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Synthesis of azomethine macrocycles by condensation of dicarbonyl compounds with diamines without using metal ions as template agents

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Abstract. Different strategies for the synthesis of symmetrical and unsymmetrical macrocyclic Schiff bases in the absence of metal ions are considered. General methods for performing macrocyclisation under thermodynamic or kinetic control are analysed. The key factors influencing the structure of macrocyclic azomethines are discussed. The bibliography includes 215 references.

I. Introduction

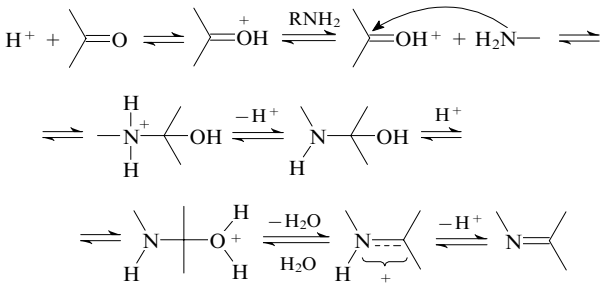
Schiff bases (azomethines) contain the RC═N group and are widely used in organic synthesis, for example, as intermediates in the synthesis of amines. Some azomethines have high biological activities, including antitumour,[1,2] bactericidal[3] or antiviral activity.[4] Schiff bases containing additional electron-donating groups belong to an important class of heteropolydentate ligands involved in mono- or polynuclear complexes with metals. Macrocyclic azomethines can trap metal ions with large radii and high coordination numbers, including lanthanides and actinides, in their cavities and form bi- and polynuclear complexes, in which two or more metal atoms are located in one cavity in close proximity to each other and which are characterised by unusual magnetic properties[5] and catalytic activity.[6] Some azomethine complexes have non-linear optical properties.[7] Macrocyclic azomethines are prone to form discotic liquid crystals.[8] In recent years, it has been demonstrated[9] that macrocyclic Schiff bases can also recognise and selectively bind anions, thus acting as artificial anionic receptors.

The most general procedure for the synthesis of azomethines is based on acid-catalysed condensation of carbonyl compounds with primary amines discovered by Schiff[10] in 1864. The classical Schiff reaction generally proceeds with high yield (Scheme 1).

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Scheme 1



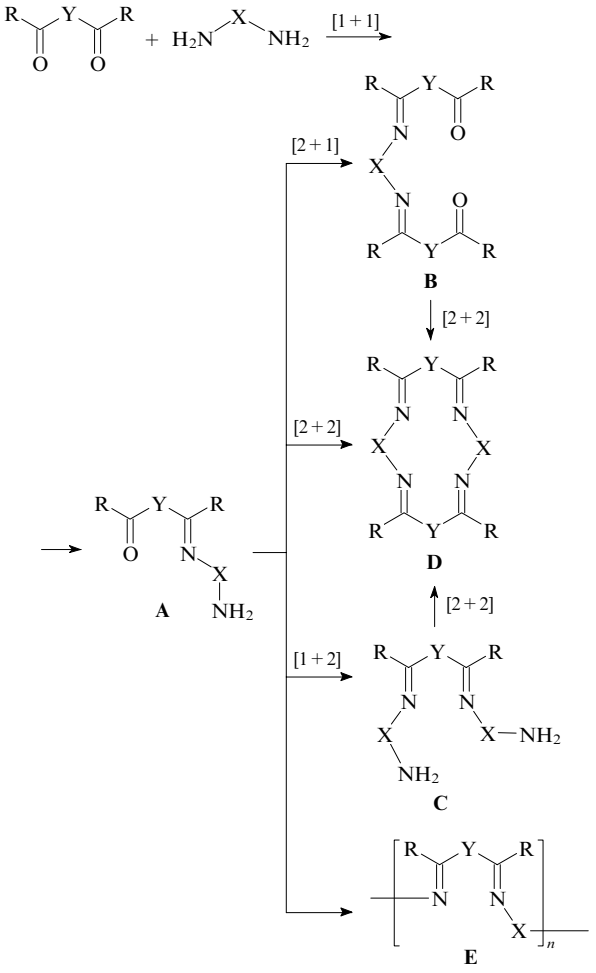
Since all steps in this transformation sequence are reversible, the process performed under thermodynamic control affords an equilibrium mixture of products, which can be considered as a dynamic combinatorial library.[11] An understanding of the factors determining the equilibrium in this system is of key importance for the achievement of chemoselectivity.

The reactions of dicarbonyl compounds with diamines are much more complicated and can afford a large set of cyclic and acyclic condensation products (Scheme 2). In the first step, one molecule of a dicarbonyl compound reacts with one diamine molecule to give the acyclic [1 + 1]-condensation product **A**, which can then form either the [2 + 1] product **B** with the second molecule of the dicarbonyl compound or the [1 + 2] product **C** with the second diamine molecule. In addition, compound **A** can undergo either cyclisation to give the [2 + 2] macrocycle **D** or polycondensation to form linear oligomers **E** with different molecular mass. In turn, bis-azomethines **B** and **C** can give the macrocyclic [2 + 2]-condensation product **D** in the subsequent reaction with diamine or the dicarbonyl compound, respectively.

The rate-determining step of the reaction depends on the acidity of the medium and it is either the addition of amine at the double bond of the carbonyl group in acidic medium or elimination of the water molecule in neutral medium. Hence, the proton-donor properties of the solvent have a substantial effect on the composition of the products, particularly, in the case of the assembly of large rings or if the starting compounds have complex geometry.

The classical scheme of processes involved in the reaction of diamines with dicarbonyl compounds was reported in several reviews (see, for example, Refs 12 and 13).

Scheme 2



In the synthesis of macrocycles, the addition of a template agent is the most efficient way of preventing polycondensation. Systematic studies of the template effect were initiated by Busch and co-workers [14–17] in the early 1960s. Template agents are generally classified into several types depending on the nature of dominant interactions with the starting compounds (donor-acceptor, electrostatic or hydrophobic interactions, π,π stacking, hydrogen bonding). The principal studies on the template synthesis were covered in sufficient detail in two volumes of *Topics in Current Chemistry*.[18,19] The anionic template effect was considered in depth in several review articles [20–22] included in the special issue of *Coordination Chemistry Reviews* and also in reviews.[23,24] In the last decade, investigations on the synthesis of macrocyclic Schiff bases in the presence of metal ions and the properties of the resulting complexes were summarised in more than ten publications (see, for example, reviews [13,25–28] and monographs [29]). The metal template synthesis has been covered in depth in publications by Vigato and co-workers.[30,31] Recently, Sessler and co-workers [32] have published a review on the synthesis of pyrrole-containing macrocyclic Schiff bases by different methods.

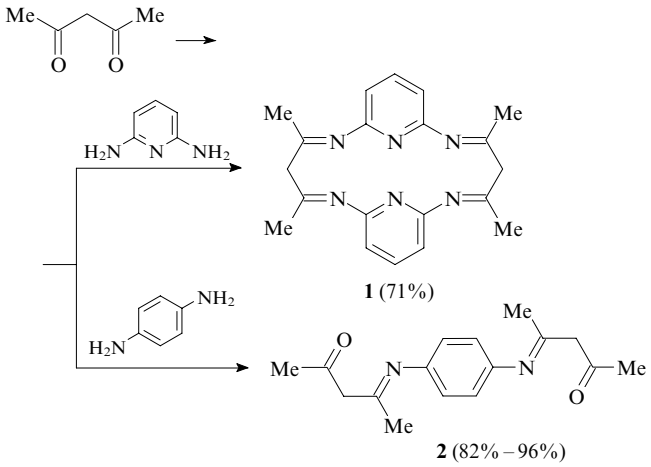
The metal template synthesis of macrocyclic Schiff bases has been studied in most detail. However, this method has two substantial drawbacks. First, the reactions with dicarbonyl compounds and diamines as the starting components generally produce symmetrical complexes. Hence, the template synthesis is unsuitable for the preparation of unsymmetrical macrocyclic Schiff bases. Second, metal-free compounds cannot be synthesised by this method. The selective condensation in the presence of a template agent is provided by strong binding of a metal ion in the cavity of the macrocycle. In many cases, demetallation of complexes can be performed only with the use of simultaneous reduction of imino groups to amino groups.

In the last two decades, considerable efforts were made to develop template-free methods for the synthesis of Schiff bases. In the present review, we analyse main approaches to the synthesis of macrocyclic azomethines by the self-assembly method in the absence of template agents. These data are considered from other points of view and are substantially extended and revised compared to the data published in our earlier review.[33]

II. Symmetrical macrocyclic Schiff bases

Symmetrical macrocyclic Schiff bases are generally synthesised by $[n+n]$-condensation reactions, where $n = 2$, 3 or 4.

Schiff bases prepared from diamines and carbonyl compounds of the aliphatic series are unstable and readily undergo hydrolysis. These macrocyclic ligands are usually synthesised by the template method. On the contrary, azomethines generated from aromatic or heteroaromatic diamines and aliphatic dicarbonyl compounds are rather stable and can be isolated as free ligands. For example, the condensation of acetylacetone with equimolar amount of 2,6-diaminopyridine in methanol in the presence of catalytic amounts of hydrochloric acid affords the corresponding [2 + 2] macro-cycle **1**.[34]



The [2 + 1]-condensation product of acetylacetone with *p*-phenylenediamine, *viz*., compound **2**, was prepared in high yield in the presence of a large excess of the dicarbonyl compound.[35]

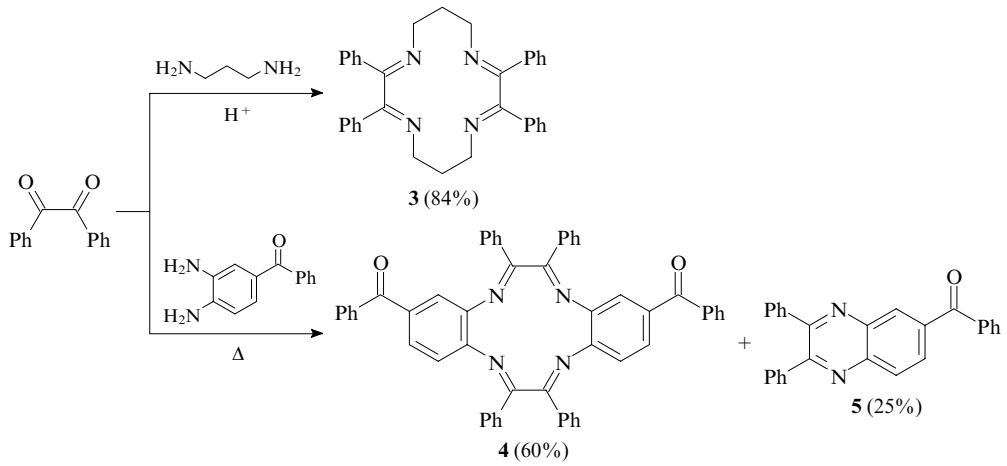
Even more stable Schiff bases can be synthesised from aliphatic or aromatic diamines and dicarbonyl derivatives of aromatic and heteroaromatic series. These compounds are used in the synthesis of polydentate ligands by self-assembly reactions more often than other reagents.

Aromatic diketones generally react with aliphatic diamines in ethanol in the presence of catalytic amounts of acids to form the corresponding [2 + 2]-condensation products. For example, the reaction of benzil with 1,3-diaminopropane produces macrocyclic Schiff base **3**.[36]

This reaction with aromatic diamines proceeds under prolonged reflux and gives not only macrocyclic [2 + 2]-condensation product **4** but also quinoxaline derivative **5** as a [1 + 1]-condensation product (Scheme 3).[37]

The composition of the products synthesised by the reactions of dicarbonyl compounds with diamines is determined by several factors, among which the nature of the starting compounds is of most importance. As a rule, the target products can be prepared in good yields by varying the concentration and the ratio of the reagents, the nature of the solvent, the temperature and the catalyst. The reactions of dicarbonyl

Scheme 3



compounds with aliphatic α,ω-diamines were studied in most detail. For these reactions, the conditions of the synthesis of stoichiometrically controlled condensation products were found.

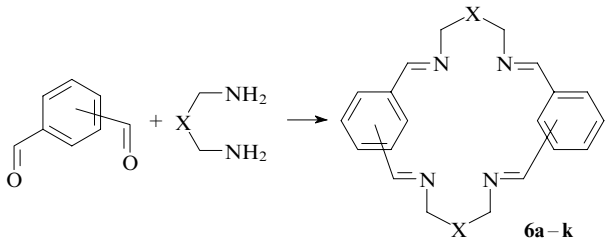
Two amino groups of aliphatic diamines separated by a hydrocarbon bridge react independently of each other. Hence, the reactions involving these groups cannot, as a rule, be terminated after the formation of acyclic [1 + 1]-condensation products. In the absence of metal salts, most of these reactions produce oligomeric compounds.[38,39] However, [2 + 2] macrocyclic compounds can be prepared as the major products by carefully choosing the ratio and the concentration of the reactants and the nature of the solvent.[40]

Intermolecular reactions giving oligomers are generally suppressed using high-dilution conditions (the concentration is 10^{-2}–10^{-3} mol litre^{-1} or lower) and stoichiometric amounts of the components. The solvent is chosen such that the starting reagents are readily soluble, whereas the target product is poorly soluble. Taking into account the fact that the resulting macrocyclic Schiff bases are less polar than the starting compounds, polar solvents, such as methanol, ethanol and acetonitrile, are the solvents of choice. The reactions can be performed either at room temperature over a long period of time (> 12 h) or by refluxing for 0.5–4 h. Many efficient syntheses of [2 + 2] macrocycles based on aromatic and heteroaromatic dicarbonyl compounds, which were performed under these conditions, were documented. The composition of the reaction products depends primarily on the nature of the aromatic moiety of dicarbonyl compounds and the presence of substituents in these compounds, whereas the geometry and conformations of the fragments involved in the reaction are insignificant.

The macrocyclisation reactions systematised according to the type of the starting dicarbonyl compounds are considered below.

1. Cyclocondensation of diamines with aromatic dicarbonyl derivatives

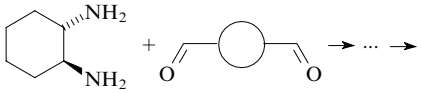
The condensation of isophthalaldehyde and terephthalaldehyde with diamines in dilute solutions (~10^{-2}–10^{-3} mol litre^{-1}) of lower alcohols or acetonitrile affords [2 + 2]-macrocyclic Schiff bases **6a**–**k**. (Most of macrocyclic compounds based on phthalaldehyde were synthesised by the template method.[29])

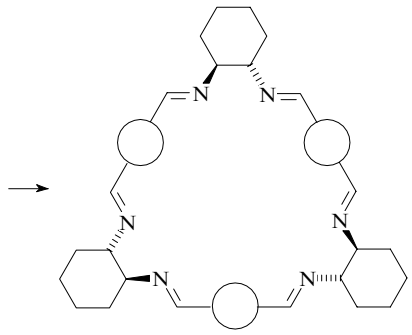


Compound **6**	X	Isomer	Yield (%)	Ref.
a	absent	1,3	88	41
b	CH_2NMeCH_2	1,3	10	42
c	CH_2NHCH_2	1,3	60–70	40
d	CH_2NHCH_2	1,4	–	43
e	CH_2NTsCH_2	1,3	87	42
f	$(CH_2SCH_2)_2$	1,3	71	41
g	$(CH_2SCH_2)_2$	1,4	48	44
h	1,2-$C_6H_4(CH_2SCH_2)_2$	1,3	86	45
i	1,2-$C_6H_4(CH_2SCH_2)_2$	1,4	96	45
j	1,3-phenylene	1,3	–	46
k	1,3-phenylene	1,4	–	43

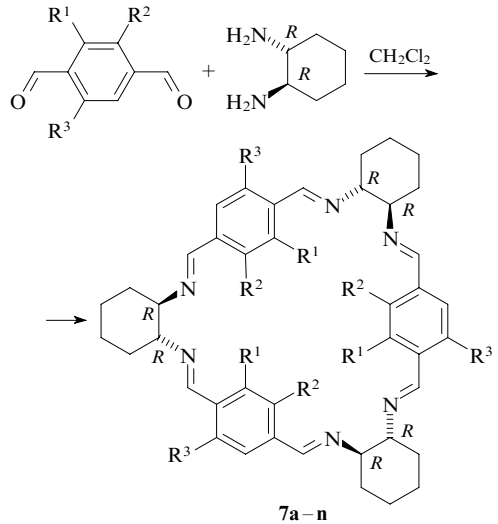
X-Ray diffraction studies showed that, in the crystals, such macrocyclic compounds adopt a stair-like conformation with the parallel arrangement of the aromatic rings. The [2 + 2]-condensation product of isophthalaldehyde with 1,3-bis(aminomethyl)benzene, *viz*., compound **6j**, contains two pairs of mutually parallel aromatic rings, which form a cavity inside the ligand (Fig. 1).[46] The azomethine groups in this compound are in the *cis*,*trans* conformation with respect to the aromatic ring.

Unlike acyclic aliphatic diamines, diaminocyclohexanes have a rather rigidly fixed configuration. In *trans*-1,2-diaminocyclohexane, both amino groups are in equatorial positions, and the $H_2N-C-C-NH_2$ dihedral angle is close to 60°. Because of this, *trans*-1,2-diaminocyclohexane behaves like an almost planar building block, which is prone to form [3 + 3] macrocycles in the reactions with structurally rigid dicarbonyl compounds with the linear arrangement of carbonyl groups.





For example, the reactions of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with terephthalaldehyde and its derivatives afford [3 + 3]-condensation products **7a**–**i**. Low yields of some macrocyclic compounds are attributed to the necessity of performing repeated reprecipitation of the resulting compounds to isolate analytically pure samples, although the yields determined from the spectroscopic data are no lower than 80%–85%.



7a–**n**

Compound **7**	R^1	R^2	R^3	Yield (%)	Ref.
a	H	H	H	90	47
b	H	Me	Me	97	48
c	H	OMe	OMe	90	48, 49
d	H	OEt	OEt	18	50
e	H	OPr^n	OPr^n	17	50
f	H	OBu^n	OBu^n	32	50
g	H	OBn	OBn	23	50
h	H	$OCH_2C_6H_4F$-4	$OCH_2C_6H_4F$-4	29	50
i	OMe	OMe	H	25	49
j	H	OMe	Et	8	50
k	H	OMe	Bu^n	13	50
l	H	OMe	Bn	15	50
m	H	OMe	$(CH_2)_2OMe$	5	50
n	H	OMe	Me	46	50

The use of a low-polarity aprotic solvent (dichloromethane) made it possible to perform reactions at high concentrations of the reactants ($\sim$0.1 mol litre^{-1}) and obviate oligomerisation. According to the results of calculations by the molecular mechanics method, the position of the conformational equilibrium for model compound **8**, which differs from macrocycles **7** by the absence of one azomethine group, is favourable for the closure of the [3 + 3] macrocycle.[47] Apparently, the cyclic structure is generated from this conformation of the acyclic [3 + 3] precursor.

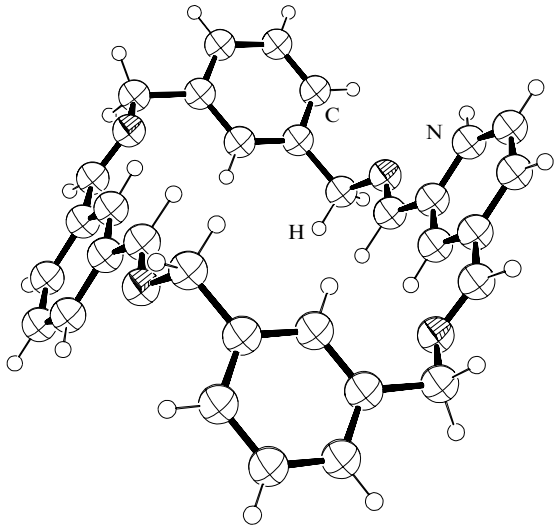
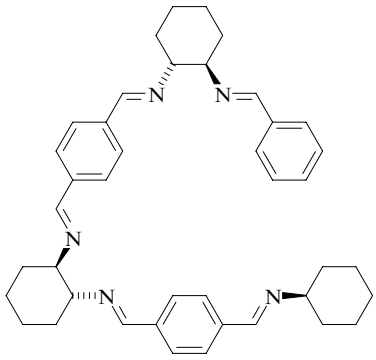


Figure 1. X-Ray diffraction structure of compound **6j**.[46] (All structures shown in the figures in the present review were retrieved from the Cambridge Structural Database.)



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The X-ray diffraction data for compound **7a** show that the cyclohexane fragments in [3 + 3] azomethine molecules are in one plane, whereas the benzene rings are virtually perpendicular to this plane and form a trihedral prism (Fig. 2).[47, 51]

A detailed study of this reaction of a series of 2,5-disubstituted terephthalaldehydes showed that their condensation

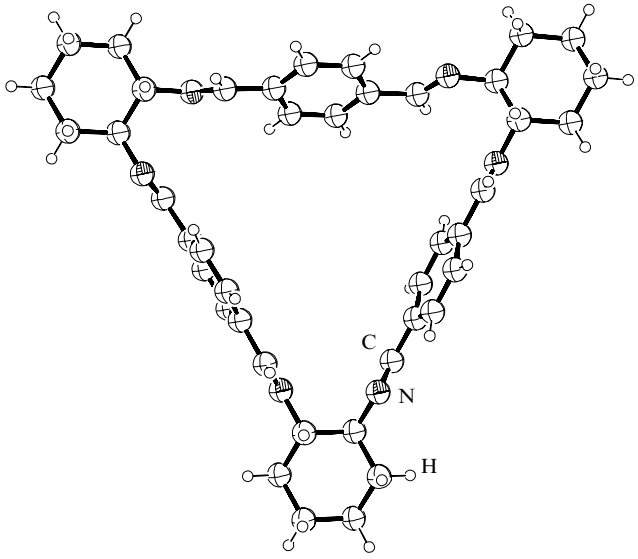
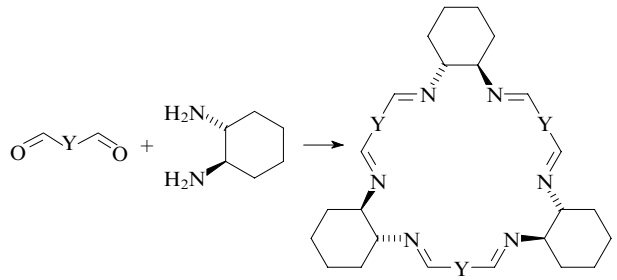


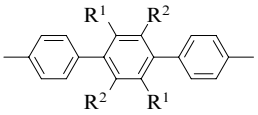
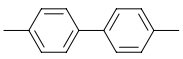
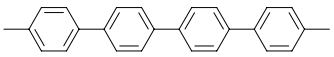
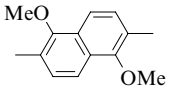
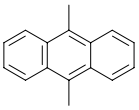
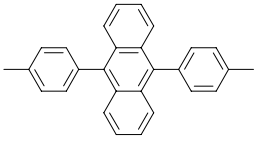
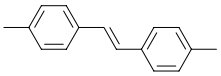
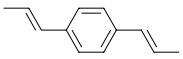
Figure 2. Structure of [3 + 3] azomethine **7a**.[47]

with *trans*-(*R*,*R*)-1,2-diaminocyclohexane is stereospecific and affords only one of two possible stereoisomeric macrocycles. As a result, only highly symmetrical [3 + 3]-condensation products **7j**–**n** are formed.[50]

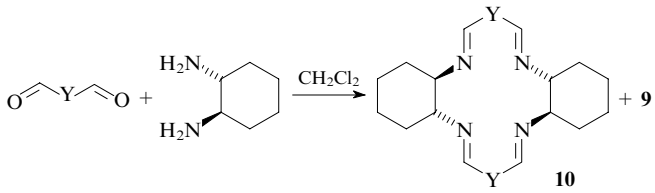
The reaction with *trans*-(*R*,*R*)-1,2-diaminocyclohexane was successfully extended to other aromatic dicarbonyl compounds containing formyl groups in the *para* positions with respect to each other. For example, [3 + 3] macrocycles **9** were synthesised in yields from moderate to high.



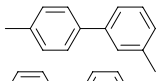
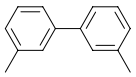
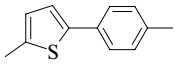
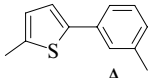
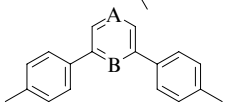
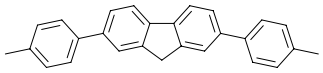
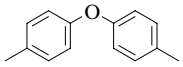
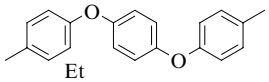
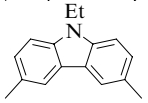
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Y		Yield (%)	Ref.
	$R^1 = H, R^2 = Me$	18	52
	$R^1 = R^2 = F$	55	53
	$R^1 = R^2 = H$	99	54
		32–67	54, 55
		57	52
		14	52
		80	54
		99	55
		68	55
		58	55

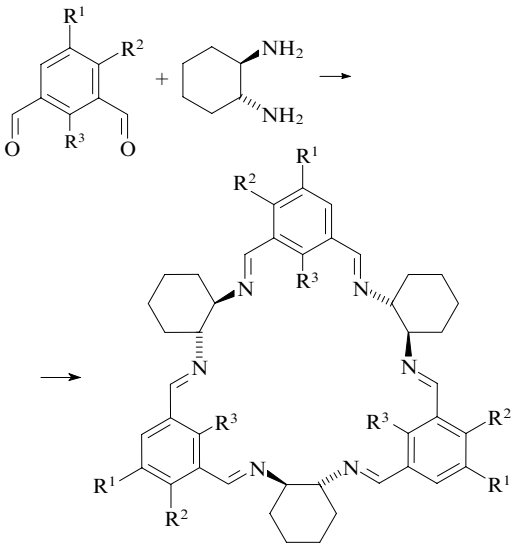
A consideration of the results of macrocyclisation in terms of geometry of the starting compounds (the geometric approach) leads to the conclusion that changes in the mutual orientation of the carbonyl groups in dialdehydes should determine the direction of the process. Actually, the deviation of the angle between the formyl substituents from 180° results in mixtures of cyclic compounds **9** and **10**, [2 + 2] macrocycles being the major reaction products, upon reactions of such dialdehydes with *trans*-(*R*,*R*)-1,2-diaminocyclohexane.



10

Y	**10** : **9**	Yield **10** (%)	Ref.
	97 : 3	67	53
	98 : 2	72	53
	95 : 5	72	53
	98 : 2	66	53
 A = B = CH	90 : 10	79	53
A = N, B = CH	90 : 10	78	53
A = CH, B = N	88 : 12	81	53
	85 : 15	34	53
	–	42	52
	–	68	56
	–	42	56
	–	30	48

By contrast, the condensation of substituted isophthalaldehydes, in which the mutual arrangement of the carbonyl groups seemingly hinders the formation of [3 + 3] macrocycles, with *trans*-(*R*,*R*)-1,2-diaminocyclohexane in concentrated (0.1 mol litre^{-1}) solutions in dichloromethane gives [3 + 3]-macrocyclic azomethines **11a**–**f** in good yields.

