrole 75



Recently, American and Russian chemists in their cooperative research have found that the result of the reaction of diamide of 2,6-pyridinedicarboxylic acid **71** with dialdehydes strongly depends on the nature of the anion of the Bronsted acid used as catalyst. In the presence of 2.5 equivalents of trifluoroacetic acid, [1+1]-condensation products **72** and **73** were formed in 90% yield (Scheme 133) as the corresponding trifluoroacetates.[11,171,190] By contrast, use of other acid catalysts (e.g., HCl, H_3CCO_2H, HNO_3, H_2SO_4, and H_3PO_4) led to precipitation and yielded salts of macrocycles **72** and **73** contaminated with various oligomeric products.[11,171]

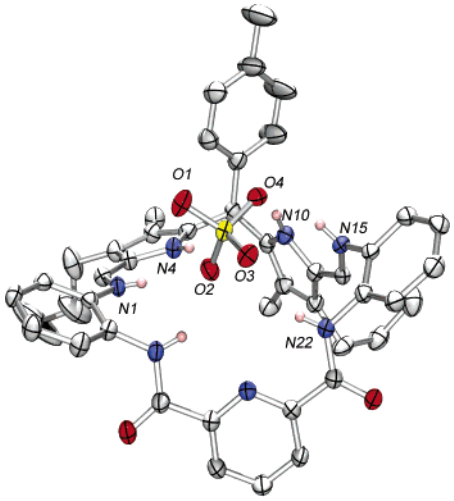


Figure 2. Structure of salt **74**·H_2SO_4. This figure was generated using data downloaded from The Cambridge Crystallographic Data Centre (CCDC) and corresponds to a structure originally reported by Sessler et al.[11]

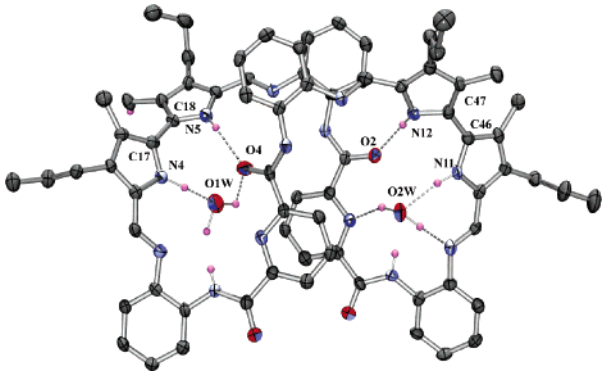


Figure 3. Structure of macrocycle **76**·$2H_2O$ according to X-ray analysis. This figure was generated using data downloaded from The Cambridge Crystallographic Data Centre (CCDC) and corresponds to a structure originally reported by Sessler et al.[191]

Macrocycles **73** and **74** are capable of binding tetrahedral anions when acting as artificial anionic receptors.[171,190] These data suggest that the binding ability of macrocycle and the yield in the cyclocondensation are closely related. The structure of salt **74** with sulfuric acid was determined by X-ray analysis (Figure 2).

Reaction of **71** with diformyldipyrrole **75** in methanol in the presence of various acids leads to different results[191] (Scheme 134). According to the data from mass spectrometry, in the presence of nitric acid, only oligomers are formed, which are also the main products in the reactions catalyzed by HCl or HBr, although a small amount of the [1+1]-macrocycle is formed in the mixture in these cases. In the presence of acetic and trifluoroacetic acids, the major reaction product becomes the salt of [2+2]-macrocycle **76** with an admixture of a minor amount of oligomers. Only when sulfuric acid is used as a catalyst is the salt of [2+2]-macrocycle **76** with two molecules of sulfuric acid formed without admixtures of oligomerization products.[191] The structure of **76**, isolated from its salt by treating with triethylamine, was determined by X-ray analysis (Figure 3).