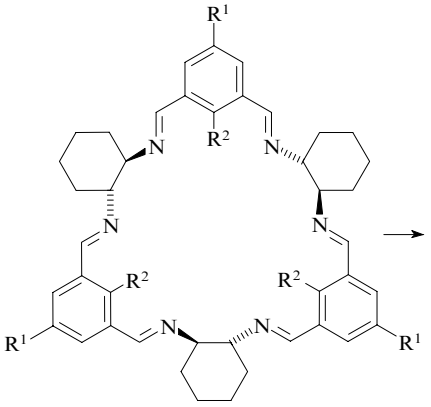


11a–**f**

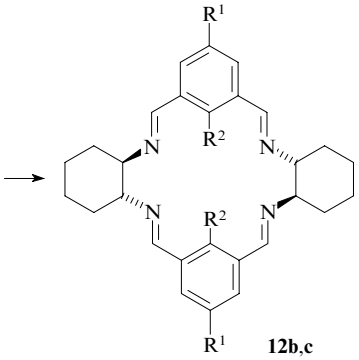
Compound **11**	R^1	R^2	R^3	Yield (%)	Ref.
a	H	H	H	90	47
b	Me	H	H	75	48, 49
c	H	H	Me	67	48

Compound **11**	R^1	R^2	R^3	Yield (%)	Ref.
d	OMe	OMe	OMe	70	48
e	Me	OH	H	78	57
f	Me	H	OTs	59	50

Under these conditions, [3 + 3]-macrocyclic products **11** are formed under kinetic control, but the reaction mixtures contain also [2 + 2] Schiff bases as the products formed under thermodynamic control. The latter were detected in the ESI (electrospray ionisation) mass spectra of the reaction mixtures produced in the synthesis of compounds **11b**,**c**.[48] In addition, the [3 + 3]-condensation products can undergo the rearrangement into the corresponding [2 + 2] macrocycles **12b**,**c** in quantitative yield upon prolonged refluxing (12–72 h) in dichloromethane.[48]



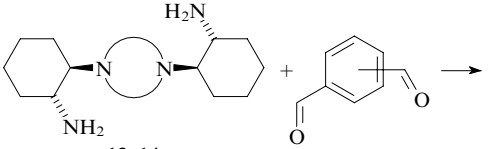
11b,**c**



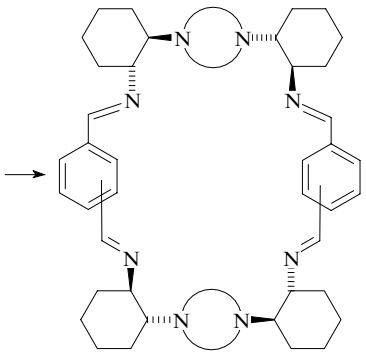
12b,**c**

R^1 = Me, R^2 = H (**b**); R^1 = H, R^2 = Me (**c**).

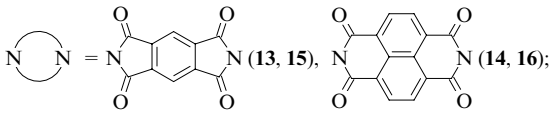
This geometric approach does not operate in the reactions of tetramines **13** and **14** with aromatic dicarbonyl compounds. For example, the reactions of diamine **13** with iso- and terephthalaldehydes give [2 + 2]-condensation products **15a** and **15b**, respectively.[58]



13, **14**

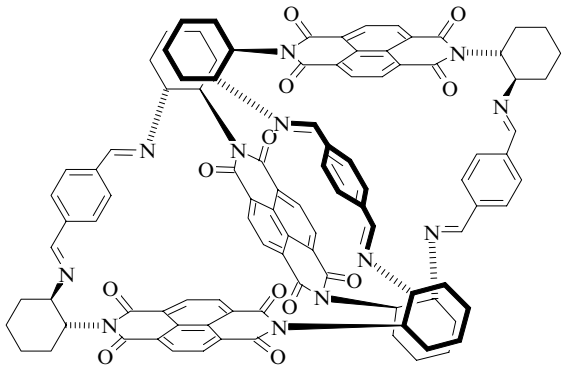


15a,**b**; **16a**



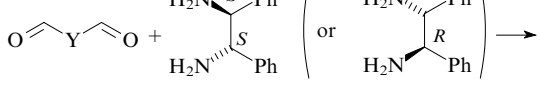
1,3 isomers (**a**), 1,4 isomers (**b**).

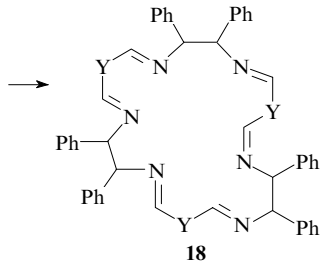
However, the reaction of geometrically similar diamine **14** with terephthalaldehyde afforded [3 + 3]-condensation product **17**, whereas isophthalaldehyde gave, as expected, [2 + 2] macrocycle **16a**.[58] The results of molecular simulation (PM3 method) show that [3 + 3]-condensation product **17** adopts a figure eight-like conformation due to the π,π-stacking interaction between the benzene ring of the terephthalate fragment and the naphthalene system.[58] Apparently, this interaction determines the reaction pathway.



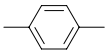
17

Stereoisomeric (*R*,*R*)- and (*S*,*S*)-1,2-diamino-1,2-diphenylethanes contain two bulky benzene rings serving as conformational anchors. These substituents rather rigidly fix the mutual arrangement of the amino groups. The angle between these groups, like that in *trans*-1,2-diaminocyclohexanes, is close to 60°. Because of this, the reactions of these diamines with dicarbonyl compounds proceed analogously to the reactions of *trans*-1,2-diaminocyclohexanes. For example, the reactions of these diamines with iso- or terephthalaldehyde in dichloromethane at room temperature produce [3 + 3] macrocycles **18**.[49]



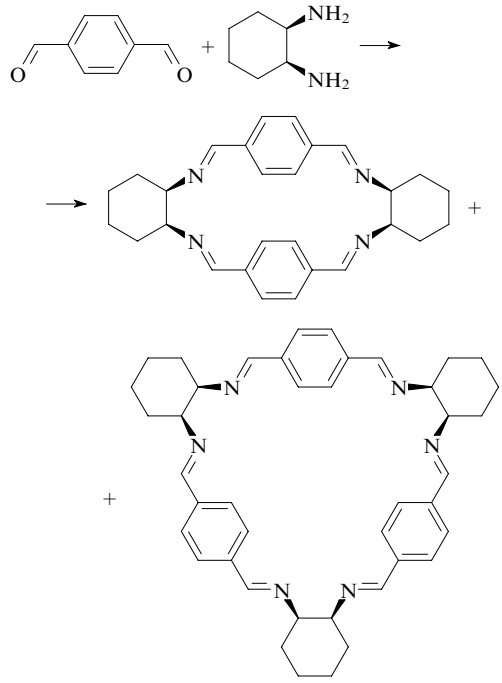


18

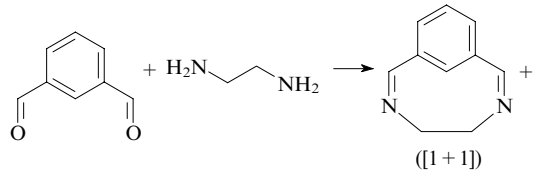
Y	Stereo-configuration	Yield (%)
	*S*,*S*	17
	R,*R*	19
	*S*,*S*	20

An investigation of the behaviour of [3 + 3] macrocycles **18** demonstrated that these compounds are decomposed in chloroform to give oligomeric condensation products. Apparently, [3 + 3] azomethines are generated under kinetic control, whereas oligomers are produced under thermodynamic control. It cannot be ruled out that thermodynamic stability is determined by the solvation effect, *i.e.*, it depends on the nature of the solvent.

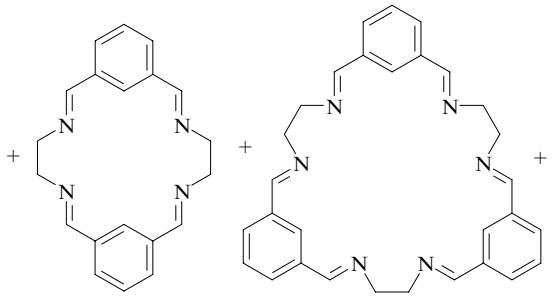
The amino groups in *cis*-1,2-diaminocyclohexane are in the equatorial and axial positions. This change in the geometry leads to changes in the reactivity with respect to dicarbonyl compounds. *cis*-1,2-Diaminocyclohexane, unlike the *trans* isomer, reacts with terephthalaldehyde to give a mixture of [2 + 2]- and [3 + 3]-condensation products (mass spectrometric data), with the latter greatly predominating.[59]



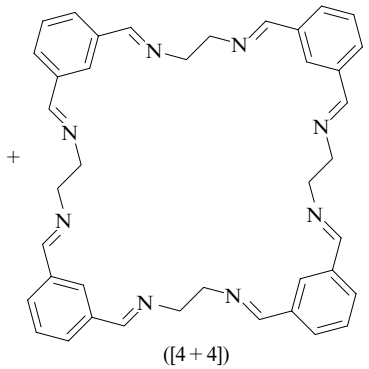
Complex mixtures are also produced in the reactions of acyclic 1,2-ethylenediamine.



([1 + 1])



6a ([2 + 2]) ([3 + 3])

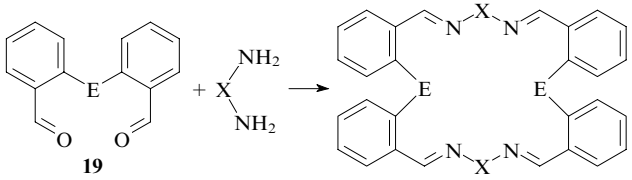


([4 + 4])

The field desorption (FD) mass spectrometric study demonstrated[60] that the reaction of isophthalaldehyde with ethylenediamine in methanol gives a combinatorial library of [1 + 1]-, [2 + 2]-, [3 + 3]- and even [4 + 4]-condensation products.

By contrast, these reactants afford only one reaction product, *viz.*, [2 + 2] macrocycle **6a** (see above), in acetonitrile. Presumably, the use of protic methanol instead of aprotic acetonitrile leads to an increase in the condensation rate and, as a consequence, to a decrease in the selectivity of the reaction.

Dicarbonyl derivatives containing several benzene rings, including those linked to each other through heteroatoms, react analogously to monocyclic compounds. For example, the reactions of bis(2-formylphenyl) chalcogenides **19** (E = Se or Te) with aliphatic diamines in boiling acetonitrile produce the corresponding macrocyclic Schiff bases.[61,62]

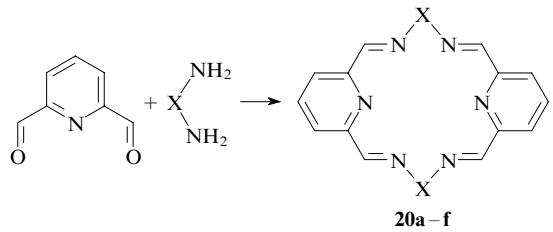


19

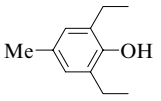
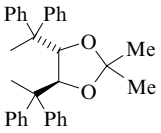
E = Se, Te; X = $(CH_2)_n$ (n = 3, 6) (yield for E = Se is 61%), CH_2CHMe (71%), $(CH_2)_2NH(CH_2)_2$ (32%), $CH_2(CH_2NHCH_2)_2CH_2$ (60%).

2. Cyclocondensation of diamines with pyridine dicarbonyl derivatives

On the whole, pyridine dicarbonyl derivatives are very reactive in nucleophilic addition reactions to the carbonyl group because of the electron-withdrawing character of the pyridine ring, due to which they readily form Schiff bases. However, the selectivity of such reactions is, as a rule, low. Examples of the selective formation of macrocyclic systems from pyridine dicarbonyl derivatives in the absence of template agents are few in number, whereas products of their template condensation in the presence of metal ions are widely known.[13] As a rule, diformylpyridines react with various diamines in dilute solutions in acetonitrile (more rarely, in methanol) to form [2 + 2] macrocycles **20a**–**f** in satisfactory yields.



20a–f

Compound **20**	X	Solvent	Yield (%)	Ref.
a	$(CH_2)_3$	MeCN	62	63
b	$CH_2C{\equiv}CCH_2$	MeOH	86	64
c	$(CH_2)_2NMe(CH_2)_2$	MeCN	60	42
d	$(CH_2)_2NH(CH_2)_2$	MeCN	60–70	40, 43
e		MeOH	45	65
f		–	–	66

Data on the three-dimensional structures of macrocyclic Schiff bases based on pyridine derivatives are scarce. According to the available data, two pyridine rings in [2 + 2] macrocycle **20f**, which was synthesised from 2,6-diformylpyridine and *trans*-4,5-bis[(1-amino-1,1-diphenyl)methyl]-2,2-dimethyldioxolane, are linked to each other by the π,π-stacking interaction and are spaced by 3.3 Å (Fig. 3).[66] The azomethine groups of the macrocycle are in the *trans*,*trans* conformation, resulting in the lipophilic character of the cavity.

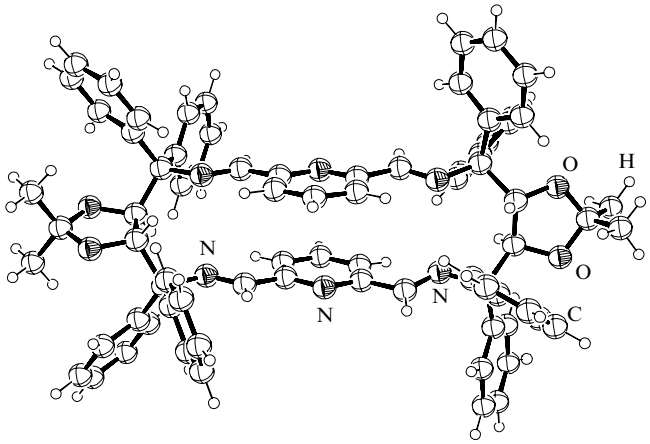
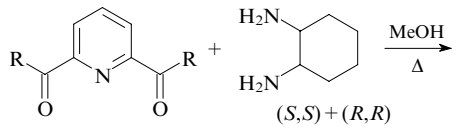
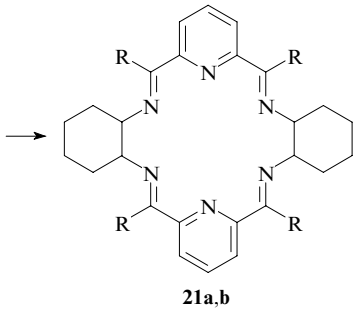


Figure 3. Structure of [2 + 2] macrocycle **20f**.[66]

The condensation of *trans*-1,2-diaminocyclohexane with 2,6-diformyl- or 2,6-diacetylpyridine (refluxing in methanol) gives [2 + 2]-macrocyclic Schiff bases **21a**,**b** in both dilute and concentrated solutions.[67]



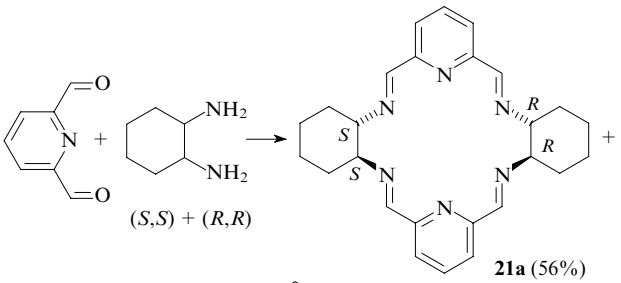
(*S*,*S*) + (*R*,*R*)



21a,**b**

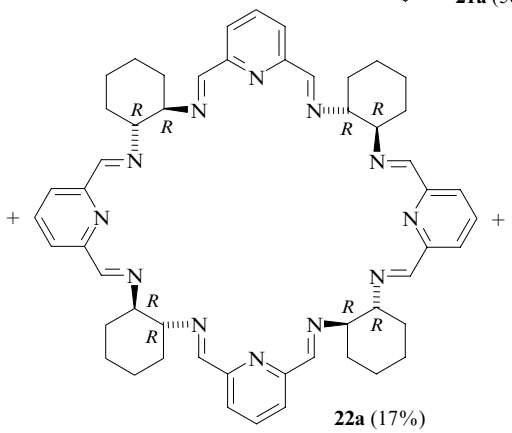
R = H (**a**, 68%), Me (**b**, 57%).

The detailed study of this reaction with diformylpyridine and racemic *trans*-diamine demonstrated that this reaction gave a mixture of [2 + 2]- (**21a**) and [4 + 4]-condensation products (**22a**),[68] which were isolated and characterised by different physicochemical methods, and [3 + 3] macrocycle **23a**, which was detected by the NMR method. No formation of macrocycles diastereomeric with macrocycles **21a**, **22a** and **23a** was observed. The self-organisation of the achiral and racemic starting compounds gives rise to the only stereoisomer even in the case of [4 + 4] macrocyclisation.

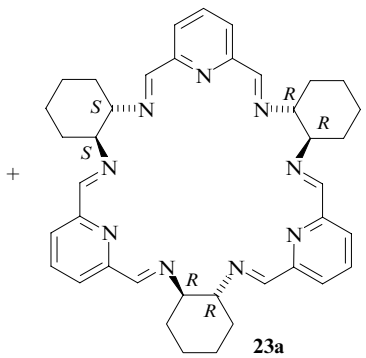


(*S*,*S*) + (*R*,*R*)

21a (56%)



22a (17%)



23a

The reaction of 2,6-diformylpyridine with *trans*-(*R*,*R*)-1,2-diaminocyclohexane also yields a mixture of [2 + 2]-, [3 + 3]- and [4 + 4]-condensation products, with the [3 + 3]-condensation product substantially predominating.[68]

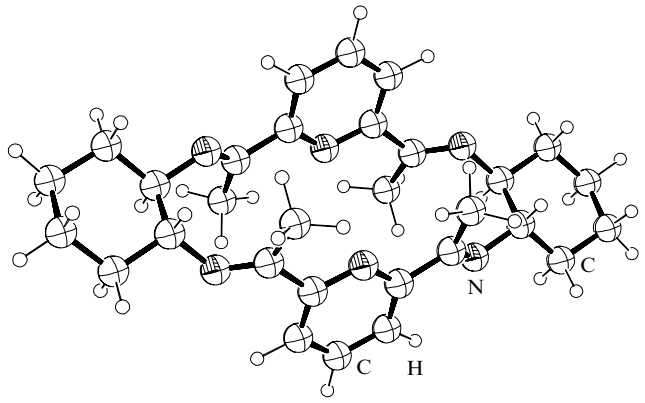
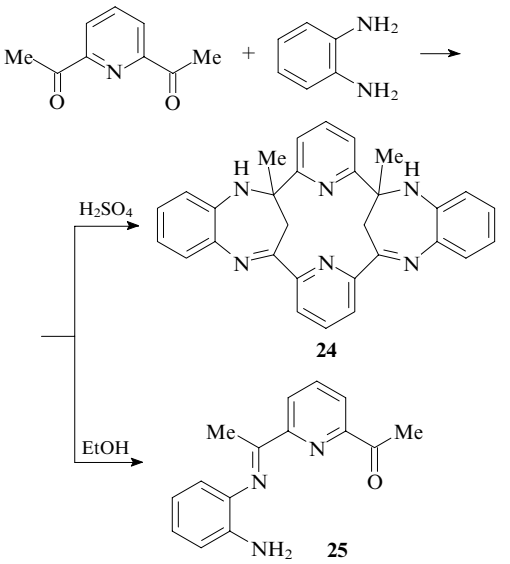


Figure 4. Structure of [2 + 2] macrocycle **21b**.[67]

The structures of [2 + 2] macrocycles **21** containing the *trans*-(*R*,*R*)-1,2-diaminocyclohexane fragments substantially differ from those of azomethines containing aliphatic diamine fragments because the cyclohexane ring is geometrically more rigid. Macrocycle **21b** adopts a stair-like conformation with the coplanar pyridine rings (Fig. 4).[67] The pyridine nitrogen atoms are spaced by 3.6 Å due to the fact that all azomethine groups are in the *trans*,*trans* conformation.

The reactions of *o*-phenylenediamine with pyridine dicarbonyl derivatives in the presence of sulfuric acid also produce macrocycles. Initially, the [2 + 2]-macrocyclic structure has been assigned to the condensation product of 2,6-diacetylpyridine with *o*-phenylenediamine.[69] However, a more detailed investigation showed that the closure of the macrocycle in this product is followed by intramolecular alkylation at the C=N bond to give product **24**.[70]

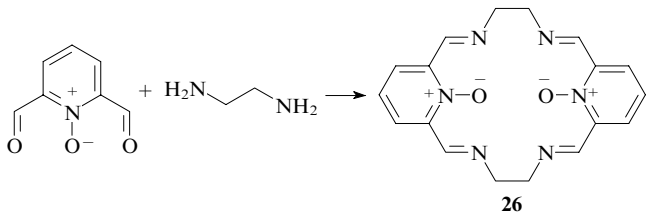


24 **25**

In the absence of acids, pyridine dicarbonyl derivatives behave abnormally in the reactions with *o*-phenylenediamines. For example, the reaction of 2,6-diacetylpyridine with *o*-phenylenediamine in ethanol in the absence of acid catalysts affords only [1 + 1]-condensation product **25**, which reacts with neither the dicarbonyl compound nor diamine.[70]

This inertness of bifunctional derivatives can be explained, for example, in terms of the electron-withdrawing properties of the pyridine ring. Since the carbonyl group in the resulting [1 + 1]-Schiff bases **25** is involved in the chain of direct polar conjugation with the amino group, the reactivity of each group substantially decreases.

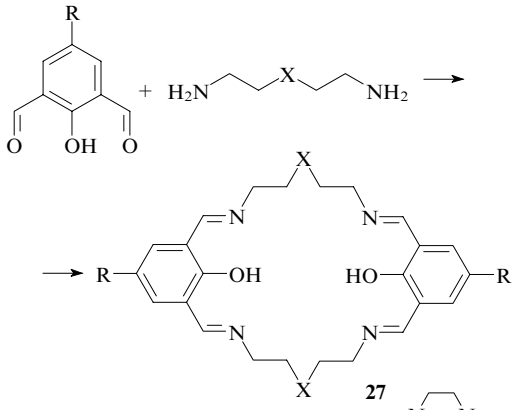
From this point of view, investigations of the behaviour of 2,6-diformylpyridine *N*-oxide under analogous conditions are of obvious interest. However, the reaction of this compound only with 1,2-ethylenediamine was documented.[71] This reaction proceeds under reflux in methanol and gives [2 + 2] macrocycle **26**.



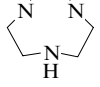
26

3. Cyclocondensation of diamines with dicarbonyl derivatives of phenols and their thio analogues

The reactions of diamines with dicarbonyl derivatives of phenols were studied in most detail. Due to the presence of the proton-donating hydroxy group, such dicarbonyl compounds can catalyse self-condensation with diamines. Although the acidity of dicarbonyl derivatives of phenols is not too high (pK_a of salicylaldehyde is 8.37),[72] the autocatalytic reactions of phenol derivatives with diamines in alcohols proceed easily. The corresponding macrocycles are formed in high yields, although with low selectivity. The reactions of long-chain aliphatic and heteroaliphatic diamines with 4-substituted 2,6-diformylphenols readily proceed in dilute ($\sim 10^{-2}$ mol litre^{-1}) methanolic or ethanolic solutions to give [2 + 2]-macrocyclic Schiff bases **27** in quantitative yields.[73–79]

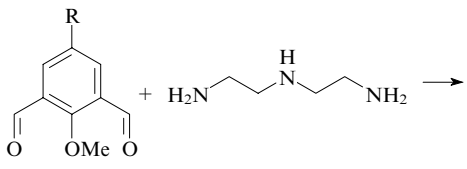


27

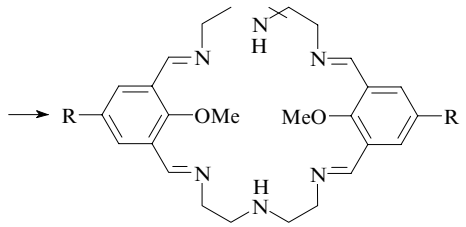
R = Cl, Me; X is absent,[73] NH,[74,75] S,[75] O,[75,76] ,[77]

$O(CH_2)_2O$,[76,78] $O(CH_2CH_2O)_2$,[76] NHC(O)C(O)NH.[79]

As demonstrated above (see Section II.1), dicarbonyl derivatives of phenol ethers react similarly to benzene analogues containing no OR groups. This is the basic difference between derivatives of phenol ethers and phenols. However, the reaction of 2,6-diformylanisoles **28** with diethylenetriamine produces [2 + 2]-macrocyclic Schiff bases **29**.[80]



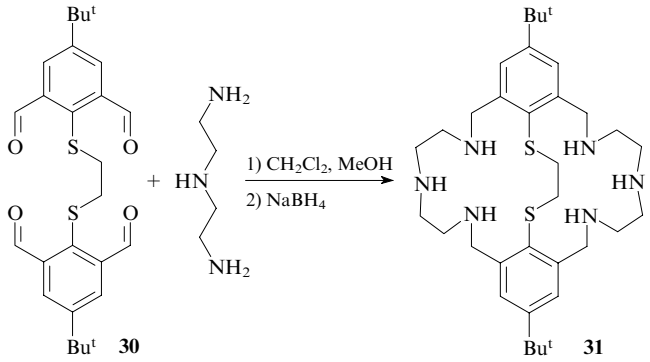
28



29 (65% – 80%)

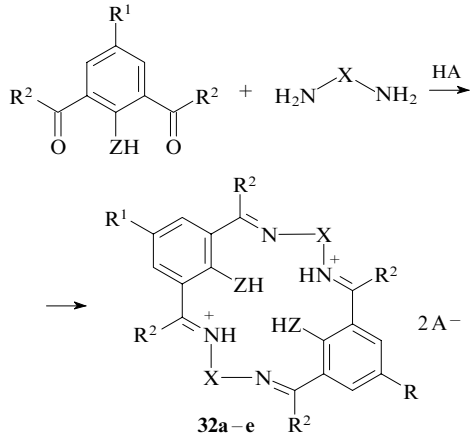
R = Br, Cl, Me, OMe.

The condensation proceeds more easily if two dicarbonyl fragments are linked to each other by a bridge of an appropriate length to form one molecule. For example, diethylenetriamine reacted with bis-sulfide **30** to give the corresponding macrobicyclic Schiff base, which was reduced to the corresponding polyamine **31** in a total yield of >90%.[81]



30 **31**

Under standard conditions (heating in alcohols), dicarbonyl derivatives of phenols do not form macrocyclic Schiff bases in the reactions with ethylene- and propylenediamines.[41,43] However, these compounds can be synthesised by performing the reaction in dilute methanolic solutions ($\sim 10^{-2}$ mol litre^{-1}) in the presence of two equivalents of a strong protic acid (HBr). Macrocyclic [2+2] Schiff bases **32a**–**f** thus synthesised were isolated as salts.[82,83]



32a–**e**

Compound **32**	X	R^1	R^2	Z	A
a	$(CH_2)_2$	Me	H	O	Br
b	$(CH_2)_2$	Bu^t	Me	O	Br
c	$(CH_2)_3$	Me	H	O	Br
d	$(CH_2)_3$	Me	Me	S	Br
e	$CH_2CH(OH)CH_2$	Me	H	S	Br
f	$(CH_2)_4$	Me	H	O	ClO_4

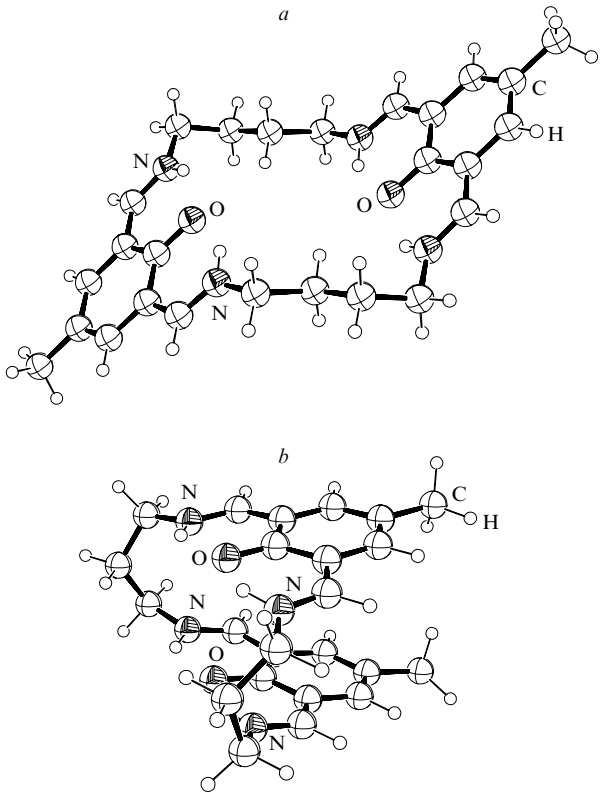
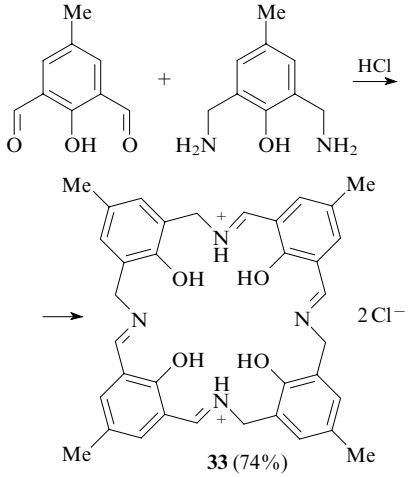


Figure 5. Molecular structures of doubly protonated macrocycles **32f** (*a*)[84] and **32c** (*b*).[85]

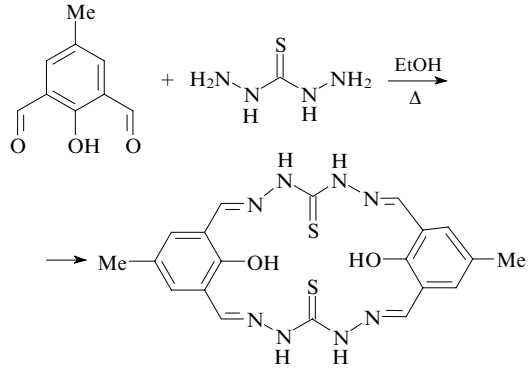
The structures of dications **32a**–**e** depend on the number of the carbon atoms (*n*) in aliphatic α,ω-diamines. If *n* = 2 or 4, the molecules adopt a stair-like conformation. Macrocycle **32f** [R^1 = Me, R^2 = H, Z = O, X = $(CH_2)_4$, A = ClO_4] formed from 1,4-diaminobutane (Fig. 5*a*) is an example.[84] Macrocycle **32c** containing an odd number of carbon atoms (*n* = 3) adopts a horseshoe conformation because of the close proximity of two aromatic rings of the phenolic fragments located at a distance of 3.6–4.1 Å (Fig. 5*b*).[85,86] Under conditions of acid catalysis, 2,6-bis(aminomethyl)-4-methylphenol reacts with 2,6-difor-myl-4-methylphenol to give [2+2] macrocycle **33**.[87]



33 (74%)

In the reactions with dicarbonyl compounds, thiocarbohydrazide behaves like aliphatic diamines. For example, the condensation of this compound with an equimolar amount of

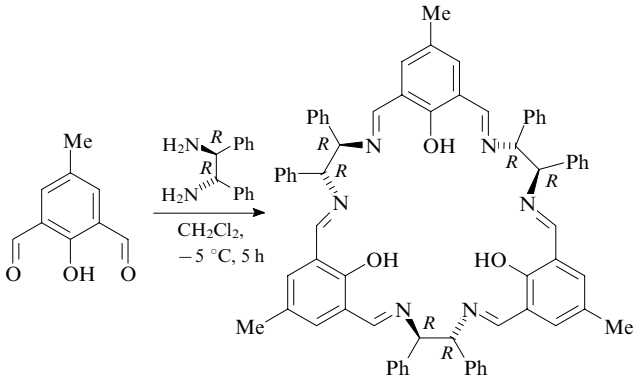
2,6-diformyl-4-methylphenol in boiling ethanol affords [2 + 2] macrocycle **34**.[88]



34 (70%)

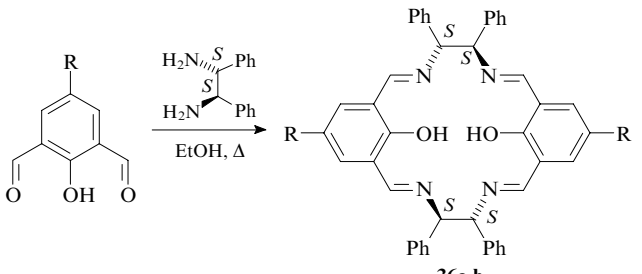
The reactions of dicarbonyl derivatives of phenols with 1,2-diaminoalkanes in dichloromethane instead of ethanol produce lower cyclooligomers. As mentioned in the Introduction, the addition of amine at the carbonyl group is the rate-determining step of the reactions giving azomethines in acidic medium. Hence, the use of a less polar aprotic solvent, which prevents dissociation of the hydroxy group of phenol, instead of polar ethanol readily performing the proton solvation is an appropriate solution.

The reaction of 2,6-diformyl-4-methylphenol with (*R*,*R*)-1,2-diamino-1,2-diphenylethane in dichloromethane at −5 °C produced [3 + 3] macrocycle **35**, which was isolated in 99% yield uncontaminated with other azomethines (mass spectrometric data).[89] The structure of compound **35** is shown in Fig. 6.



35 (99%)

By contrast, the reaction of 4-substituted 2,6-diformylphenols with (*S*,*S*)-1,2-diamino-1,2-diphenylethane in boiling ethanol produces [2 + 2] macrocycles **36a**,**b**.[90]



36a,**b**

R = H (**a**), Bu^t (**b**).

From the above it follows that enantiomerically pure 1,2-diphenylethylenediamines give [3 + 3] macrocycles as the major products under kinetic control and [2 + 2] products under thermodynamic control. An analogous situation is observed

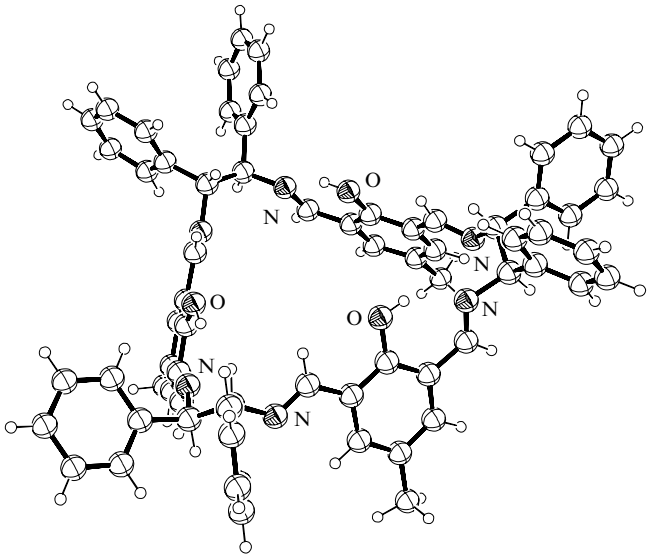
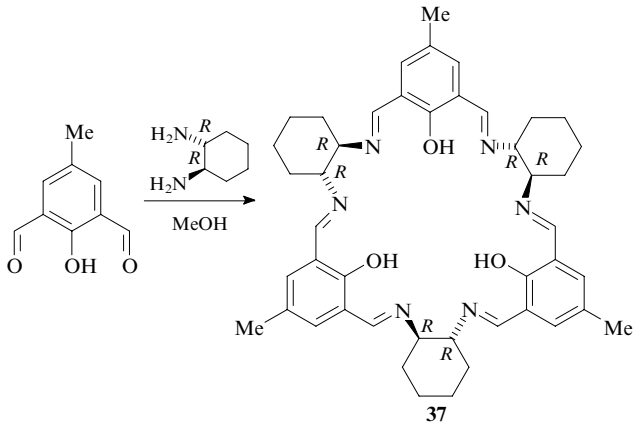


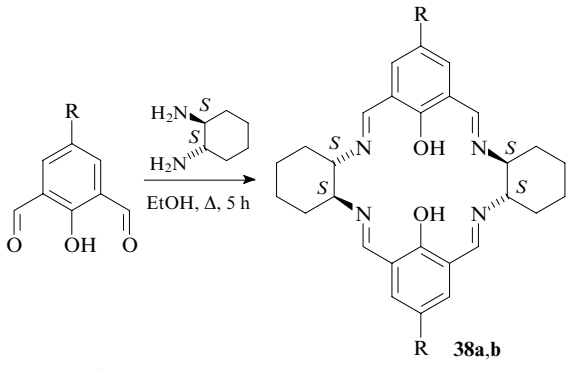
Figure 6. Structure of [3 + 3] macrocycle **35**.[89]

in the reactions of diformylphenols with *trans*-1,2-diaminocyclohexanes even when carried out in alcohols.

For example, the reaction of *trans*-(*R*,*R*)-1,2-diaminocyclohexane with 2,6-diformyl-4-methylphenol in a concentrated (0.1 mol litre^{-1}) methanolic solution at −5 °C or at room temperature produces [3 + 3]-macrocyclic azomethine **37** in quantitative yield.[57,89,91,92] However, according to the results of the study,[90] *trans*-(*S*,*S*)-1,2-diaminocyclohexane reacts with 4-substituted 2,6-diformylphenols under reflux in ethanol for 5 h to give [2 + 2] products **38a**,**b**. This is circumstantial evidence that the formation of [2 + 2]-condensation products is thermodynamically controlled.



37

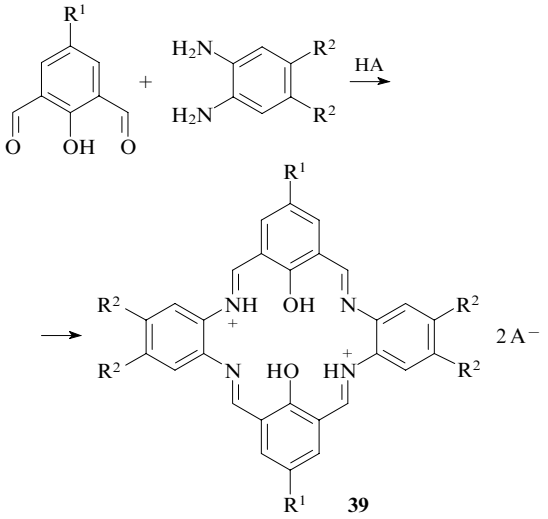


38a,**b**

R = H (**a**), Bu^t (**b**).

The structures of the [3 + 3] macrocycles synthesised by the reactions of 1,2-diaminocyclohexane with diformylphenols substantially differ from those obtained in the reactions with diformylbenzenes containing no OH groups (see Fig. 2). In the former case, the molecules adopt a bowl conformation due to which they can be considered as analogues of calix[3]arenes.[89]

The reactions of *o*-phenylenediamine and its derivatives with 2,6-diformylphenols in alcohols easily proceed only in the presence of acids and give salts of [2 + 2] macrocycles **39**, like the reactions with 1,2-ethylenediamine.[39]



39

R^1 = Me, Bu^t; R^2 = H, Me.

The X-ray diffraction data show that structures of macrocycles **39** are planar, and the hydrogen atoms are localised at the oxygen atoms of the phenolic groups and the nitrogen atoms of the azomethine fragments (Fig. 7).[39] Consequently, the macrocycles prepared by the reactions of diformylphenols with aromatic diamines are structurally different from their aliphatic analogues (see above), in which all endocyclic hydrogen atoms are located at the nitrogen atoms of the azomethine groups.

Different, in principle, macrocycles were synthesised by the reactions of 2,6-diformylphenols with *o*-phenylenediamine in the absence of acids. These reactions afford mixtures of [2 + 2]-macrocyclic Schiff bases **40**, in which two of four imino groups are reduced, as well as 2,6-bis(benzimidazol-2-yl)phenols **41**.[74,93,94] Macrocyclic compound **40** (R^1 = Me, R^2 = H) was synthesised in 60% yield by the reaction of *o*-phenylenediamine with 2,6-diformyl-4-methylphenol in the presence of catalytic amounts of hydrochloric acid (Scheme 4).[39]

The theoretical investigation of the mechanism of formation of macrocycles **40** by the density functional theory method[94] demonstrated that the first step of this reaction

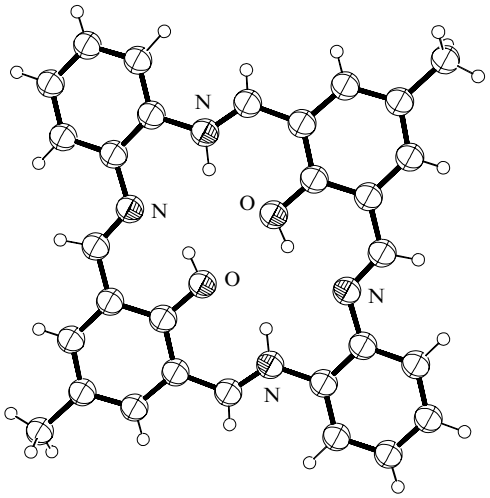
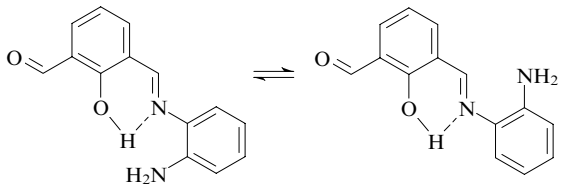


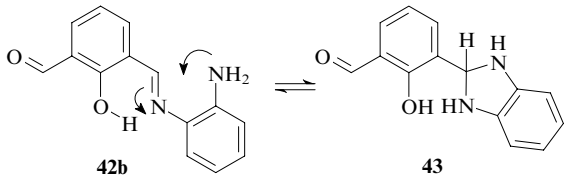
Figure 7. Structure of dication **39** (R^1 = Me, R^2 = H).[39]

(like the reaction of 2,6-diacetylpyridine with *o*-phenylenediamine) gives the [1 + 1]-condensation product, which can be represented as two rotamers **42a** and **42b**.



42a (0 kcal mol^{-1}) **42b** (3.18 kcal mol^{-1})

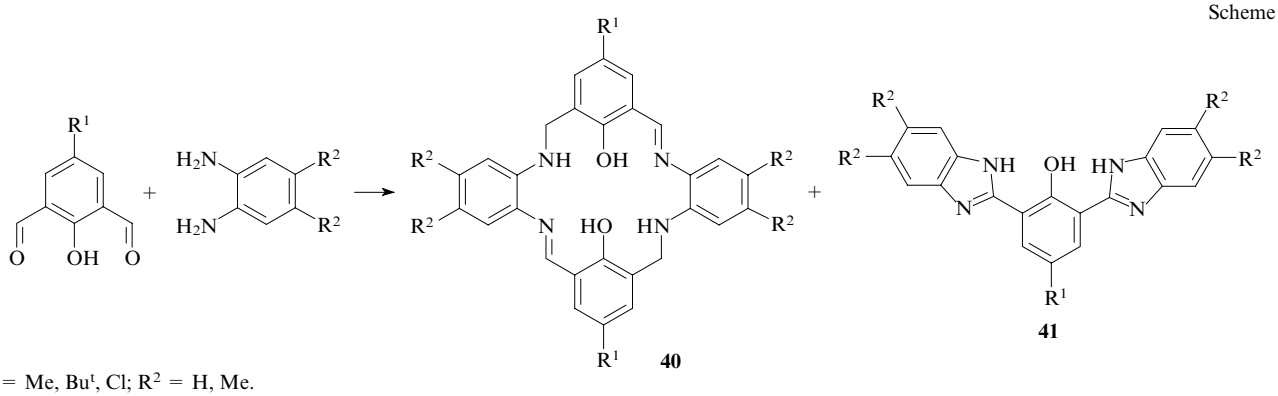
The most stable conformer **42a** exists in equilibrium with isomer **42b**, whose energy is 3.18 kcal mol^{-1} lower. In the latter isomer, the distance between the nitrogen atom of the amino group and the carbon atom of the imino group is about 3.5 Å, which is favourable for intramolecular cyclisation.



42b **43**

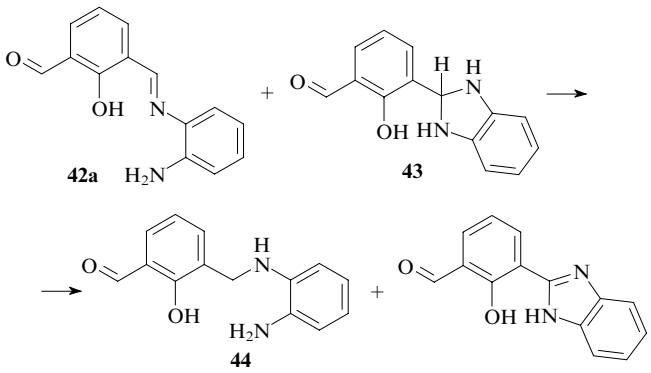
The resulting benzimidazoline **43** is a strong reducing agent. The reaction of **43** with [1 + 1] Schiff base **42a** leads to reduction of the latter to diamine **44**. According to the results of calculation, this process is exothermic (27.3 kcal mol^{-1}).

Scheme 4



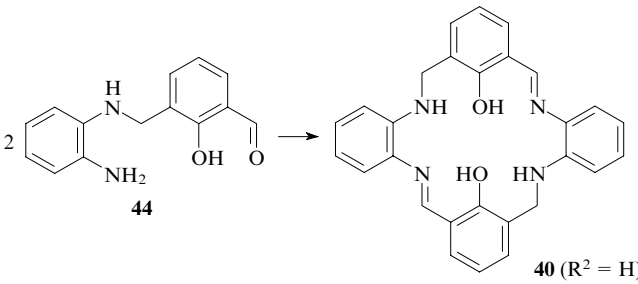
40 **41**

R^1 = Me, Bu^t, Cl; R^2 = H, Me.



Two molecules of diamine **44**, in which the carbonyl and amino groups are separated from each other, are readily involved in the usual Schiff condensation yielding compound **40** ($R^1 = R^2 = H$). This reaction is exothermic ($\Delta H^\circ = -0.12$ kcal mol^{-1}, $\Delta G^\circ = -9.15$ kcal mol^{-1}).

The X-ray diffraction structure of macrocyclic compound **40** ($R^1 = Bu^t$, $R^2 = H$) is planar (Fig. 8). In the crystal structure, the molecules are disordered so that the CH_2NH and CH═N groups randomly replace each other,



due to which the differences in the lengths of the double and single CN bonds are not observed (the standard HC═N and H_2C-N bond lengths are 1.303 and 1.460 Å, respectively).[93] Apparently, the crystal structure contains several tautomeric forms, in which the hydrogen atoms are in the vicinity of different nitrogen atoms. In addition, the crystal structure can contain zwitterions, in which all three or four nitrogen atoms are protonated and the negative charges are located on one or two oxygen atoms [the C–O bond lengths are 1.33(1) and 1.34(1) Å and are similar to the standard $C(sp^2)-OH$ and $C(sp^2)-O^-$ bond lengths, respectively].

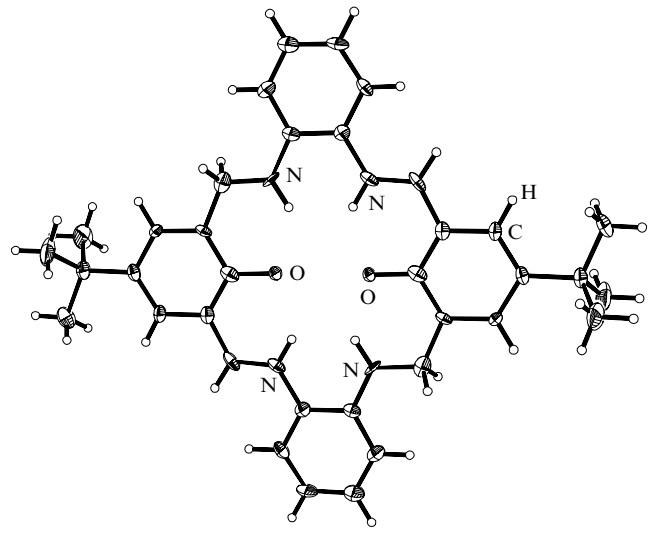
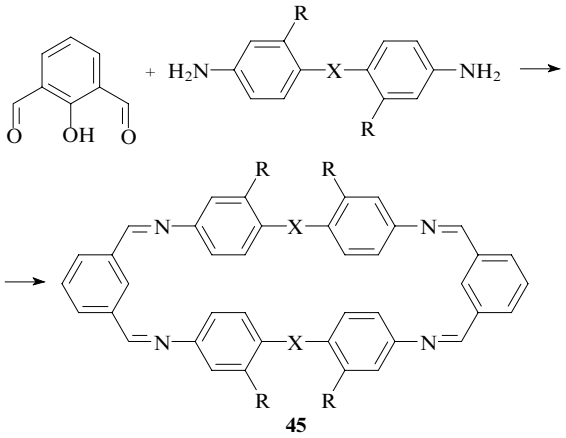


Figure 8. X-Ray diffraction structure of macrocycle **40** ($R^1 = Bu^t$, $R^2 = H$).[93]

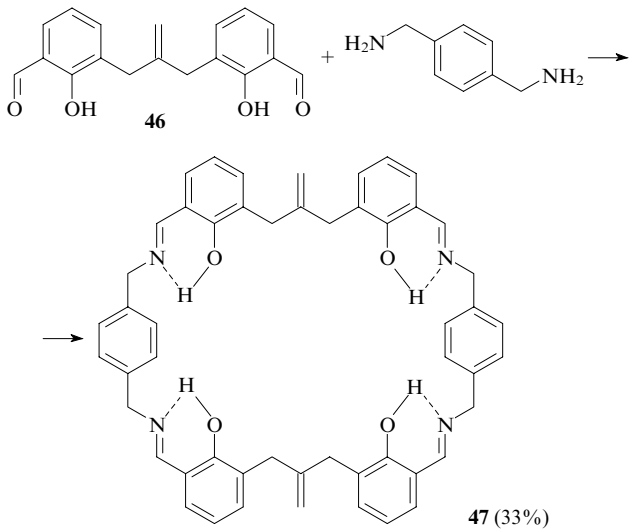
In the reactions with dicarbonyl compounds, polycyclic aromatic diamines containing amino groups in different aromatic rings behave like aliphatic α,ω-diamines. For example, the condensation of 2,6-diformylphenol in methanol with equimolar amounts of diamino derivatives of biphenyl, diphenylmethane and 1,2-diphenylethane afforded the expected [2 + 2] macrocycles **45**.[95,96]



X is absent: R = Me, OMe; X = $(CH_2)_n$ (n = 1, 2), R = H.

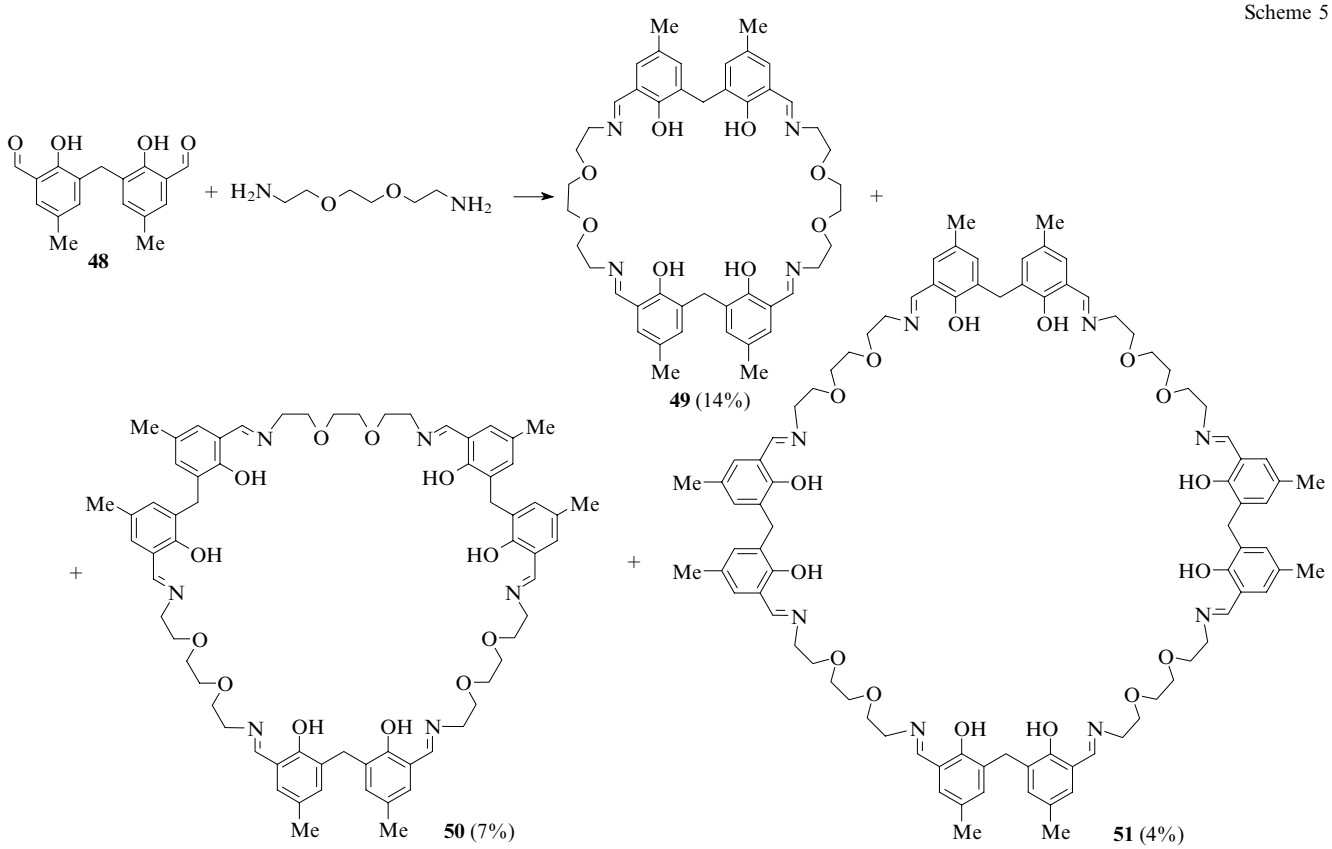
Schiff bases that are formed in reactions of diformyl derivatives of polyphenols or their thio analogues with diamines, are of great interest as ligands. Unexpected results were obtained in the reaction with dicarbonyl compounds containing the hydroxy group that undergoes deprotonation, particularly, if the hydroxy and carbonyl groups are in the *ortho* positions with respect to each other. In this case, there are conditions favourable for the formation of strong hydrogen bonds both in the starting dicarbonyl compound and its cyclocondensation products with diamines, resulting in an increase in thermodynamic stability of such compounds. In addition, the absence of the direct polar conjugation between the carbonyl groups in dicarbonyl compounds results in an increase in their reactivity with respect to diamines.