Macrocycle **76** is capable of strongly binding tetrahedral anions: HSO_4^- (1:1; $K_a = 63\,500 \pm 3000\ M^{-1}$) and $H_2PO_4^-$

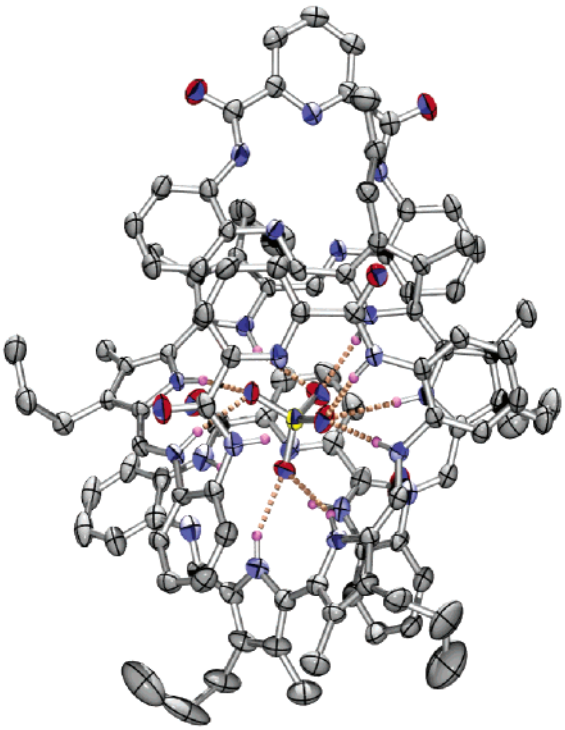


Figure 4. Structure of macrocyclic complex **77**·H_2SO_4 according to X-ray analysis. This figure was generated using data downloaded from The Cambridge Crystallographic Data Centre (CCDC) and corresponds to a structure originally reported by Sessler et al.[191]

(2:1; $K_{a1} = 191\,000 \pm 15\,400$ M^{-1}; $K_{a2} = 60\,200 \pm 6000$ M^{-1}; $K_a = 107\,000 \pm 9600$ M^{-1}, where $K_a = (K_{a1} \times K_{a2})^{0.5}$. This macrocycle weakly binds acetate ion (1:1, $K_a = 26\,000 \pm 2400$ M^{-1}) and does not bind other anions (chloride, bromide, and nitrate).[191]

Macrocycle **76** is quite stable under normal conditions in methanol solution. When **76** is left in an acetonitrile solution in the presence of tetrabutylammonium hydrosulfate or dihydrophosphate, the macrocycle is rearranged quantitatively into the sulfate salt of the expanded macrocycle **77**; the latter can be rationalized as a [3+3]-condensation product[191] (Scheme 135). The structure of sulfate salt **77** was determined by X-ray analysis[191] (Figure 4). In this complicated supramolecular complex the doubly protonated macrocycle is doubly twisted. The sulfate dianion is strongly bonded to the inner cavity by an array of hydrogen bonds. The nearest environment of the sulfate dianion bonded in the cavity is shown in Figure 5.

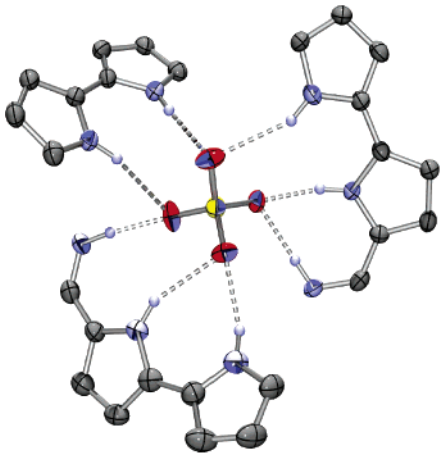
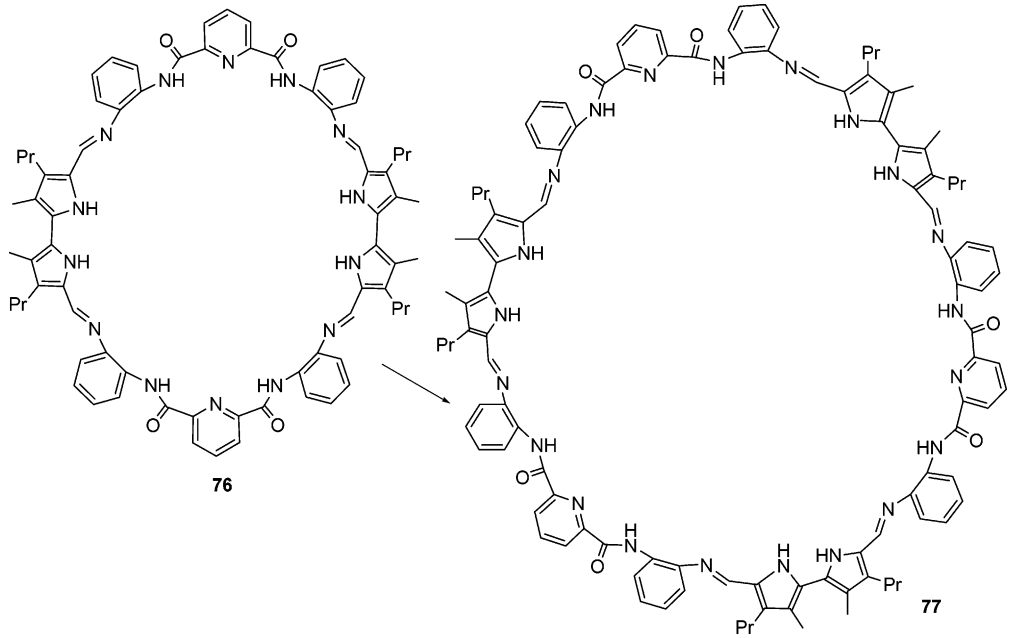