The reaction of diformyl derivative **46** with 1,4-bis(aminomethyl)benzene in THF at room temperature affords [2 + 2]-macrocyclic Schiff base **47**.[97]



The condensation of bis-phenol **48** with 3,6-dioxa-1,8-diaminooctane in a chloroform–methanol mixture under high-dilution conditions affords a mixture of [2 + 2], [3 + 3],

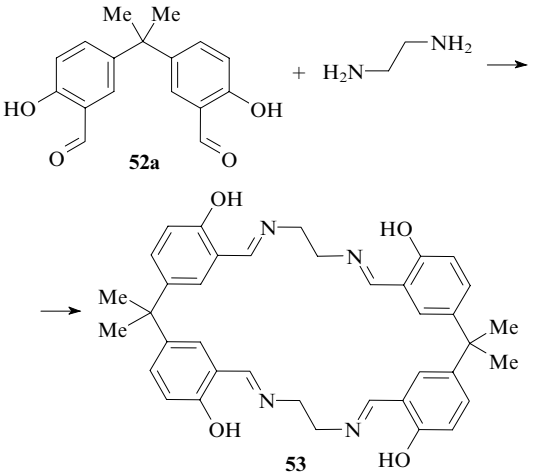
Scheme 5



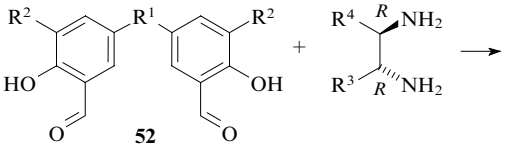
[4 + 4], [5 + 5], [6 + 6] and even [7 + 7] macrocycles. Some of these products (compounds **49**–**51**) were isolated in the individual state. The high-molecular-mass products were detected by MALDI-TOF mass spectrometry.[98] It should be noted that the [1 + 1]-condensation product was not found in the mixture (Scheme 5).

The X-ray diffraction data for [2 + 2]-condensation product **49** show that, in the crystal, this macrocycle adopts a twisted, figure eight-like, conformation due to the π,π-stacking interaction between two of four phenol fragments (Fig. 9).[98] This suggests that the template reaction in which the π,π-stacking plays the organising role is possible, because cyclooligomer **49** is produced in the maximum yield.

In the reactions with aliphatic diamines, polyphenols containing the salicylaldehyde fragments linked to each other by bridges in the *para* position with respect to the hydroxy group show reactivity similar to that of monophenols. For example, the reaction of bis-phenol **52a** with ethylenediamine produces [2 + 2]-macrocyclic Schiff base **53**.[99]



The reactions of bis-phenols **52** with salts of chiral diamines in alcohols in the presence of potassium carbonate under microwave irradiation also afford [2 + 2] macrocycles.[100]



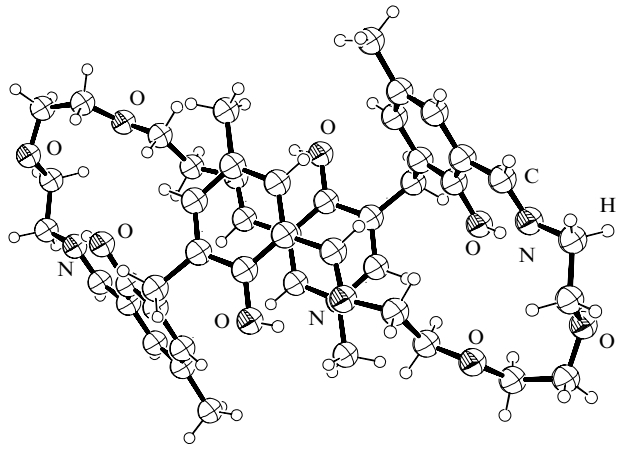
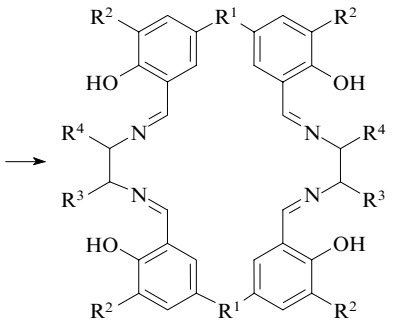
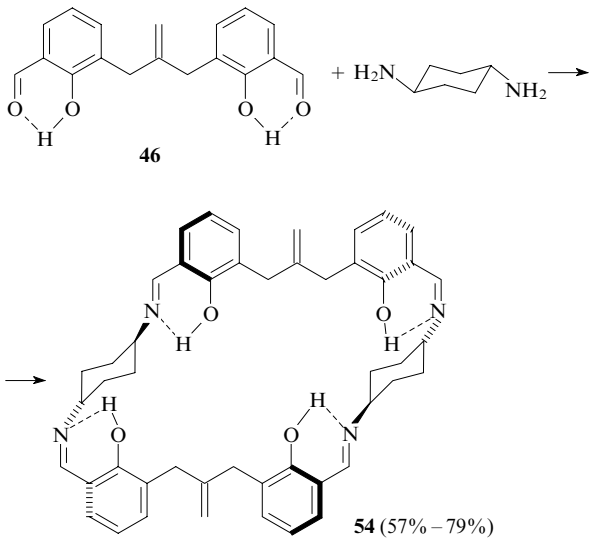


Figure 9. X-Ray diffraction structure of [2 + 2] macrocycle **49**.[98]



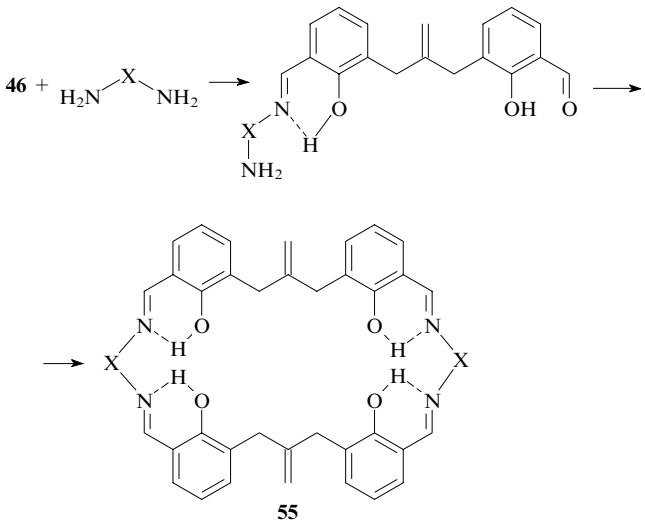
$R^1 = CH_2$: R^2 = H, Br, NO_2, Bu^t; $R^1 = CMe_2$: R^2 = H, Br;
$R^1 = SO_2$, R^2 = H; R^1 is absent, R^2 = H;
$R^3 - R^4 = (CH_2)_4$, CH_2NBnCH_2; $R^3 = R^4 = CO_2Bn$.

The reaction of *trans*-1,4-diaminocyclohexane with a dicarbonyl derivative of bis-phenol **46**, in which the carbonyl groups are fixed by strong hydrogen bonding, produced [2 + 2]-macrocyclic Schiff base **54**.[97]



54 (57% – 79%)

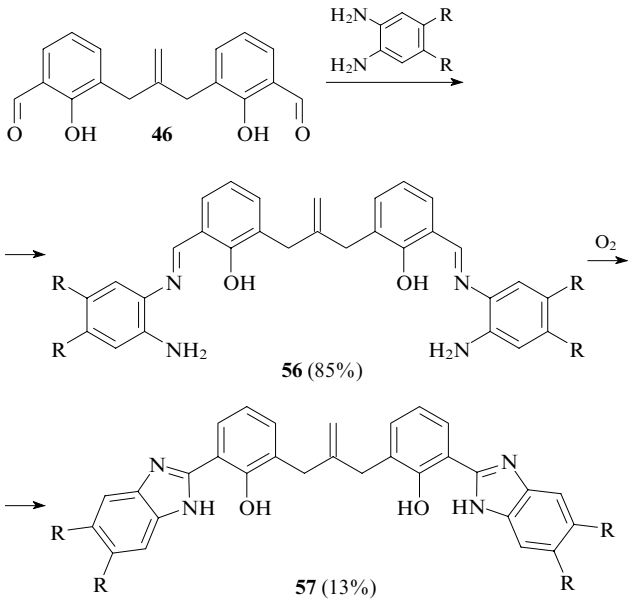
Because of the absence of direct polar conjugation between the carbonyl groups in dicarbonyl compound **46**, these groups are involved in the reactions with diamines independently of each other, which allows the synthesis of stoichiometrically controlled products. The reaction of 0.1 M solutions of dialdehyde **46** with aromatic diamines (in a ratio of 1 : 1) in THF or DMF at room temperature afforded the corresponding [2 + 2] macrocycles **55**.[97] The reaction was demonstrated to give initially [1 + 1]-condensation products. The ^{1}H NMR spectroscopic study showed that these compounds are stabilised (like the final products) by strong hydrogen bonding between the phenolic hydroxy groups and the azomethine nitrogen atoms.[97]



55

X is 1,2-phenylene (90% – 97%), 1,3-phenylene (58% – 64%), 1,4-phenylene (76% – 98%), 1,5-naphthylene (90% – 97%).

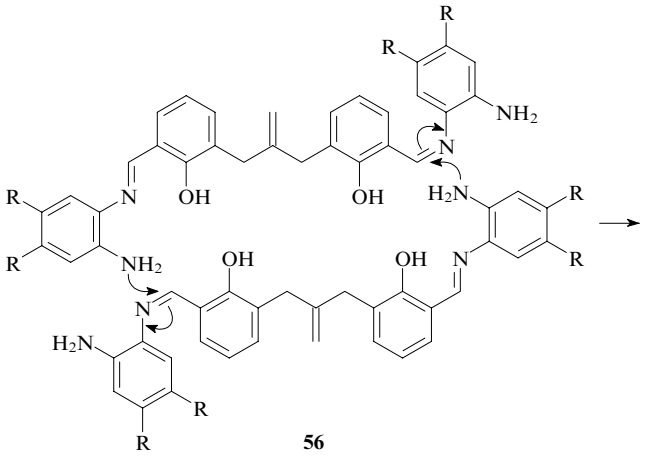
The reactions of dilute (0.04 mol litre^{-1}) methanolic solutions of dialdehyde **46** with an excess of *o*-phenylenediamine or its 4,5-dimethoxy derivative at room temperature yielded acyclic [1 + 2]-condensation products **56**.[101]



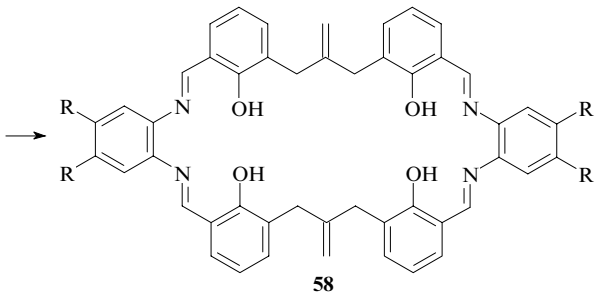
R = H, OMe.

Diamines **56** thus synthesised are very sensitive to atmospheric oxygen and, like the [1 + 1]-condensation products involving 1-R-2,6-diformylphenols (see above), are oxidised to the corresponding benzimidazole derivatives **57**. This process is the major side reaction in the synthesis of these azomethines.[101]

The X-ray diffraction study showed that two molecules of [1 + 2] azomethine **56** in the unit cell are located so that the nitrogen atoms of the amino groups of one molecule are located close to the carbon atoms of the azomethine fragments of the adjacent molecule.



56

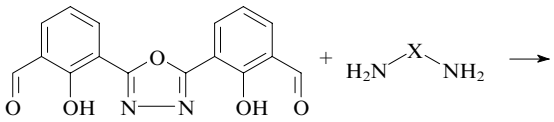


58

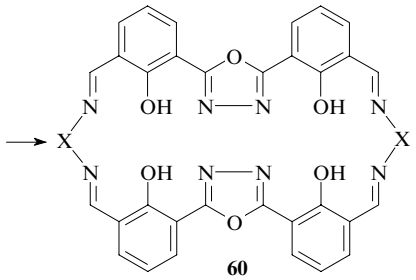
R = H (71%), OMe (37%).

It was hypothesised that the dimeric structure is retained in solution. Upon prolonged storage of solutions, two molecules of compound **56** undergo condensation to form [2 + 2] macrocyclic Schiff base **58**, which is accompanied by elimination of two *o*-phenylenediamine molecules.[101]

The condensation of dicarbonyl derivatives of polyphenols with diamines proceeds analogously even if two fragments of salicylaldehyde are linked to each other by a rigid bridge. For example, the reaction of equimolar amounts of dialdehyde **59** with diamines in dilute acetonitrile solution (0.01 mol litre^{-1}) produces [2 + 2]-macrocyclic azomethines **60**.[102]



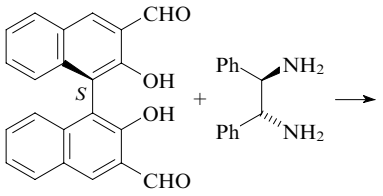
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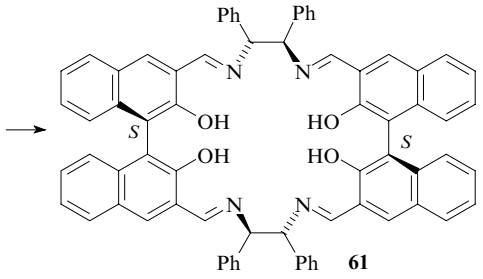


60

X = CH_2CH_2, *o*-phenylene.

Important results giving a new insight into the formation of macrocycles were obtained in the study of the reaction of 3,3′-diformyl-2,2′-dihydroxybinaphthyl with (*R*,*R*)-1,2-diamino-1,2-diphenylethane. For example, dialdehyde having the *R* configuration forms only oligomers,[103, 104] whereas the *S* enantiomer undergoes [2 + 2] condensation to give macrocycle **61**.[105]





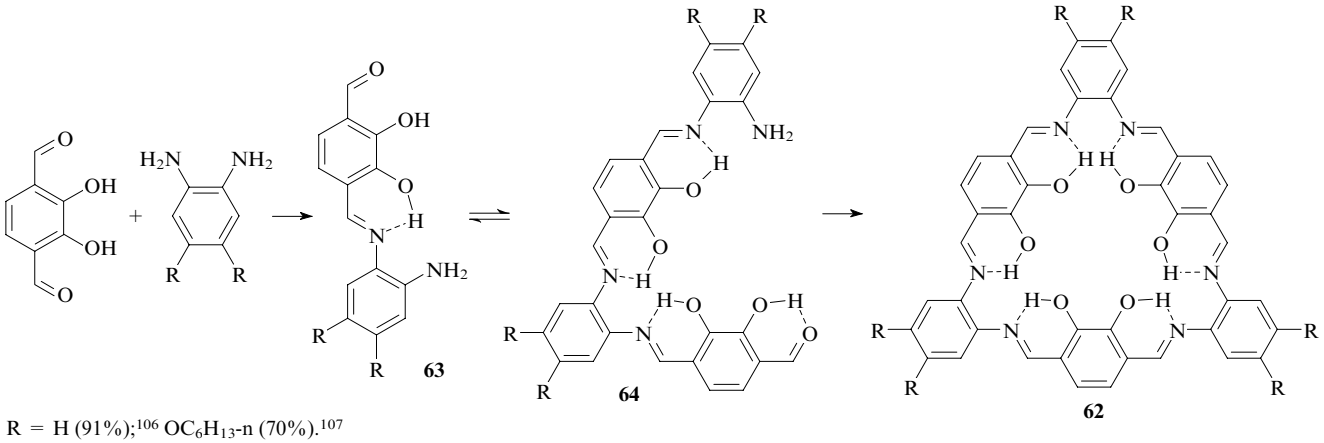
61

The selective reaction of the *S* enantiomer of dialdehyde with optically pure diamine allowed the resolution of racemic 3,3′-diformylbinaphthyl and the isolation of the pure *S* enantiomer in 50% – 60% yield (with respect to theoretical).[105]

Unlike dicarbonyl derivatives of polyphenols, diformylpyrocatechols react with aromatic dialdehydes to form only [3 + 3]-condensation products. Apparently, this is a consequence of the rigid structural preorganisation of the reactants. In some sense, the same factor of self-organisation of macrocycles, which was responsible for the predominant formation of [3 + 3] macrocycles in the reaction of terephthalaldehyde with *trans*-1,2-diaminocyclohexanes (see Section II.1), plays the decisive role.

The reaction of 3,6-diformylpyrocatechol with *o*-phenylenediamines in acetonitrile in the absence of catalysts proceeds in complete agreement with the geometry of the reaction components and affords [3 + 3]-condensation products **62**. The reaction proceeds through the formation of acyclic [1 + 1]- (**63**) and [2 + 2]-condensation products (**64**). In this case, the macrocycles are stabilised by hydrogen bonds, which was demonstrated by ^{1}H NMR spectroscopy.[106, 107] Thermodynamically most stable [3 + 3] macrocycle **62** precipitates from the reaction mixture, resulting in the shift of the equilibrium toward the formation of this product (Scheme 6).

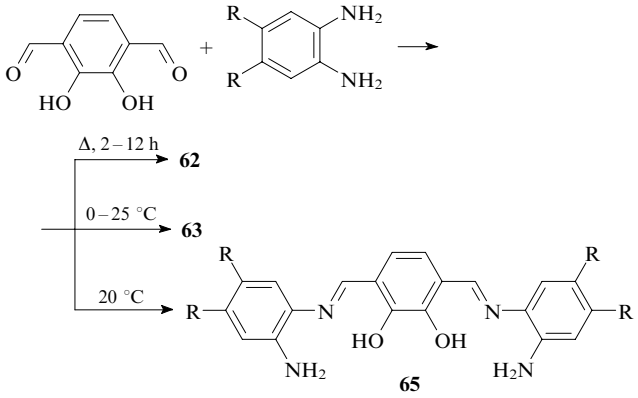
Scheme 6



63 **64** **62**

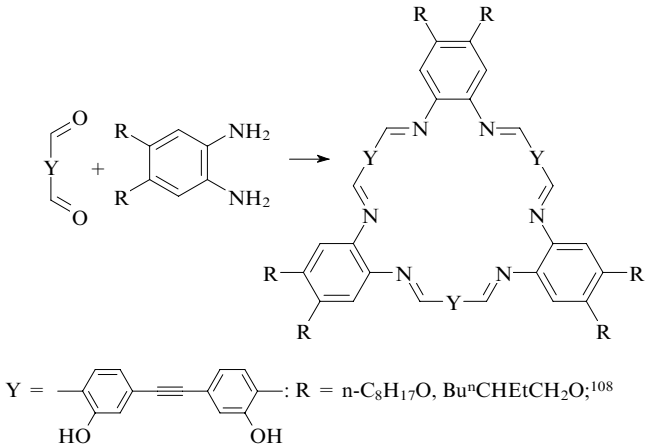
R = H (91%);[106] OC_6H_{13}-n (70%).[107]

This reaction in a boiling chloroform – acetonitrile mixture also produces [3 + 3] macrocycles **62**, a much longer reaction time being required for the reactions with long-chain amines [1,2-diamino-4,5-di(hexyloxy)benzene].[8] In this case, [1 + 1]-, [1 + 2]- and [2 + 1]-condensation products were also detected in the reaction mixture. The position of the equilibrium in this dynamic combinatorial library substantially depends on the reaction conditions. Since [3 + 3] macrocycle **62** is the thermodynamically controlled reaction product, it is formed as the major product upon prolonged refluxing of the reaction mixture. The reaction under kinetic control (low temperature and short reaction time) gives predominantly [1 + 1]-condensation product **63** and at room temperature, [1 + 2]-condensation product **65**. All these compounds were demonstrated [8] to be intermediates in the reaction affording the [3 + 3] macrocycle.



Other diformylphenols with analogous arrangement of the carbonyl groups are also involved in the reactions with *o*-phenylenediamines. Their reactions with *o*-phenylenediamines in a chloroform – acetonitrile mixture yield [3 + 3]-condensation products (Scheme 7).[108, 109]

Scheme 7



X-Ray diffraction studies showed that the resulting antiaromatic 48p-electron macrocycles are non-planar (Fig. 10).[106, 109] Due to this geometry, the conjugation between the aromatic rings is absent, the antiaromaticity is violated, and these compounds become unstable.

The analogous reaction in commercial chloroform produces [3 + 3] macrocycles **62** along with partially reduced derivatives **66** in low yields (10% – 20%). The reduction products

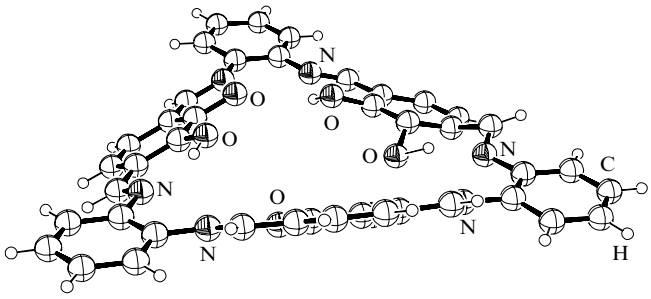
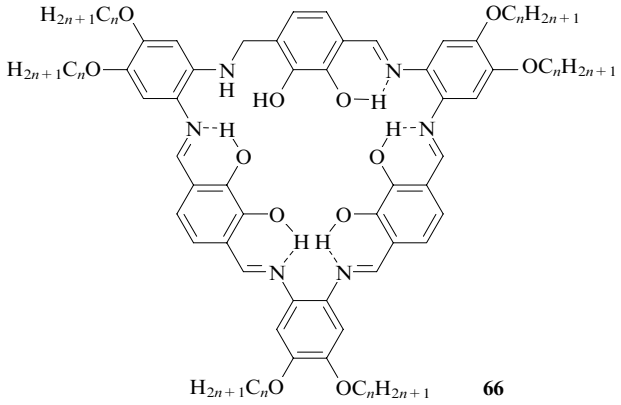


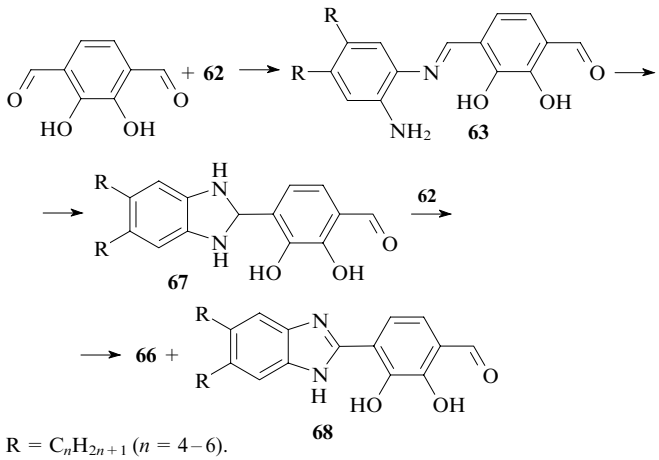
Figure 10. Structure of macrocycle **62** (R = H).[106]

were not detected if the reaction was carried out in chloroform purified from traces of moisture and acids.[8, 110]



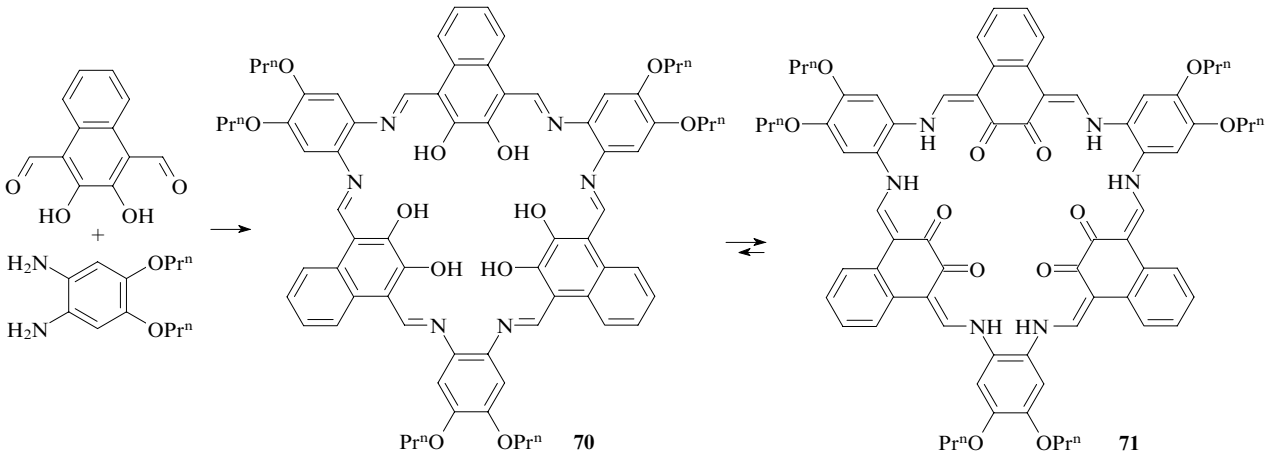
The mechanism of formation of reduced product **66** is presented in Scheme 8.[110] The reaction of [3 + 3] macrocycle **62** with the starting dialdehyde in commercial chloroform affords products of the macrocycle cleavage, including [1 + 1]-condensation product **63**. The latter can undergo intramolecular cyclisation analogous to that described above for phenol derivatives to form benzimidazoline derivative **67**, which is involved in reduction of [3 + 3] macrocycle **62** yielding compound **66**. The transfer of the hydrogen atom to the carbon atom of the imino group occurs from the carbon atom of benzimidazoline, which was confirmed experimentally with the use of an isotope label.[110]

Scheme 8

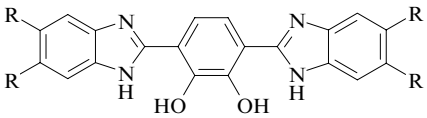


Reduction of [3 + 3] macrocycles **62** is accompanied by oxidation of benzimidazoline **67** to benzimidazole **68**, which

Scheme 9



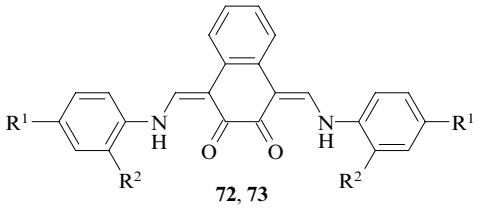
was detected in the reaction mixture along with reduced macrocycle **66** and bis(benzimidazoline) derivative **69**.[8,110]



69

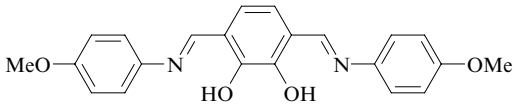
The extension of [3 + 3]-condensation of *o*-phenylenediamines with aromatic 1,4-dialdehydes to naphthalene derivatives resulted in macrocycle **70**, which exists in equilibrium with keto-enamine tautomeric form **71** (Scheme 9).[111]

Tautomerisation of azomethine to the corresponding enamine leads to the removal of antiaromaticity of [3 + 3] macrocyclic Schiff base, the second aromatic ring in naphthalene remaining intact. Studies of model compounds by quantum chemical methods and X-ray diffraction showed[111] that azomethine derivatives of 1,4-diformyl-2,3-dihydroxynaphthalene, *viz*., compounds **72** and **73**, unlike their pyrocatechol analogue **74**, exist in the keto-enamine form.



72, **73**

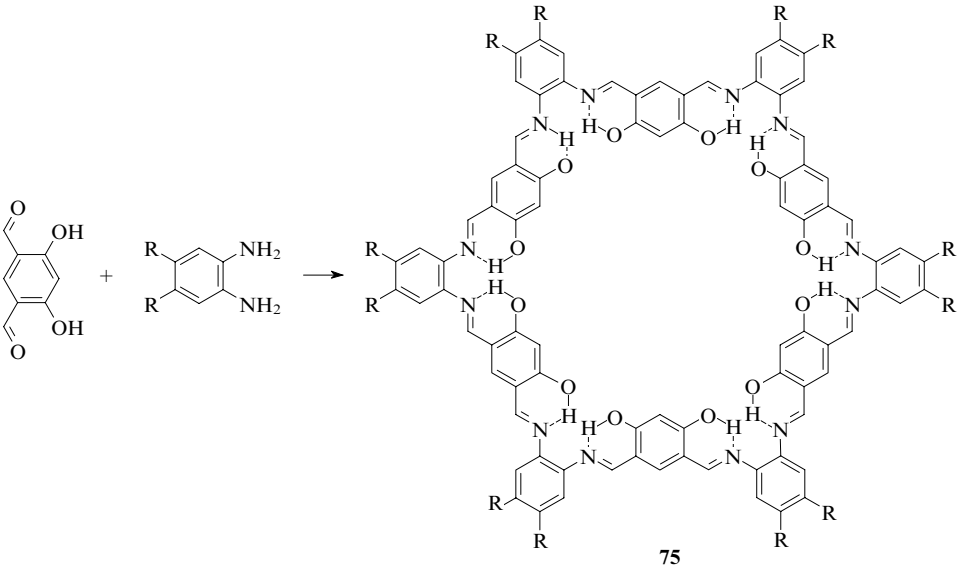
R^1 = OMe, R^2 = H (**72**); R^1 = H, R^2 = NHBoc (**73**), Boc is *tert*-butoxycarbonyl.



74

The formation of hydrogen bonds is a powerful driving force for the self-organisation of macrocycles. This is most clearly illustrated by the formation of macrocycles **75** as a result of [6 + 6] condensation of diformylresorcinol with *o*-phenylenediamine (Scheme 10).[112]

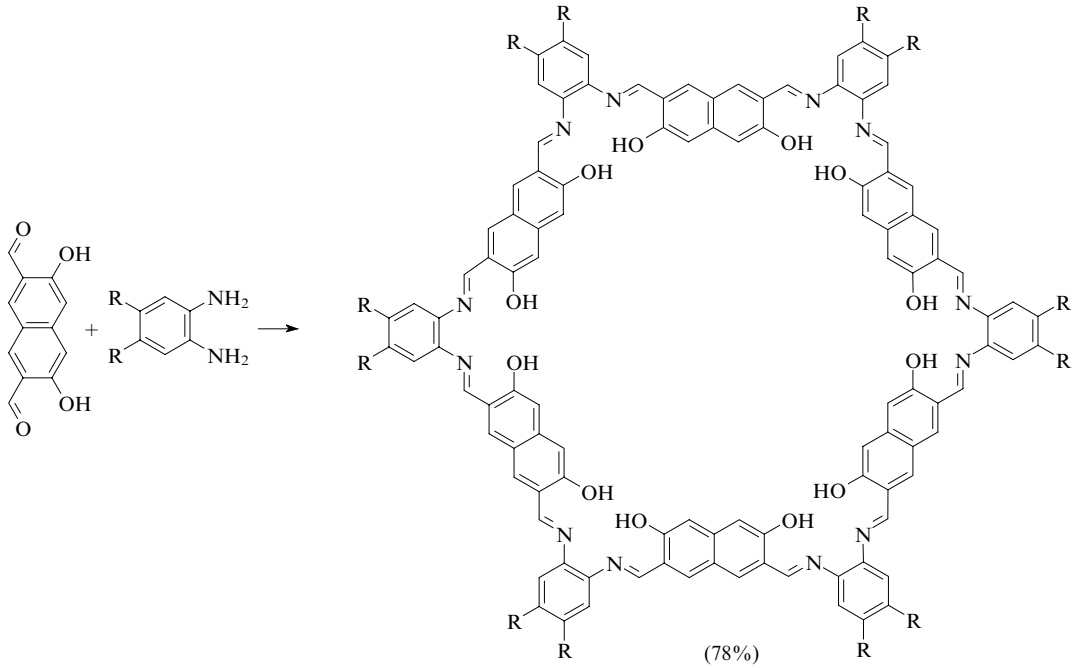
Scheme 10



75

R = OC_6H_{13}-n (19%), OC_5H_{11}-n (25%).

Scheme 11



R = OC_6H_{13}-n.

The fact that the analogous reaction of 2,7-diformyl-3,6-dihydroxynaphthalene was successful suggests that this [6 + 6] macrocyclisation for rigidly preorganised dihydroxydiformyl derivatives of polycyclic aromatic compounds has the general character (Scheme 11).[112]

4. Cyclocondensation of diamines with dicarbonyl derivatives of five-membered carbo- and heterocycles

a. 2,5-Diformyl derivatives of furan and thiophene

2,5-Diformylfuran and -thiophene readily react with aliphatic diamines to form [2 + 2]-macrocyclic Schiff bases **76a**,**b** and **77a** – **g** if the amino groups are separated by a chain of three or more atoms. Dilute solutions of these compounds in acetonitrile or methanol are used. The behaviour of these dicarbonyl compounds is completely analogous to that of related benzene derivatives (Scheme 12).

The three-dimensional structure of one of these compounds, *viz*, the reaction product of 2,5-diformylthiophene with 3-oxapentane-1,5-diamine **77e**, was established (Fig. 11).[118]

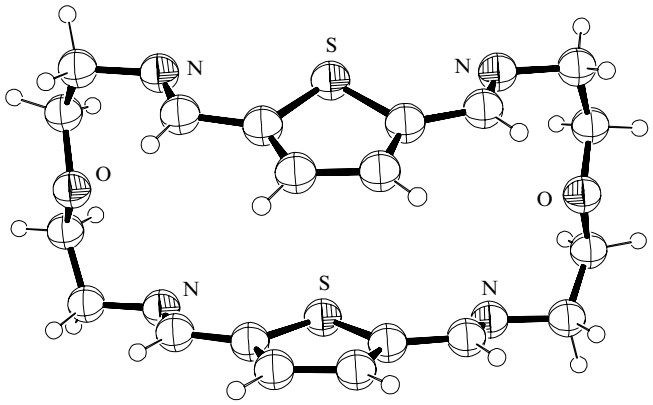
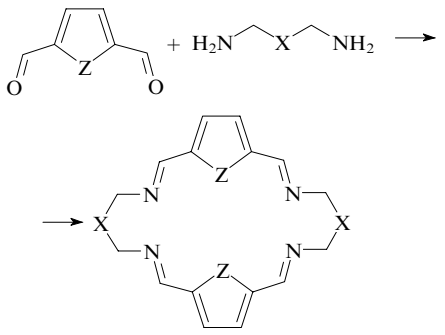


Figure 11. Structure of [2 + 2] macrocycle **77e** (n = 1).[118]

Scheme 12

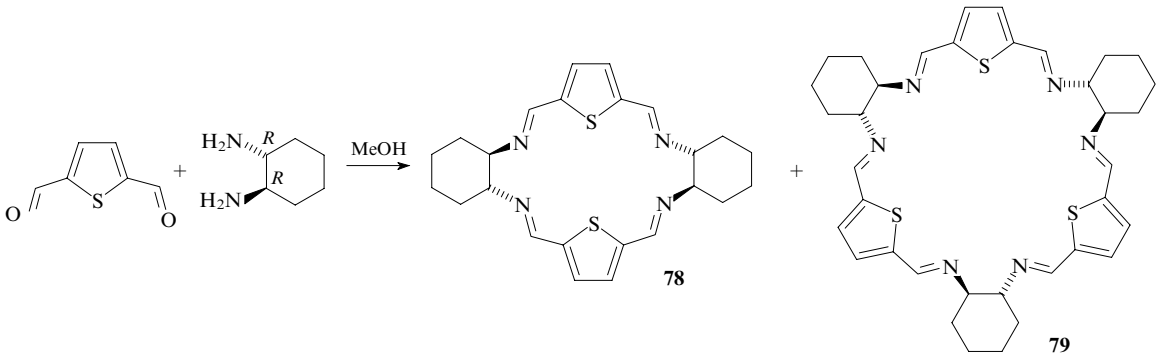


76a,**b**; **77a** – **g**

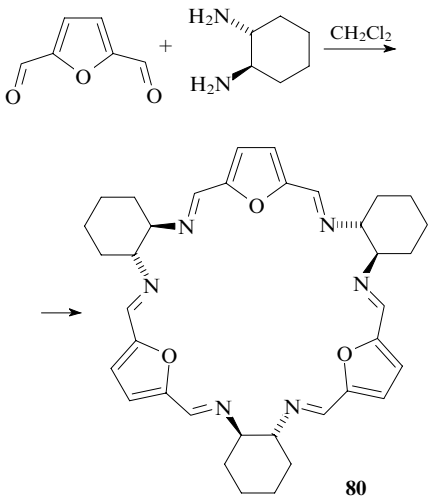
Compound	X	Z	Yield (%)	Ref.
76a	CH_2NHCH_2	O	–	43
76b	$(CH_2OCH_2)_n$ (n = 1 – 3)	O	60 – 70	40
77a	CHOH	S	50 – 55	113
77b	CH_2NHCH_2	S	–	114
77c	$CH_2NBu^tCH_2$	S	48	115, 116
77d	CH_2SCH_2	S	70	114, 117
77e	$(CH_2OCH_2)_n$ (n = 1 – 3)	S	60 – 70	114, 117
77f	$(CH_2)_n$ (n = 1 – 3)	S	50 – 90	117
77g	$(CH_2)_2NH(CH_2)_2$	S	50 – 90	117

With a geometrically more rigid diamine, *viz*., *trans*-(*R*,*R*)-1,2-diaminocyclohexane, more complex processes occur compared to the reactions with flexible aliphatic amines. For example, the reactions of 2,5-diformylthiophene in methanol at room temperature produce [2 + 2] (**78**) and [3 + 3] macrocycles (**79**). Studies by mass spectrometry showed that these products are present in a mixture in equal amounts.[119] The replacement of methanol by dichloromethane results in the formation of only one reaction product, *viz*., [3 + 3] macrocycle **79** (35% yield) (Scheme 13).[48]

Scheme 13



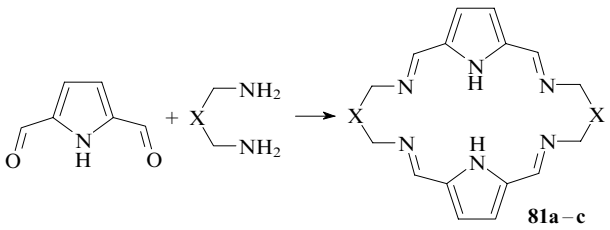
The condensation of 2,5-diformylfuran with *trans*-(*R*,*R*)-1,2-diaminocyclohexane at room temperature in dichloromethane gives [3 + 3] azomethine **80** in quantitative yield.[52]



Such different results obtained for related 2,5-diformyl derivatives of furan and thiophene provide conclusive evidence that the formation of [3 + 3] macrocycles depends on the nature of the solvent. In weakly polar dichloromethane, the reactions afford only [3 + 3]-condensation products, whereas a series of products are formed in polar methanol.

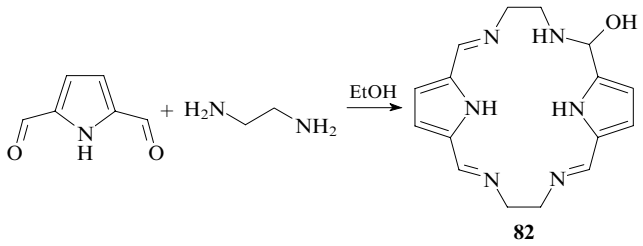
b. Diformyl derivatives of pyrrole and compounds with several pyrrole rings

Unlike oxa and thia analogues, α,α′-dicarbonyl derivatives of pyrrole are less reactive toward amines. Hence, the synthesis of pyrrole-containing macrocycles requires the use of a catalyst (acids). A rather few azomethine macrocyclic compounds (for example, compounds **81a**–**c**) were synthesised by direct reactions of 2,5-diformylpyrrole with aliphatic diamines.

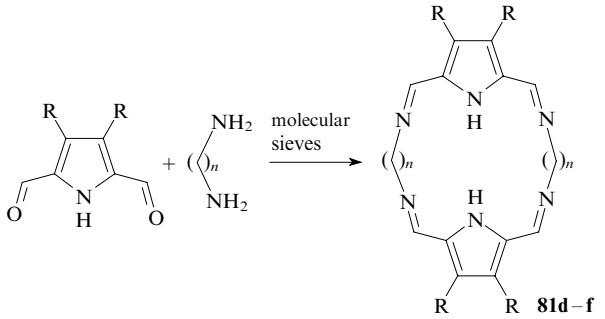


X = CHOH (**a**, 50%–55%),[123] CH_2NHCH_2 (**b**),[43, 114] CH_2 (**c**, 66%).[63]

However, not all reactions yield macrocyclic azomethines. For example, the reaction of ethylenediamine with 2,5-diformylpyrrole in ethanol stops at the formation of hemiaminal **82**, which is the intermediate of the [2 + 2]-condensation reaction.[38]

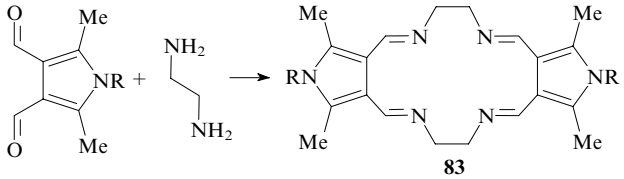


The addition of molecular sieves to the reaction mixture favours the completion of the reaction giving rise to macrocycles. Under these conditions, the reactions of diformylpyrrole derivatives with ethylenediamine and propylenediamine produced compounds **81d**–**f**.[120]



n = 2: R = H (**d**), Me (**e**); *n* = 3, R = Me (**f**).

Unlike the 2,5 isomers, 3,4-diformylpyrroles react with diamines in the absence of acids and molecular sieves to give [2 + 2] macrocycles **83** in high yields.[121]

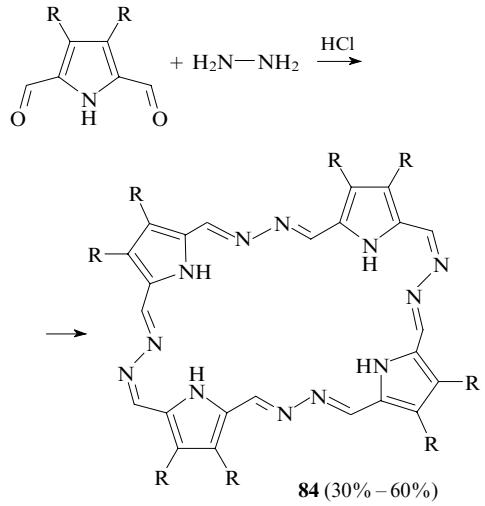


R = H, Me, Et.

The reactions of 3,4-dialkoxy-2,5-diformylpyrroles with hydrazine,† which can, in principle, be considered as the simplest diamine, yielded unexpected results. The reactions in

† The template synthesis affords the corresponding [2 + 2] macrocycles.

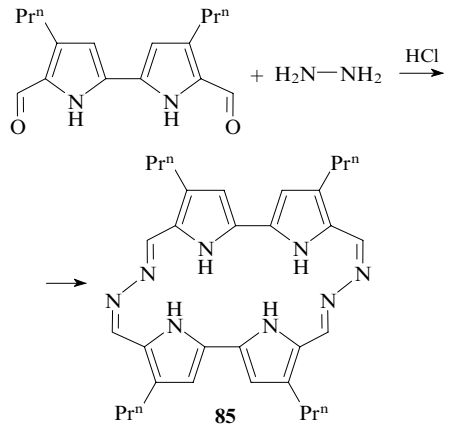
methanol in the presence of HCl afford [4 + 4] macrocycles **84** as the condensation products.[122]



84 (30% – 60%)

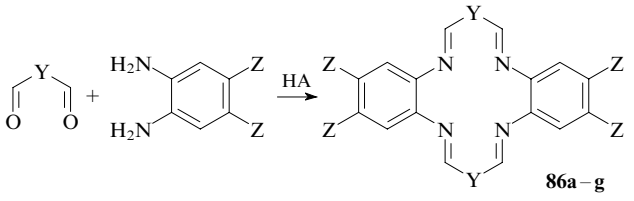
R = OC_nH_{2n+1} (n = 1, 6, 10, 14).

By contrast, the reaction of hydrazine with 5,5′-diformyl-4,4′-dipropyl-2,2′-bipyrrole gives [2 + 2]-condensation product **85**.[123]

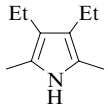
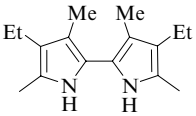
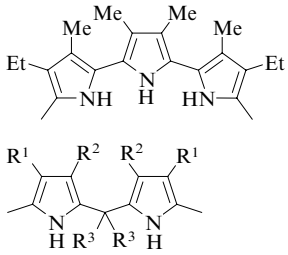


85

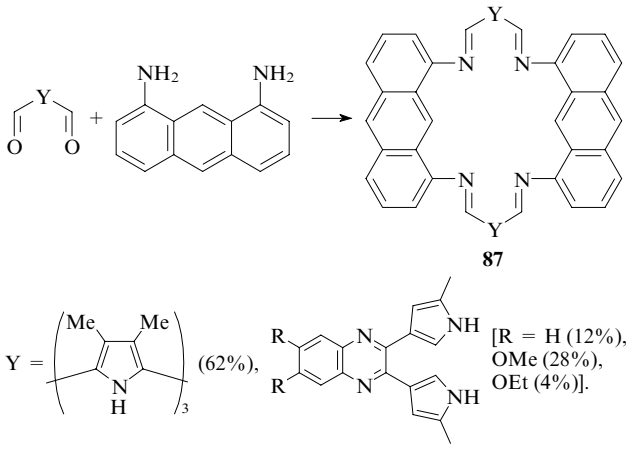
Since aromatic diamines are much less nucleophilic than aliphatic diamines, the reactions of the former with diformyl derivatives of pyrrole proceed only in the presence of acid catalysts. As a rule, the reactions give [2 + 2]-condensation products, *i.e.*, compounds **86a** – **g**, in good yields.



86a – **g**

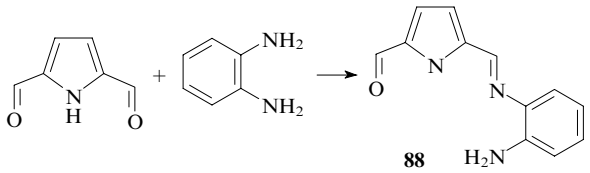
Compound **86**	Y	Z	Yield (%)	Ref.
a		OMe	100	124
b		OMe	95	125
c		OMe	60	126
d	$R^1 = R^2 = H$, $R^3 = Me$	H	98	127, 128
e	$R^1 = R^2 = H$, $R^3 = Me$	OMe	66	127
f	$R^1 = Me$, $R^2 = Et$, $R^3 = H$	H	91	127
g	$R^1 = R^2 = H$, $R^3 = Ph$	H	48	128, 129

The reactions of 1,8-diaminoanthracene with diformyl derivatives of the pyrrole series in methanol in the presence of acids also produce [2 + 2]-macrocyclic Schiff bases **87**.[126, 130]



87

In the absence of acids, 2,5-diformylpyrrole reacts with *o*-phenylenediamine in ethanol to give only [1 + 1]-condensation product **88**, which is involved in reactions with neither the dicarbonyl compound nor the diamine without additional activation.[131]



88

Since the carbonyl group in the resulting [1 + 1] Schiff base **88** is also involved in the chain of direct polar conjugation with the amino group, both groups become substantially less reactive. Two azomethine molecules in the crystal of **88** are linked to each other to form a stable dimer through four hydrogen bonds between the amino groups and the hydrogen atoms of the pyrrole rings and the oxygen atoms of the carbonyl groups (Fig. 12).[131] The energy of formation of this dimer estimated by quantum chemical calculations in terms of density functional theory [131] is 15.4 kcal mol^{-1}. Apparently, the dimeric structure is retained in solution, which additionally decreases the ability of this azomethine to be involved in further condensation.

c. Diformyl derivatives of pyrazole

Data on macrocyclic azomethine derivatives of five-membered heterocycles containing more than one heteroatoms are scarce. Only several successful syntheses of macrocycles from 3,5-

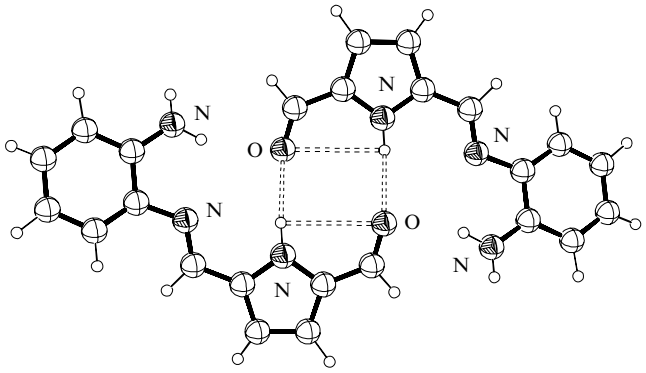
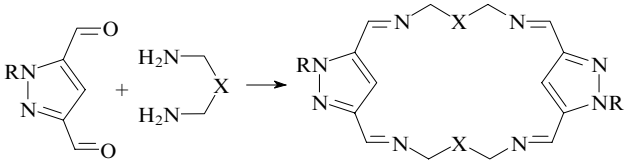


Figure 12. Structure of the dimer of product **88**.[131]

diformylpyrazoles in the absence of metal ions were documented. In alcohols or acetonitrile, the reactions of 1-substituted 3,5-diformylpyrazoles with diamines containing no additional nitrogen atoms produce macrocyclic Schiff bases **89**.[132, 133]

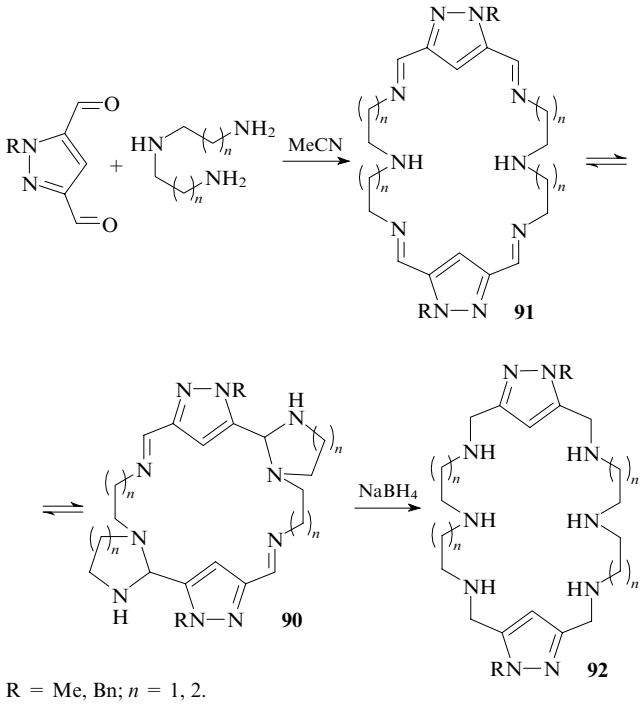


89

R = H, Me, Bn; X is *m*-phenylene (30%),CH_2OCH_2 (90% – 94%).

Under the same conditions, the reaction of diethylenetriamine or dipropylenetriamine gave pentacyclic products **90** in 80% yield.[132] Presumably, the reaction initially produces [2 + 2]-macrocyclic azomethine **91**, which undergoes intramolecular cyclisation, *viz*., the nucleophilic addition of the secondary amino group at the C=N bond.[132, 133] Most likely, this process is reversible because reduction of Schiff bases **90** to compounds **92** is accompanied by the opening of both imidazolidine rings.[133, 134]

The intramolecular nucleophilic addition at the C=N bond was observed also in the template condensation of diformyl derivatives of pyrazole with diamines containing additional donor atoms (for example, with 1,3-diamino-2-hydroxypropane, diethylenetriamine, *etc*.).[135 – 138] This process was demonstrated to be reversible, and the equilibrium can be shifted by adding ions of various metals or performing transmetallation of the resulting complexes.