Figure 5. Nearest coordination environment of the sulfate anion in **77**·H_2SO_4 complex. This figure was generated using data downloaded from The Cambridge Crystallographic Data Centre (CCDC) and corresponds to a structure originally reported by Sessler et al.[191]

This result is remarkable since it indicates that reaction of **71** with **75** in the presence of tetrahedral anions proceeds via the template scheme. Evidently the sulfate of [2+2]-macrocycle **76** is a thermodynamically controlled reaction product in methanol, while the sulfate of [3+3]-macrocycle **77** is a thermodynamically controlled reaction product in acetonitrile.[191] A substantial contribution of the solvent nature to formation of macrocycles is quite clear since acetonitrile significantly lowers the capability to solvate anion in comparison with methanol. Here the anionic template effect

Scheme 135. Rearrangement of Macrocycle 76 in the Presence of $(Bu_4N)^+HSO_4^-$ or $(Bu_4N)^+H_2PO_4$



is distinctly pronounced since the type of anion and reaction conditions determine the structure of the macrocycles formed.

The data presented in this section suggest that anions can be efficiently used in provoking condensation of dicarbonyl compounds with diamines under thermodynamically controlled conditions. Templating anions selectively bind one of the products of a dynamic combinatorial library formed, thus shifting the equilibrium toward formation of the most stable complex. This phenomenon provides the basis for a new efficient approach to creating artificial cationic and anionic receptors.

6. Conclusions

The material collected in this review shows that the reversibility of all consecutive-parallel reactions results in a situation where condensation of dicarbonyl compounds with diamines, under thermodynamically equilibrium conditions, provides a dynamic combinatorial library which contains many products. Appropriate choice of reaction conditions (solvent, concentrations and ratio of reactants, temperature, acidic catalyst) makes it possible to shift the equilibrium toward the target product and obtain free Schiff bases or their salts of various structures in good yields in the absence of metal cations traditionally used as template agents. The most difficult problem of designing nonsymmetric macrocycles is successfully solved by exploring the strategy of fragment-to-fragment assembling from enlarged building blocks as precursors. In this case, both metal ions and anions can be used as template agents in the final step of the synthesis. The anions are especially efficient for assembling macrocycles which contain inside the cavity several proton-donor groups capable of participating in hydrogen bonding. These anion−template condensations provide straightforward access to creating artificial anionic and cationic receptors.

Very recently Kuhnert assumed that the amine molecule could act as a template agent during condensation,[192] leading to the dynamical combinatorial synthesis of various Schiff bases. This assumption suggests that some other neutral molecules could be used as templates as well.[193] Thus, a broad variety of molecular hosts could be constructed for catalysis, biochemistry, medicine, and enzyme modeling applications. Efficient synthesis of interlocked molecules, such as catenanes,[194] is an excellent example of a new area in macrocyclic Schiff-base chemistry. The important role of polydentate Schiff bases in coordination and supramolecular chemistry, organic synthesis, as well as their biological and medical applications is the reason for the extremely fast development of this area. Recently, Lehn showed that molecular motors can be constructed on the basis of photochemical and thermal isomerization of the azomethine bond.[195] New interesting achievements in macrocyclic azomethine chemistry can be expected in the nearest future.

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