91

90

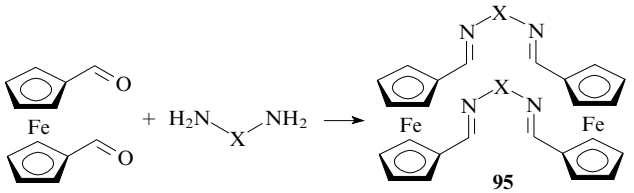
92

R = Me, Bn; *n* = 1, 2.

d. Diformyl derivatives of azulene and ferrocene

The reactions of compounds containing two carbonyl groups in a five-membered carbocycle with diamines have received little study. Only one synthesis of macrocycles by condensation of 1,3-diformylazulene with *trans*-(*R*,*R*)-1,2-diaminocyclohexane in dichloromethane at room temperature giving rise to a mixture of [2 + 2]- (**93**) and [3 + 3]-condensation products (**94**) in a ratio of 1 : 4 (Scheme 14) was documented.[48]

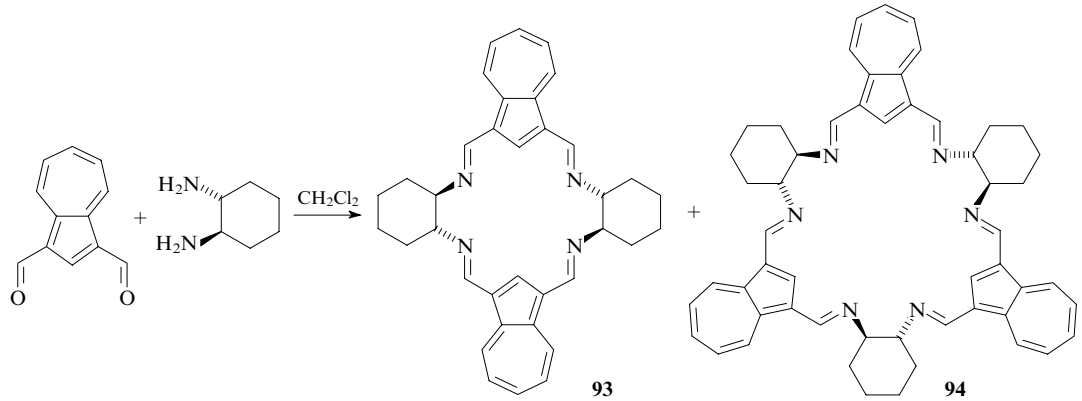
The reactions of 1,1′-diformylferrocene were studied in more detail. Due to the unique properties, this dicarbonyl organometallic compound is widely studied in supramolecular chemistry. The reactions of 1,1′-diformylferrocene with diamines in acetonitrile or chloroform at concentrations lower than 0.1 mol litre^{-1} generally produce [2 + 2]-macrocyclic Schiff bases **95**.[139, 140]



95

X = CMe_2CH_2, $CH_2CMe_2CH_2$, $CH_2C_6H_4CH_2$-3, NHC(Z)NH (Z = O, S).

Scheme 14

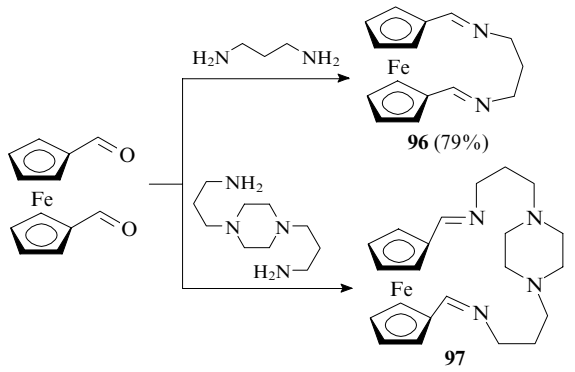


93

94

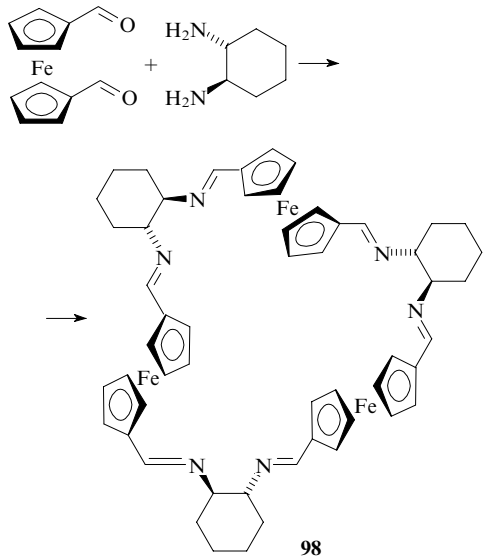
The reaction pathway substantially depends on the nature of the diamine. Aliphatic diamines and 1,3-bis(aminomethyl)benzene give [2 + 2]-cyclocondensation products, whereas 1,4-di(aminomethyl)benzene forms only oligomeric products (Ref. 139).

The carbonyl groups in 1,1′-diformylferrocene are located in different planes and can occupy different positions with respect to each other due to free rotation of the cyclopentadienyl rings. This allows the synthesis of [1 + 1] macrocycles based on this aldehyde even by the reactions of the latter with lower aliphatic diamines. For example, the reaction of 1,1′-diformylferrocene with 1,3-diaminopropane in ethanol instead of acetonitrile gives [1 + 1] macrocycle **96** as the major product.[141]



The reactions of diamines containing amino groups at a longer distance give [1 + 1] macrocycles as the major products regardless of the nature of the solvent. For example, compound **97** was synthesised by the reaction of 1,1′-diformylferrocene with 1,4-bis(3-aminopropyl)piperazine in a mixture of ethanol and chloroform at a dialdehyde concentration of 6×10^{-3} mol litre^{-1} (Ref. 139).

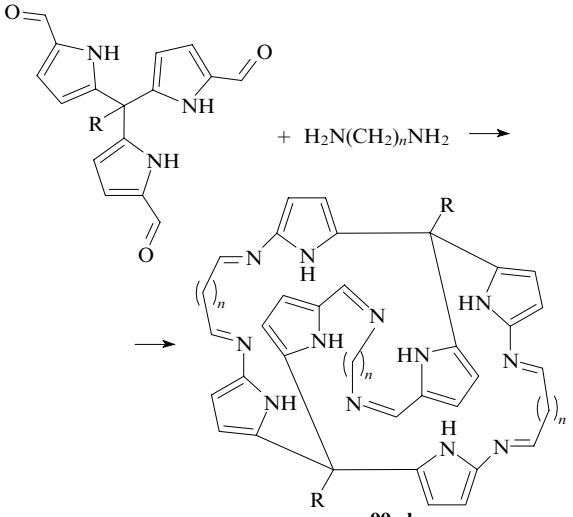
Due to ability of two cyclopentadienyl rings in 1,1′-diformylferrocene to rotate about the common axis, the reaction of this compound with *trans*-(*R*,*R*)-1,2-diaminocyclohexane gave rise to [3 + 3] azomethine **98**; however, the yield of this product was as low as 13.8%.[52] Nuclear Overhauser effect (NOE) experiments showed that the cyclopentadienyl rings in each ferrocene moiety of compound **98** in solution are turned round so that the angle between the $C_{ipso}-C(=N)$ bonds is 180°.[52]



e. Synthesis of cryptands by condensation of diformyl compounds with triamines

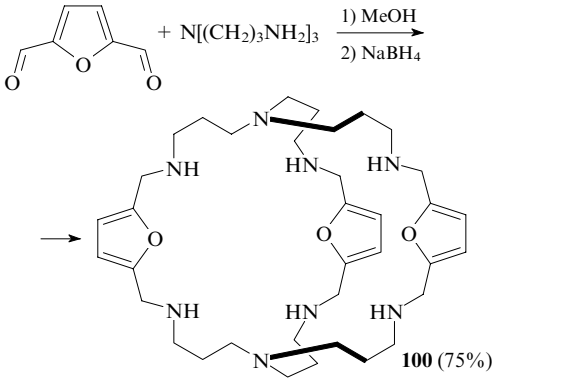
Cryptands can be assembled by the Schiff reaction of dicarbonyl compounds with triamines ([3 + 2] condensation) or of tricarbonyl compounds with diamines ([2 + 3] condensation). Only the former reaction has gained wide acceptance.

A unique example of the formation of a cryptand by the latter of condensation type was described in 2001.[142] Compounds **99a**,**b** were synthesised by the reactions of triformyl derivatives of tripyrromethanes with ethylenediamine or butylenediamine, respectively, in THF.[142]



R = Me, *n* = 2 (**a**); R = Et, *n* = 4 (**b**).

Regardless of the nature of diformyl compounds, their reactions with polyamines generally produce cryptands. The reactions in dilute solutions ($\sim 2 \times 10^{-2}$ mol litre^{-1}) in different solvents (alcohols or acetonitrile) give [3 + 2]-condensation products, *viz*., compounds **100**[143] and **101a**–**g**, in moderate or high yields. The cryptands produced in these reactions are structurally similar. Their molecules have a trihedral prismatic shape, the prisms being bound by three aromatic fragments of the dialdehyde and the nitrogen atoms of the polyamine.[154–157] Figure 13 shows the structure of cryptand **101a** prepared from 2,5-diformylfuran and tris-(2-aminoethyl)amine.[154]



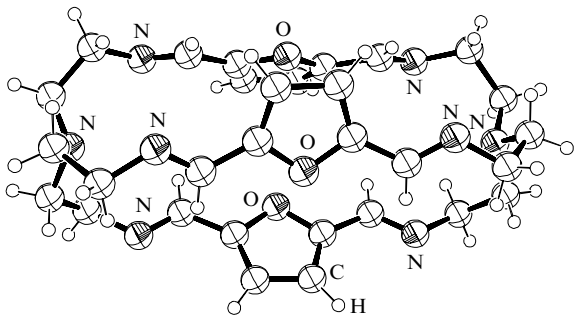
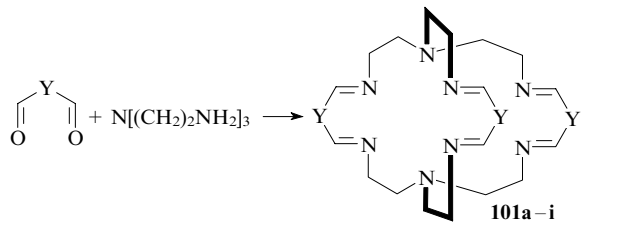
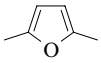
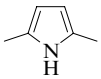
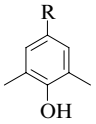
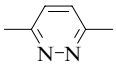
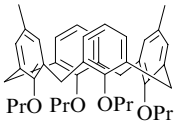
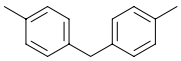


Figure 13. Structure of cryptand **101a**.[154]



Compound **101**	Y	R	Yield (%)	Ref.
a		–	62	43, 144
b		–	–	43
c		–	60	43, 145
d		–	47–56	43, 73, 145
e		OMe Me	42 63	146 147
f		Me n-C_6H_{13} H	55–65 50 –	148, 149 148 30, 150
g		–	64	151
h		–	60	152
i		–	60	153

The condensation of 2,6-diformyl-4-methylphenol with 2,6-bis[1,1-bis(aminomethyl)ethyl]pyridine in the presence of

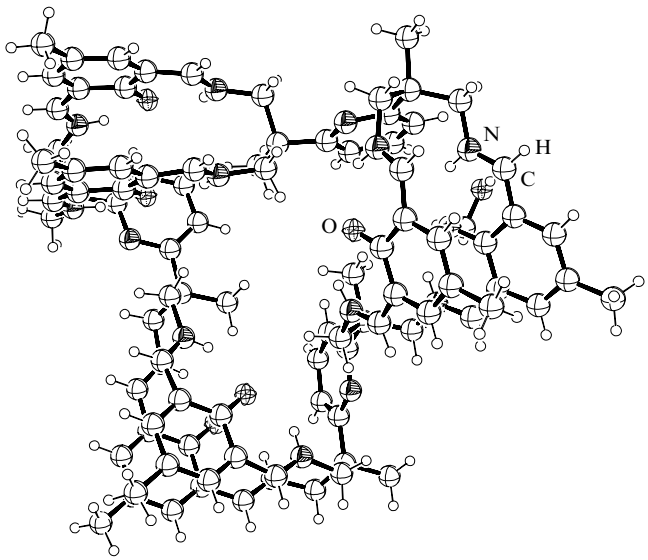
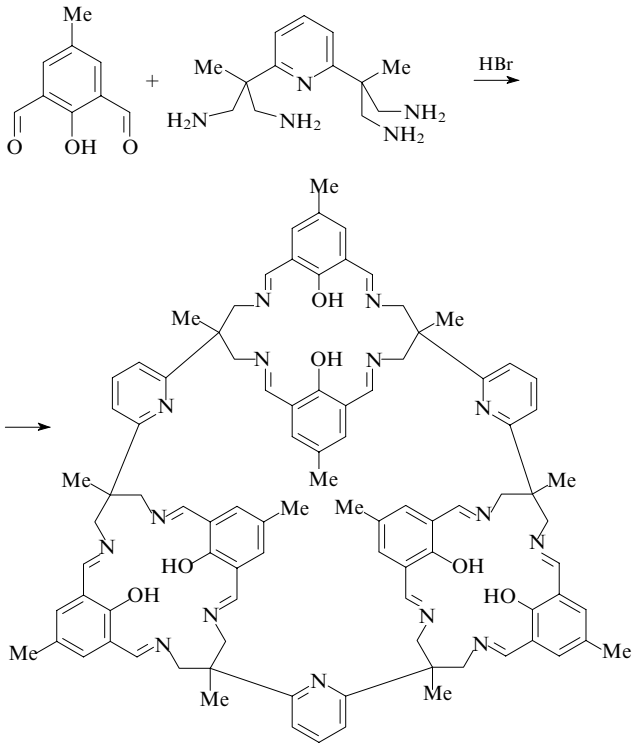


Figure 14. Structure of macrocycle **102**.[159]

Scheme 15



HBr affords polycycle **102** as the [6 + 3]-condensation product in a yield higher than 90% (Scheme 15).[158, 159]

Macrocycle **102** contains three [2 + 2] macrocyclic fragments formed by 2,6-diformyl-4-methylphenol and 1,3-propylenediamine, which are linked to each other by pyridine bridges. All three fragments, like free protonated [2 + 2] macrocycles (see Fig. 5*b*), adopt a horseshoe conformation (Fig. 14).[159]

To generalise the results considered in the present section, it should be noted that the following two methods are used most widely for the synthesis of azomethine macrocycles from dicarbonyl compounds and diamines: the condensation of $\sim 10^{-2}$ M solutions of equimolar amounts of the starting compounds in acetonitrile at room temperature and the condensation of more dilute solutions ($\sim 10^{-3}$ M) by refluxing in alcohols. The results of the reactions with aliphatic diamines are determined primarily by the reactant ratio. The synthesis according to most of other procedures affords a library of products. The isolation of individual compounds from this library can be based on low solvation of certain macrocyclic azomethines in low-polarity solvents.

The nature of diamines has the main effect on the ratio of the components. If the amino groups in diamines are separated by a long aliphatic or heteroatomic chain, these groups react independently of each other because they are spatially distant and the conjugation is absent. In reactions with monocyclic dicarbonyl compounds in the absence of acids, diamines in which the amino groups are in rather close proximity (α,β and α,γ diamines), as a rule, form oligomers. In the presence of strong acids (HCl or HBr), these reactions give salts of [2 + 2] macrocycles as the major products.

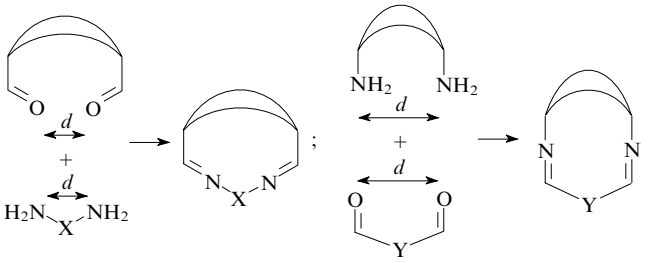
III. Unsymmetrical macrocyclic Schiff bases

An analysis of the published data shows that the condensation of dicarbonyl compounds with diamines offers great scope for the synthesis of various polydentate Schiff bases. In this class of

compounds, unsymmetrical macrocyclic compounds containing at least two coordination units of different nature (a soft unit for binding late transition metals and a hard unit for binding early transition metals) inside the macrocycle have attracted considerable attention in recent years. Heterobinuclear complexes belonging to this class are of exceptional interest for catalysis. Quantum chemical calculations demonstrated that these complexes can bind low-reactivity compounds (alkenes, carbon monoxide and dioxide, nitrogen and even alkanes) and activate them for further chemical transformations as a result of the concerted push-pull effect of two metals of radically different nature on the substrate molecule.[160] The structures and properties of heterobinuclear complexes were covered in the reviews.[29, 30, 161]

In the previous sections, we considered several special examples of the synthesis of unsymmetrical macrocyclic Schiff bases. The optimal strategy for the construction of such structures is based on the idea of the fragment assembly involving the [1 + 1] condensation of large bifunctional blocks presynthesised in the previous steps. The diamine and dicarbonyl components are most often synthesised independently, although blocks containing one amino group and one carbonyl group can, in principle, be used. The structure complementarity of the fragments, including their ability to adopt conformations favourable for cyclisation, is the main prerequisite for the last step of the macrocyclic ring closure (Scheme 16).

Scheme 16



The choice of an appropriate solvent capable of stabilising such conformations plays an exceptionally important role. The reactions can proceed both under acid catalysis and in the absence of acids. In some cases, the nature of the anion has a considerable effect on the reaction pathway in the presence of acids, which indicates that anions can act as template agents (see Section IV).

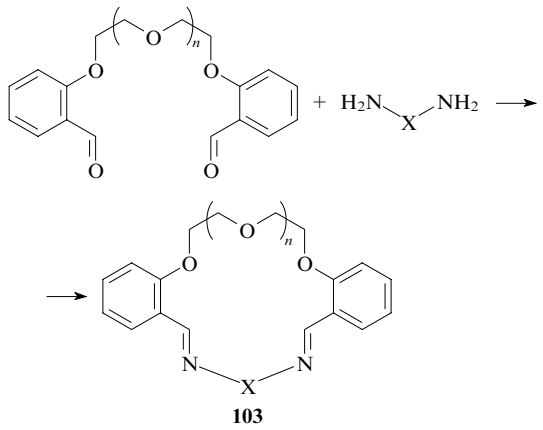
Numerous [1 + 1] condensations of bifunctional blocks with the use of metal ions as template agents were documented. In these reactions, metal ions provide preliminary coordination of the both starting polydentate building blocks by fixing the conformation favourable for cyclisation, which proceeds in the inner coordination sphere of the ion. Its coordination number determines also the size of the resulting ring. In most of the characterised reactions of this type, diamine and one of the presynthesised dicarbonyl precursors were used for the template assembly of macrocyclic Schiff bases. However, many examples of the use of mononuclear metal complexes with a dicarbonyl precursor and a diamine molecule in condensation reactions were documented. In these reactions, the metal ion located in the cavity distant from the reaction centres serves the function of retaining the dicarbonyl fragment in the conformation favourable for cyclisation. Although the carbonyl and amino groups involved in the reaction are not included in the coordination sphere of the metal ion, these transformations are always considered in depth in reviews on the template synthesis.

The assembly of macrocycles based on diamines has found little use because these compounds are difficult to synthesise. Template-free reactions of dicarbonyl compounds with diamines giving macrocyclic structures are considered in detail below.

1. Template-free fragment assembly in the absence of acids

As mentioned above, the nature of the solvent has a substantial effect on the [1 + 1] cyclocondensation pathway. The assembly of macrocycles from enlarged blocks is performed in aprotic solvents (acetonitrile, chloroform or dioxane), which rather weakly solvate polar carbonyl and amino groups of the starting compounds without hindering hydrogen bonding between these groups. Hydrogen bonds provide the organisation of the prereaction complex, in which the carbonyl and amino groups of two reactants involved in the reaction are in spatial proximity.

As an example of such condensations, let us refer to the synthesis of oxazamacrocyclic ligands **103**. In the case of *trans*-1,2-diaminocyclohexane, the yields of the products were 89% – 95%.

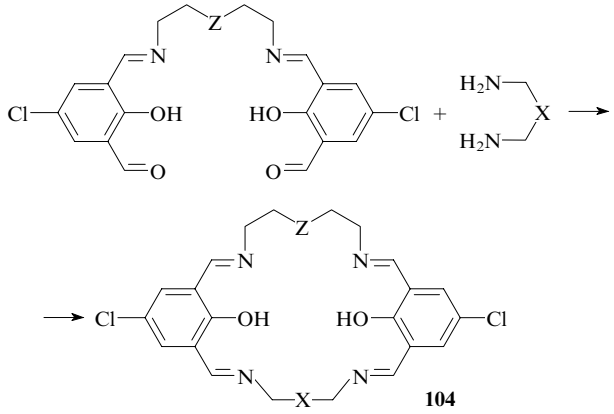


103

X = $(CH_2)_2N(CH_2CH_2NH_2)(CH_2)_2$ (n = 1);[162]

X = , n = 0–4.[163]

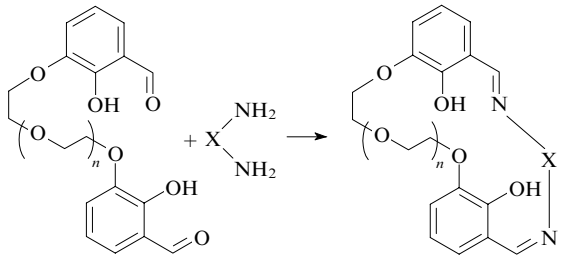
The reactions of dicarbonyl precursors with aliphatic diamines in chloroform at room temperature under kinetic control produce unsymmetrical compounds **104**.[75]



104

Z = S, NH; X is absent, CH_2ZCH_2.

The condensation in polar aprotic solvents (chloroform or acetonitrile) also affords [1 + 1] macrocycles (for example, compounds **105a** – **h**) as the major products if the reactions of aliphatic α,ω-diamines are performed with dicarbonyl derivatives, in which two salicylaldehyde fragments are separated by a flexible oligo(oxyethylene) chain.

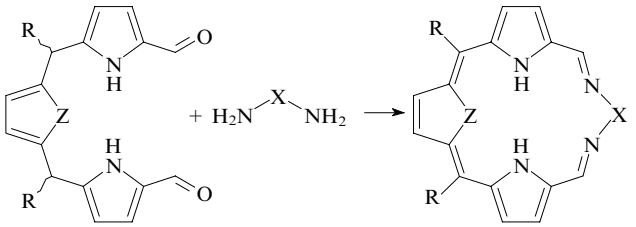


105a–h

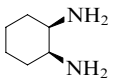
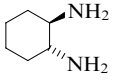
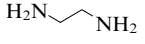
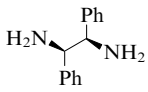
n = 1, 2.

Compound **105**	X	Yield (%)	Ref.
a	$(CH_2)_2$	62–65	164, 165
b	$(CH_2)_3$	42	166
c	$(CH_2)_2NMe(CH_2)_2$	55–60	165, 167
d	$(CH_2)_2NH(CH_2)_2$	60–70	165
e	$(CH_2)_2N(CH_2)_2$ $\vert$ $C_{11}H_{23}$-n	54–59	164
f	$(CH_2)_3NH(CH_2)_3$	54–59	164
g	CH_2CHCO_2H	69–70	164
h	$(CH_2)_2CHCO_2H$	69–70	164

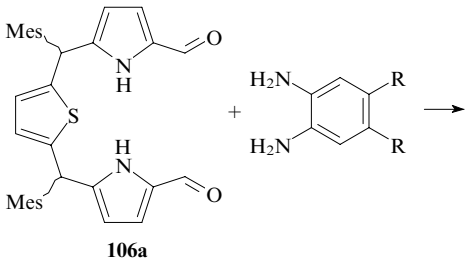
High dilution is yet another prerequisite for the synthesis of [1 + 1]-condensation products. The reactions of dicarbonyl blocks **106**, in which the carbonyl groups located in different parts of the molecules are in spatial proximity, with 1,2-diamines and hydrazine afford [1 + 1]-condensation products **107** in moderate yields only in chloroform at concentrations of 2×10^{-3} mol litre^{-1} in the presence of molecular sieves. Under these conditions, the condensation is accompanied by dehydrogenation of the macrocyclic system.



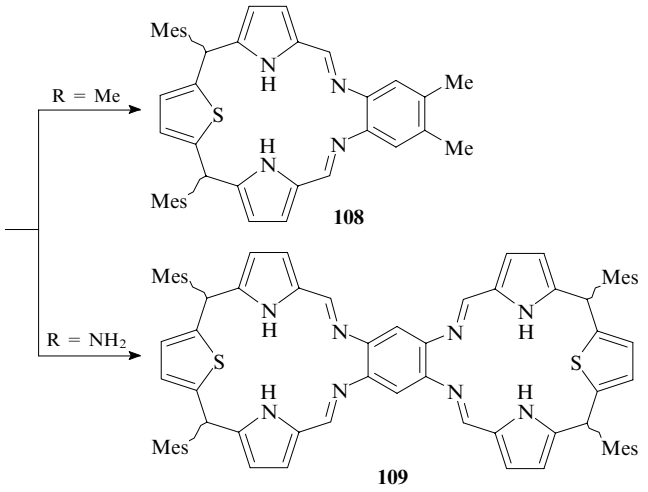
106 **107**

Diamine	Z	R	Yield (%)	Ref.
$H_2N(CH_2)_nNH_2$ (n = 2–4)	S	2,4,6-$Me_3C_6H_2$ (Mes)	–	167
	S	Mes	–	168
	S	Mes	–	168
	S	Ph	20	169
	S S	Ph Mes	40 50	169 169
$H_2N{-}NH_2$	O	Mes	43	170

The reactions of *o*-phenylenediamine with such dicarbonyl compounds also produce [1 + 1] macrocycles. For example, the reaction of dicarbonyl derivative **106a** with *o*-phenylenediamine in chloroform in the presence of molecular sieves gives the expected [1 + 1] macrocycle **108**.[168]



106a

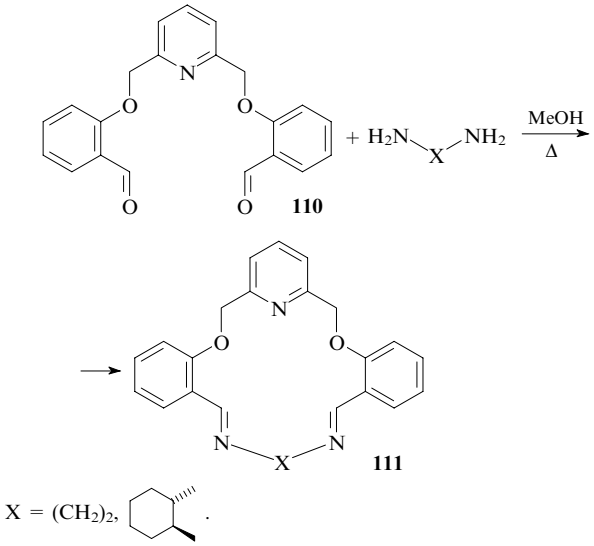


108 **109**

Interestingly, unlike the condensation with aliphatic diamines and hydrazine, the latter reaction is not accompanied by dehydrogenation to form a conjugated system. Apparently, this is associated with the fact that the completely conjugated macrocycle, which could be formed in this transformation, is antiaromatic.

The analogous condensation of compound **106a** with 1,2,4,5-tetraaminobenzene affords [2 + 1]-condensation product **109**.[168]

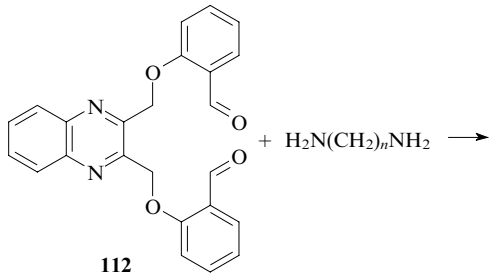
The assembly of macrocyclic Schiff bases can be performed also in methanol under thermodynamic control. For example, [1 + 1] macrocycles **111** were syntheisesed by the reaction of dicarbonyl compound **110** with 1,2-diaminoalkanes in boiling methanol.[163, 171]



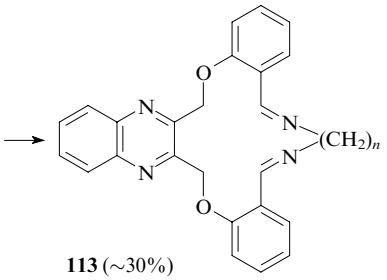
110 **111**

However, if the dicarbonyl block and diamine are non-complementary, the reactions give, as a rule, mixtures of products. For example, dicarbonyl derivative **112** reacted

with ethylenediamine to form [1 + 1]- and [2 + 2]-condensation products, which were not isolated in the individual state. By contrast, the reactions of this compound with other diamines (1,3-diaminopropane and 1,4-diaminobutane) gave only [1 + 1]-condensation products **113**.[172]



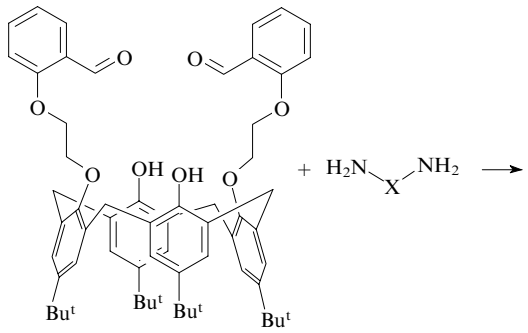
112



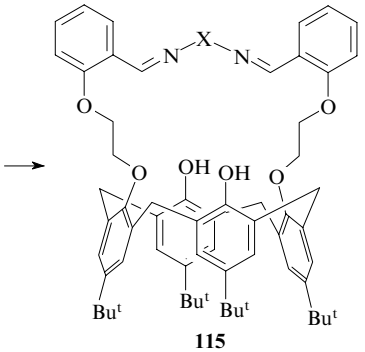
113 (~30%)

n = 3, 4.

Under prolonged reflux in a methanol–acetonitrile mixture, the dicarbonyl derivative of calixarene (**114**) reacts with diamines to form [1 + 1] macrocycles **115**.[173]



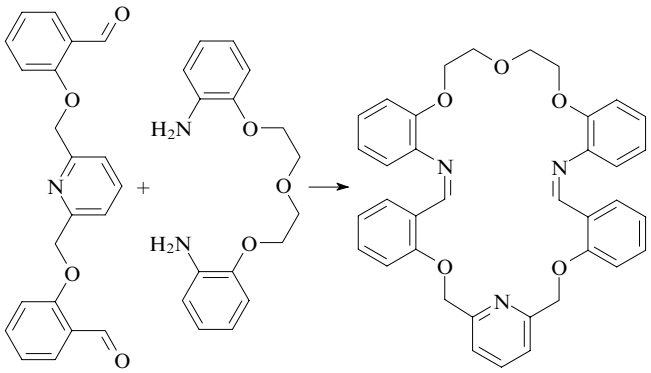
114



115

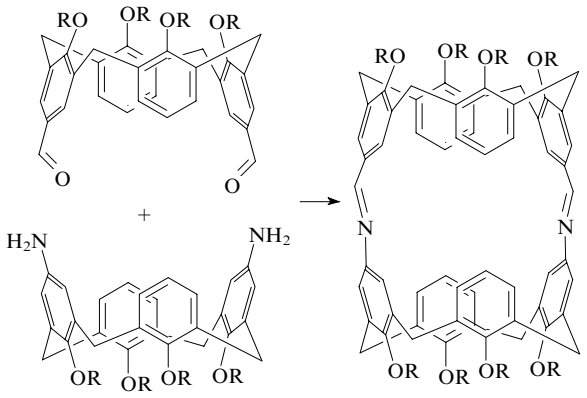
X = $(CH_2)_n$ (n = 2 (56%), 3 (86%), 4 (54%)), 1,2-phenylene (14%), $CH_2C_6H_4CH_2$-4 (96%)

Enlarged precursor blocks can react with each other to give large rings. For example, salicylaldehyde derivative **110** reacts in boiling ethanol with diamine containing the oxyethylene chain to form [1 + 1] macrocycle **116**.[174]



110 **116**

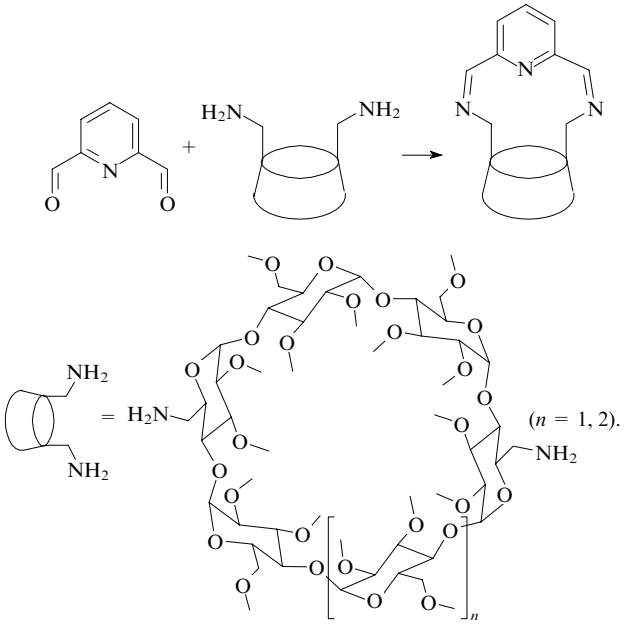
The reactions of dicarbonyl derivatives of calixarenes with complementary diamines produce [1 + 1] macrocycles **117** in high yields (74% – 92%).[175]



117

R = Pr^n, $(CH_2)_2OEt$.

Even more complex supramolecular aggregates can be synthesised by condensation of dicarbonyl compounds with per-*O*-methyldiamino derivatives of α- and β-cyclodextrins.[176] The reaction proceeds at room temperature in acetonitrile in the presence of molecular sieves A4.



(n = 1, 2).

The condensation products of 2,6-diformylpyridine with diaminocyclodextrins contain a hemispherical hydrophilic

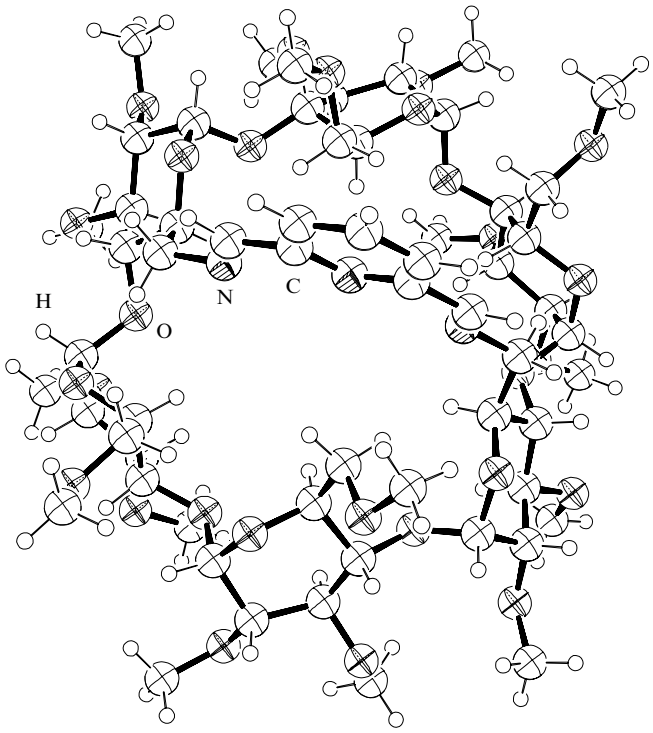
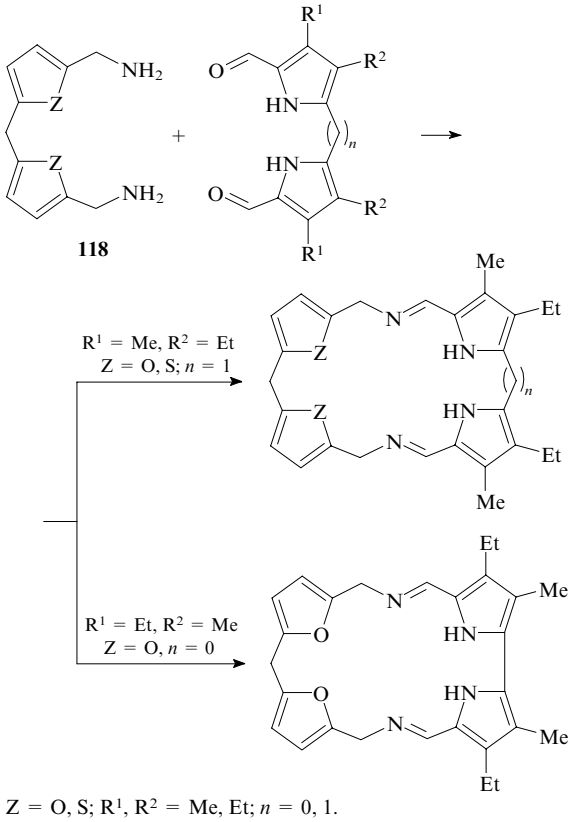


Figure 15. Structure of modified α-cyclodextrin.[176]

cavity bound by a fragment of the dicarbonyl compound (Fig. 15).[176]

The use of blocks containing two amino groups for the fragment assembly is limited by the fact that they are less widespread and are difficult to synthesise.

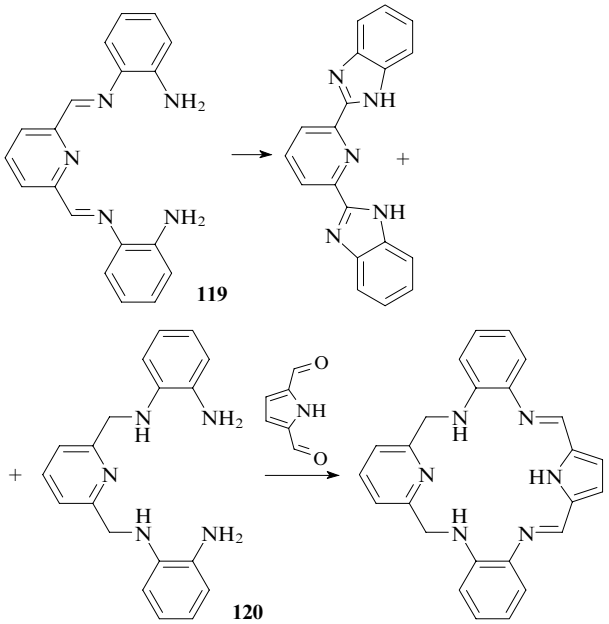
Scheme 17



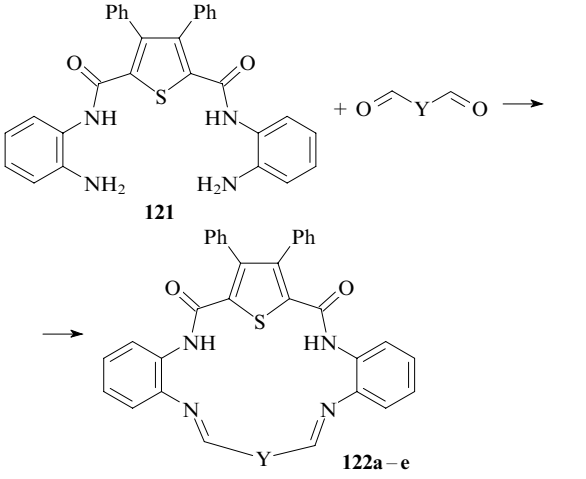
Z = O, S; R^1, R^2 = Me, Et; n = 0, 1.

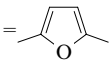
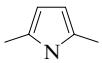
For example, the condensation of compounds **118** with dicarbonyl derivatives of bis-pyrroles (Scheme 17) can be assigned to this type of reactions.‡

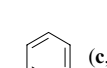
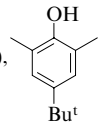
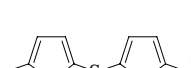
It should be noted that diamine **119**, which was synthesised by demetallation of the template [1 + 2]-condensation product of 2,6-diformylpyridine with *o*-phenylenediamine,[63] does not react with dicarbonyl compounds due to the electron-withdrawing effect of the azomethine fragments conjugated with the amino groups (see Sections II.3 and II.4). However, its reduction product **120**, which is synthesised by refluxing in toluene as a result of redox disproportionation, reacts with 2,5-diformylpyrrole to form an unsymmetrical macrocycle.[177]



On the contrary, aromatic diamines acylated at one of the amino groups by dicarboxylic acid readily form macrocycles.



Y =  (**a**, 78%),  (**b**, 60%),

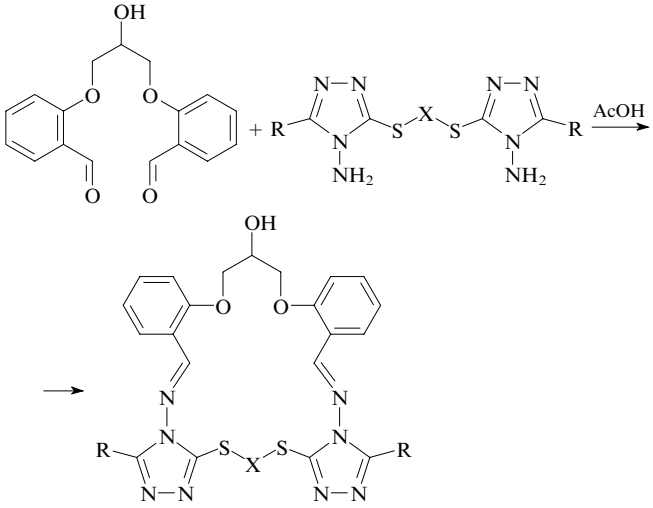
 (**c**, 85%),  (**d**, 80%),  (**e**, 83%).

‡ The data from the graduate study by A M Jasat, University of British Columbia, Vancouver, Canada, 1995.

For example, diamine **121** reacts in an aprotic polar solvent (1,4-dioxane) with various dicarbonyl compounds to give [1 + 1] macrocycles **122a**–**e**.[178] In this case, the geometry of the starting diamine imposes strict restrictions on the second reaction component (dialdehyde). Diamine **121** is planar, and dicarbonyl compounds, which can adopt planar conformations, are most active in reactions with this diamine resulting in the closure of the macrocycle because only this can give rise to a system containing a long chain of conjugation.

2. Fragment assembly in the presence of protic acids

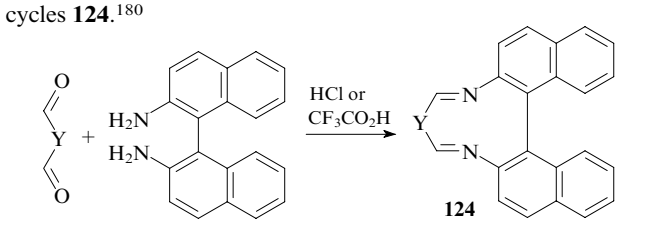
Numerous syntheses of macrocycles from dicarbonyl compounds and diamines in the presence of protic acids were documented. For example, the reaction with excess acetic acid produced 13-membered azathiacrown macrocycles **123**.[179] In this case, the acid acts as both the solvent and the acid catalyst.



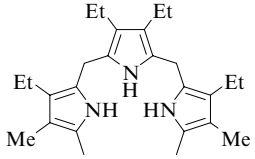
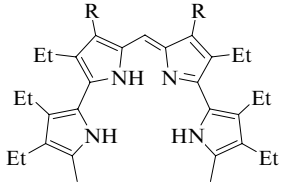
123 (40 %–50%)

R = Ph, CH_2Ph; X = $(CH_2)_n$ (n = 3, 4).

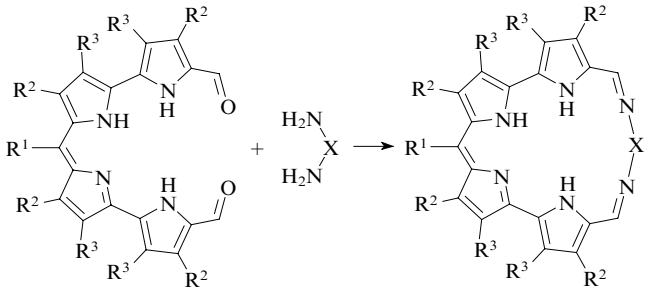
In polar protic solvents, which readily solvate amino groups (for example, in methanol), dicarbonyl derivatives of the pyrrole series are involved in condensation only in the presence of strong protic acids. For example, the condensation of dicarbonyl derivatives of the pyrrole series with optically active 2,2′-diamino-1,1′-binaphthyls in methanol in the presence of hydrochloric or trifluoroacetic acid affords macrocycles **124**.[180]



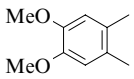
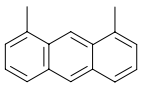
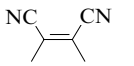
124

Y	R	Configuration of diamine	Yield (%)
	–	*R*	39
	–	*S*	30
	Et	*R*	31
	Et	*S*	36
	Me	*R*	55

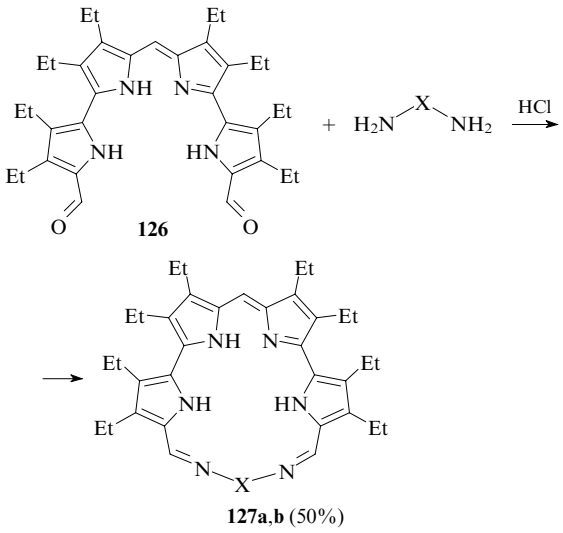
Under acid catalysis, dicarbonyl compounds react with weakly nucleophilic diamines, even with 2,3-diaminomaleonitrile, to form macrocycles **125a**–**i**.



125a–**i**

X	R^1	R^2	R^3	Compound **125**	Yield (%)	Ref.
	4-$NO_2C_6H_4$	Me	Et	**a**	95	181
	4-$NO_2C_6H_4$	Me	Me	**b**	98	181
	H	Pr^n	H	**c**	83	182
	H	Pr^n	H	**d**	80	182
	H	Et	Me	**e**	–	183
	Ph	Me	Me	**f**	70	181
	4-$NO_2C_6H_4$	Me	Me	**g**	52	181
	H	Pr^n	H	**h**	9	184
	H	Et	Et	**i**	86	184

Polypyrrole dialdehyde **126** reacts with hydrazine and 1,3-diaminoguanidine in methanol in the presence of hydrochloric acid to form the corresponding macrocycles **127a**,**b**.[184]



127a,**b** (50%)

X is absent (**a**), NHC(=NH)NH (**b**).

Macrocycles obtained from polypyrrole derivatives, which are close analogues of extended porphyrins,[185] are of interest for supramolecular chemistry because they contain a cavity inside the macrocycle, which can include substrates of various nature. For example, X-ray diffraction data show that a methanol molecule is fixed in the cavity of compound **125e** by five hydrogen bonds (Fig. 16).[183] The structures of other inclusion compounds are similar to that described above.[181]

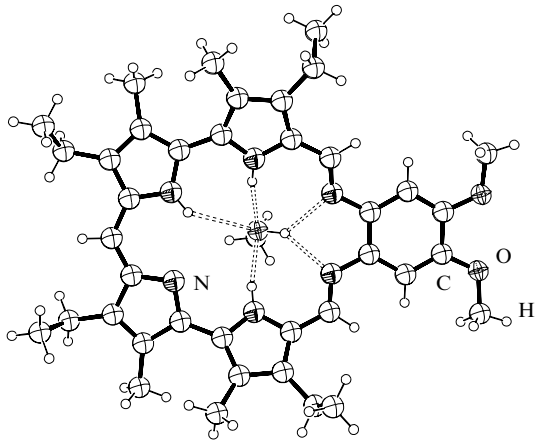
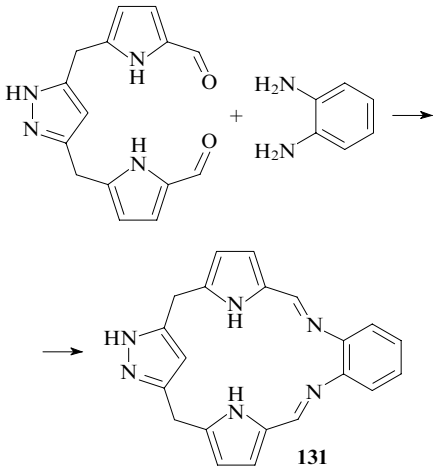


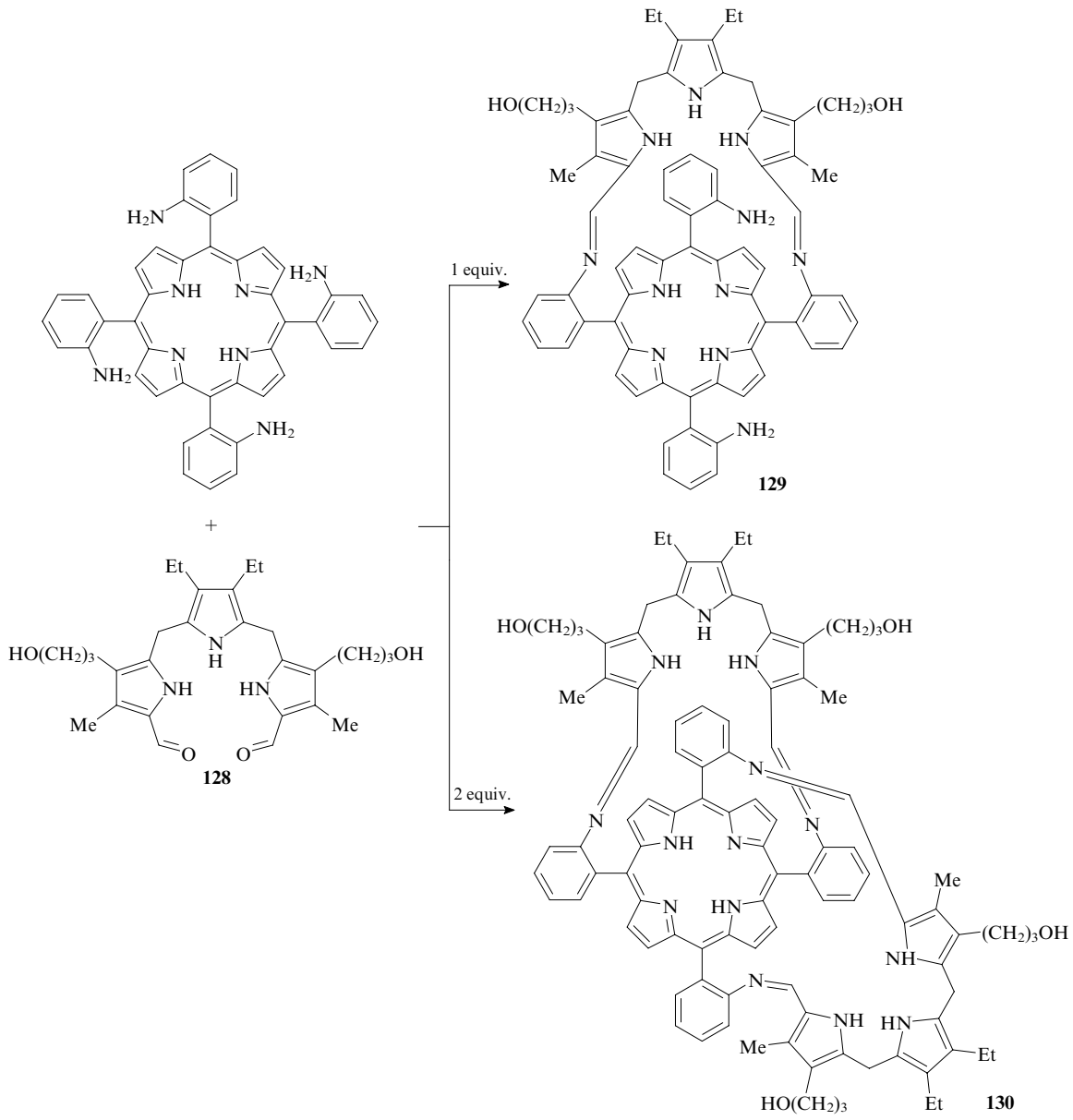
Figure 16. Structure of the inclusion complex based on macrocycle **125e**.[183]

The strategy of the fragment assembly can be used for the synthesis of three-dimensional structures. The condensation of *meso*-(2-aminophenyl)porphyrin with one or two equivalents of dialdehyde **128** in the presence of trifluoroacetic acid affords the corresponding three-dimensional polycyclic systems **129** and **130** in moderate yields (30% – 45%) (Scheme 18).[186]

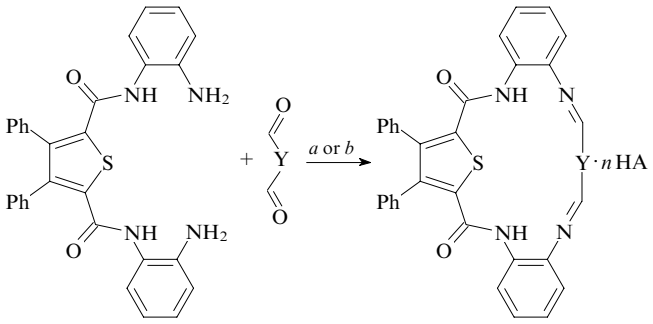
Catalysis is required also in the synthesis of heterocyclic analogues of polypyrrole macrocycles, in particular, of pyrazolepyrrole system **131**.[187]



Scheme 18

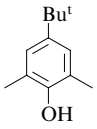
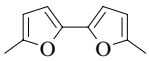
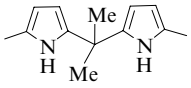
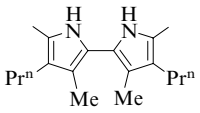


Examples of the successful assembly of macrocycles by condensation of diamines in the presence of protic acids are few in number. For instance, compound **121** reacts with various dicarbonyl derivatives in methanol only in the presence of protic acids to form salts of [1 + 1] macrocycles **122a–c,f** or free Schiff bases **122d,g,h**.[178, 188] Free macrocyclic azomethines can be isolated by treating the salts with triethylamine. Interestingly, the yield of some macrocycles in these reactions substantially depends on the nature of the acid used in the reaction.



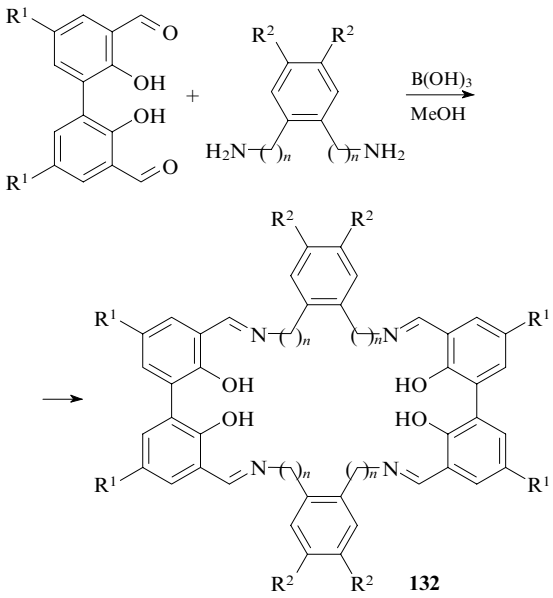
121 **122a–d,f–h**

(*a*) HA, MeOH; (*b*) (1) HA, MeOH; (2) Et_3N, CH_2Cl_2.

Compound **122**	Y	HA	Conditions	*n*	Yield (%)
a		HCl	*a*	2	73
b		HCl	*a*	2	73
c		HCl	*a*	3	42
d		HCl	*b*	0	88
f		H_3PO_4 CF_3CO_2H	*a* *a*	2/3 2	85 70
g		H_2SO_4 HCl	*b* *b*	0 0	95 65
h		HCl	*b*	0	83

IV. Anion template effect in the synthesis of macrocyclic azomethines

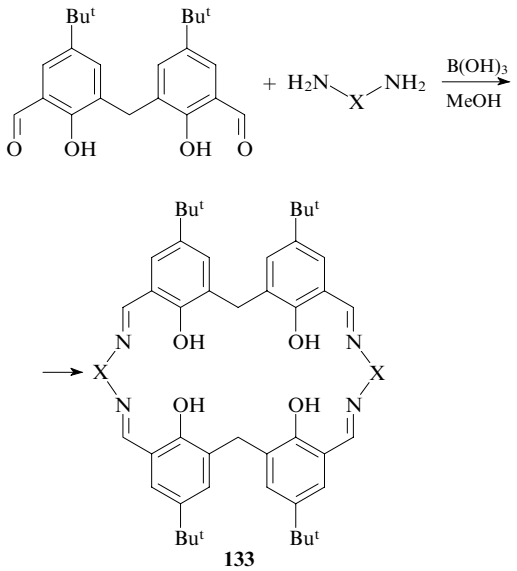
For most of the above-described reactions of dicarbonyl compounds with diamines, the nature of the Brønsted acid anion has no effect on the structure of the reaction products or their yield. However, in 1982 Corey [189] found that the cyclocondensation in the synthesis of the boron-containing antibiotic aplasmomycin efficiently proceeds only in the presence of boric acid. Corey was the first to hypothesise that the borate anion acts in this reaction as the template agent. In 1985, it was found that boric acid serves as a good catalyst for the [2 + 2] condensation of 3,3′-diformyl-2,2′-dihydroxybiphenyl with 1,4-bis(aminomethyl)benzene in methanol. In more recent years, this approach has been extended to the condensation of this dialdehyde with *o*-phenylenediamine, which allowed the synthesis of macrocycles **132**.



132

R^1 = H, R^2 = H, *n* = 1;[190] R^1 = Bu^t: R^2 = H, *n* = 0 (66%); R^2 = Me, *n* = 0 (86%).[191]

Analogously, boric acid can direct the condensation of other bis-phenol dialdehydes as well. For example, [2 + 2] macrocycles **133** were generated from various diamines in the presence of boric acid.[192]

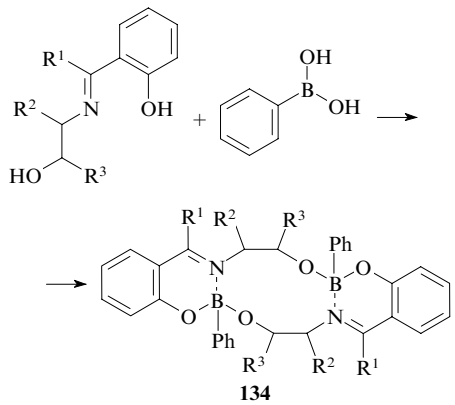


133

X = $(CH_2)_n$ (*n* = 2, 3), , *o*-phenylene.

Apparently, borate with two molecules of the diformyl derivative of bis-phenol is produced as an intermediate in this reaction. Intermediate tetrahedral borate fixes the relative arrangement of the dicarbonyl fragments favourable for the closure of a macrocycle, but renders the oligomerisation impossible. Hence, the role of boric acid as a template agent is limited only to phenol derivatives. This reaction with the use of phenylboronic acid affords boron-containing macrocycles **134**. In this case, the covalent template, *viz*., phenylboronic

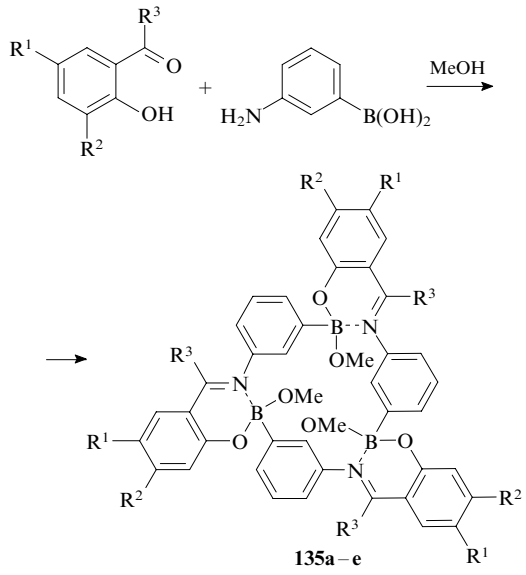
acid, remains in the molecule and forms a macrocycle through ester bonds and additional coordination with the azomethine nitrogen atom.[193, 194]



134

R^1, R^2 = H, Me; R^3 = H, Me, Ph.

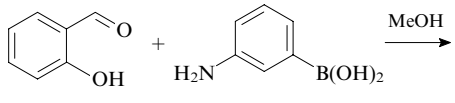
The presence of the borate group in amine molecules is favourable for the autotemplate reactions with aldehydes. The reaction of 3-aminophenylboronic acid with substituted salicylaldehydes leads to the autotemplate [3 + 3] macrocyclisation giving rise to compounds **135a–e**.

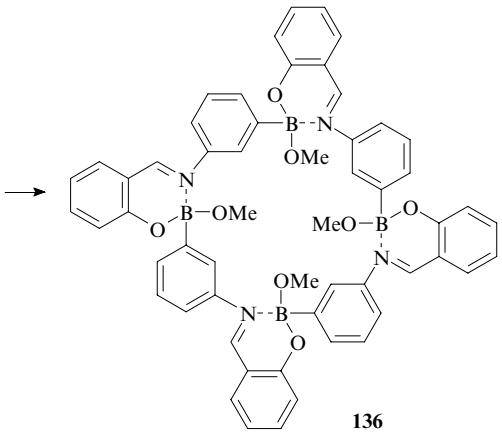


135a–e

Compound **135**	R^1	R^2	R^3	Yield (%)	Ref.
a	Bu^t	Bu^t	H	92	195
b	I	I	H	56	196
c	OH	H	H	57	196
d	H	H	Me	48	197
e	H	H	Ph	65	197

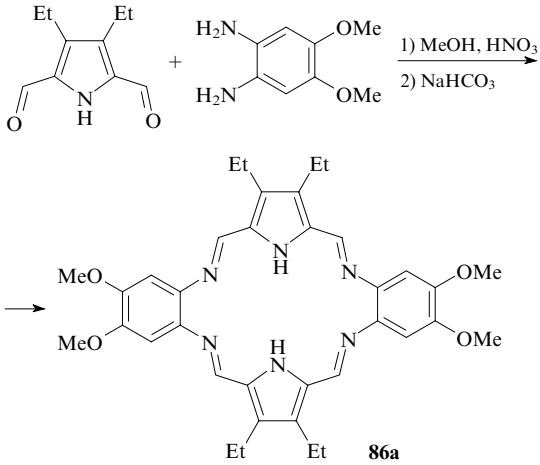
As opposed to the above-described reactions, the reaction of unsubstituted salicylaldehyde with 3-aminophenylboronic acid produces [4 + 4] macrocycle **136**.[197]





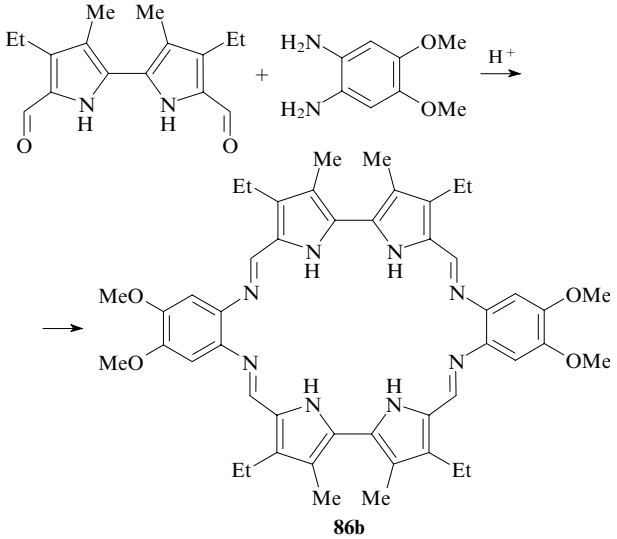
136

The possible involvement of acid anions, which are incapable of binding with dicarbonyl compounds or diamines by a strong covalent bond, has long been an open question. Sessler *et al.*[124] were among the first to find the influence of the nature of anions on the reaction pathway of dicarbonyl compounds with diamines (see Section II.4.b). It appeared that the [2 + 2] cyclisation of 3,4-diethylpyrrole-2,5-dicarbaldehyde with *o*-phenylenediamine produces compound **86a** in quantitative yield only in the presence of nitric acid.



86a

A detailed study of the reaction of 2,2′-diformylbipyrrole with *o*-phenylenediamine in the presence of various acids demonstrated that the reactions of these compounds proceed

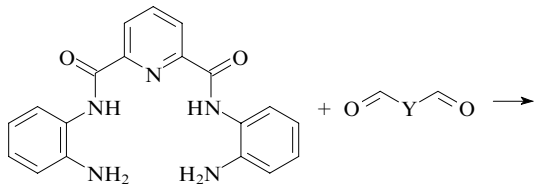


86b

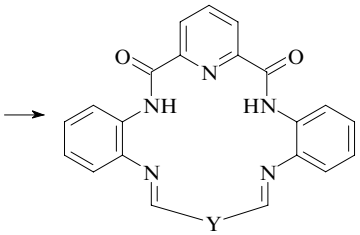
H^+ = HNO_3 (95% yield), H_2SO_4 (84%), $HClO_4$ (81%), CF_3CO_2H (74%), HCl (47%), HI (37%), HCl + $Bu^n_4NNO_3$ (> 80%).

in the presence of nitric acid to give product **86b** in a yield of up to 95%, whereas the reactions in the presence of other acids produce the macrocycle in substantially lower yields.[125]

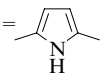
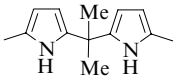
Recently, it has been found that diamide of pyridine-2,6-dicarboxylic acid and *o*-phenylenediamine (**137**) reacts with dialdehydes in the presence of trifluoroacetic or sulfuric acid to form [1 + 1]-condensation products **138a – c**. The reactions in the presence of other acids (HCl, AcOH, HNO_3 or H_3PO_4) afford mixtures of [1 + 1] macrocycles and oligomeric products.

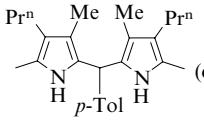


137



138a – c

Y =  (**a**, 64%),[177]  (**b**, 90%),[9, 177]

 (**c**, 90%)[198] (Tol = C_6H_4Me).

It was demonstrated[9, 177, 198] that macrocycles containing the dipyrromethane fragment can bind tetrahedral anions. The binding constants of template agents are known to correlate with the molar fraction of the receptor in a dynamic combinatorial library.[199] As mentioned in the Introduction, the synthesis of azomethines from polyfunctional derivatives gives mixtures of products. Therefore, high affinity of receptors for tetrahedral anions accounts for the template function of the latter in the macrocyclisation. However, the role of trifluoroacetic acid remains unclear. This acid can also efficiently catalyse the macrocyclisation despite that the binding constants of the resulting macrocycles with acetate ions are low.

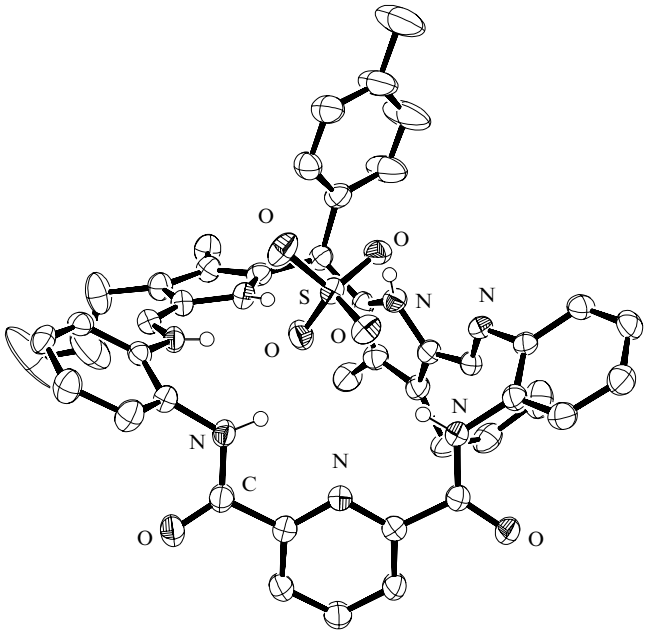
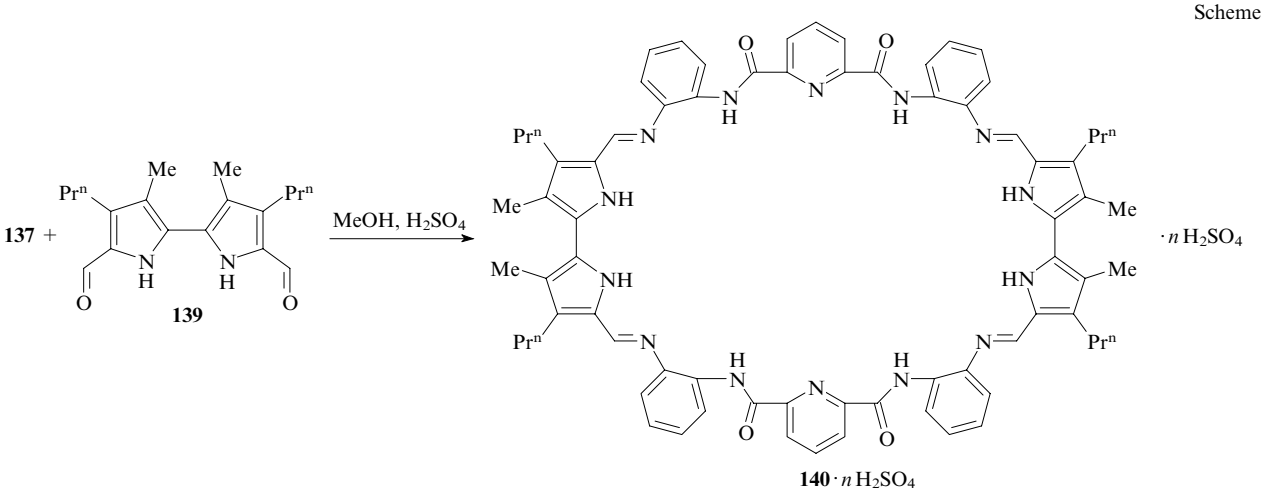


Figure 17. Structure of complex **138c** · H_2SO_4 (for clarity, the hydrogen atoms at the C atoms are omitted).[198]

The structure of the complex of ligand **138c** with sulfuric acid was determined by X-ray diffraction (Fig. 17).[198] As can be seen from Fig. 17, H_2SO_4 occurs in the complex as the dianion; macrocyclic azomethine is present as a derivative doubly protonated at the azomethine nitrogen atoms. This suggests that the synthesis of such systems requires the treatment of the reaction mixture with a base for deprotonation of azomethines.

Further study of the reactions of diamine **137** with dicarbonyl derivatives of the pyrrole series showed that the reaction of compound **137** with 2,2′-diformylbipyrrole (**139**), with carbonyl groups more remote from each other, in methanol in the presence of various acids gives different products.[200] Studies by mass spectrometry demonstrated that the reaction in the presence of nitric acid produces only oligomers. Oligomers are also the major products in the reactions catalysed by HCl or HBr, although these reactions produce small amounts of [1 + 1] macrocycles. In the presence of acetic or trifluoroacetic acids, the reaction gives the salt of [2 + 2] macrocycle **140**

Scheme 19



139

140 · $n\,H_2SO_4$

as the major product along with a small amount of oligomers. The salt of [2 + 2] macrocycle **140** containing two H_2SO_4 molecules was isolated without traces of oligomerisation products only in the presence of sulfuric acid as the catalyst.[200] This result deserves notice. It indicates that the reaction of **137** with **139** in the presence of tetrahedral anions proceeds according to the template scheme (Scheme 19).

The structure of dihydrate of compound **140**, which was isolated upon the treatment with triethylamine, was determined by X-ray diffraction (Fig. 18).[200]

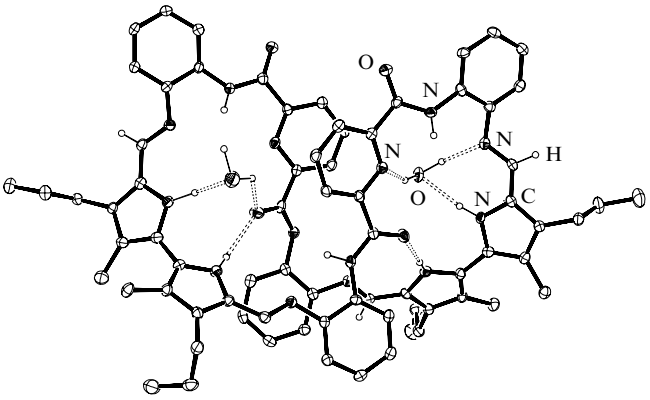
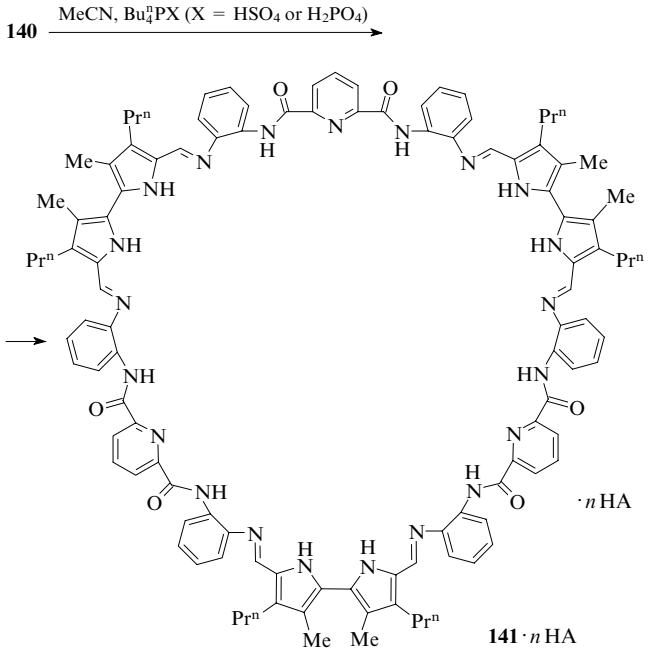


Figure 18. X-Ray diffraction structure of macrocycle **140** · 2 H_2O (aromatic and aliphatic H atoms are omitted).[200]

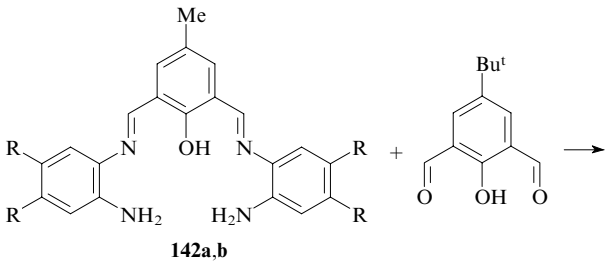
Macrocycle **140** is quite stable under standard conditions. However, storage of this compound in acetonitrile in the presence of tetrabutylphosphonium hydrosulfate or dihydrophosphate leads to its rearrangement into sulfate of macrocycle **141** in quantitative yield as a result of [3 + 3] condensation.[200]

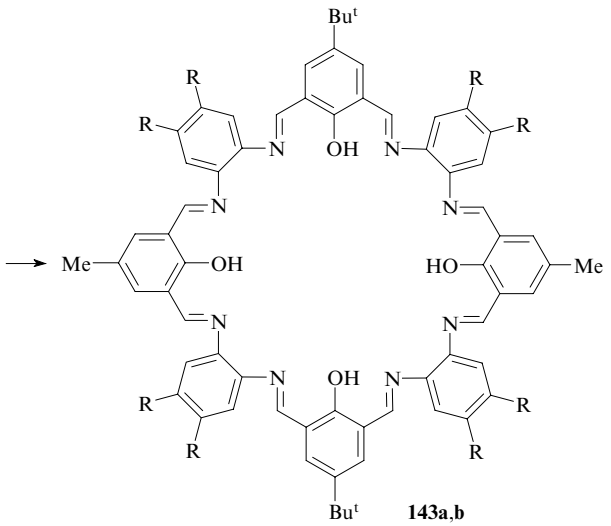


Apparently, sulfate of [2 + 2] macrocycle **140** is formed in methanol; sulfate of [3 + 3] macrocycle **141**, in acetonitrile. Evidently, the nature of the solvent has a substantial influence on the formation of macrocycles due to solvation of the anion and macrocyclic products formed in the course of the reaction.

The anion template effect is not the only factor determining the pathway of these reactions giving rise to macrocycles. As demonstrated in Section II, the results of macrocyclisation depend also on π,π-stacking interactions. The formation of macrocycles in [$n + n$]-template condensations governed by π,π interactions was documented for dicarbonyl derivatives, primarily of benzene and phenol (see Sections II.1 and II.2).

Phenolic azomethines **142a**,**b** react with 4-*tert*-butyl-2,6-diformylphenol[201] analogously to related pyridine derivative **137**. However (unlike the anion template reaction of compounds **137** and **139**), the reactions of azomethines **142a**,**b** c with this phenol proceed in the absence of template agents to give [2 + 2] macrocycles **143a**,**b** without traces of oligomerisation products.[201] The reaction in the presence of metal ions as the template agent affords a radically different macrocycle, *viz*., the [1 + 1]-condensation product.[201]





R = H (**a**), Me (**b**).

X-Ray diffraction data show that [2 + 2] macrocycle **143a** adopts a figure eight conformation due to pairwise stacking interactions between two phenolic fragments and two *o*-phenylenediamine fragments (Fig. 19).[201] In addition, this system is stabilised by numerous hydrogen bonds between the phenol hydrogen atoms and the azomethine nitrogen atoms. Evidently, the successful macrocyclisation is attributed to π,π interactions.

From the above it follows that both hydrogen bonds and other weak nonbonding interactions can be efficiently used for controlling the condensation of dicarbonyl compounds with diamines under thermodynamic control. These interactions provide the selective binding of one of the products from the dynamic combinatorial library, thus shifting the equilibrium toward the most stable complex. This phenomenon lies at the basis of an efficient approach to the design of artificial cationic and anionic receptors.

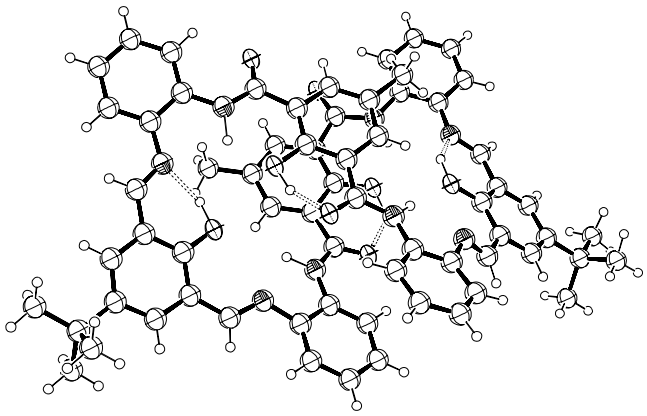
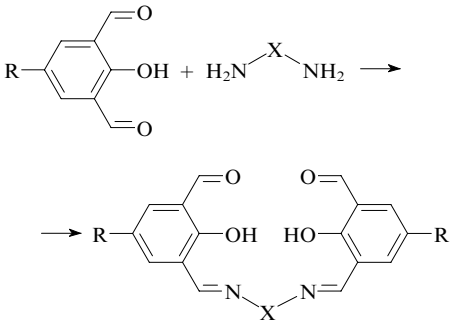


Figure 19. Structure of [2 + 2] macrocycle **143a**.[201]

V. Acyclic condensation products of dicarbonyl compounds with diamines

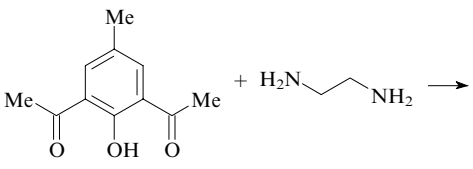
Investigations of the pathways of formation of acyclic condensation products of dicarbonyl compounds with diamines are of importance primarily in the synthesis of enlarged blocks used in the further fragment assembly of macrocycles. [2 + 1]-Condensation products are of great interest as building blocks for the assembly of unsymmetrical macrocycles by performing their reactions with diamines of different structure. Several successful syntheses of these compounds by the reactions of diformyl derivatives of phenols with aliphatic diamines (the reactant ratio was 2 : 1) were documented. The condensation can be performed in boiling acetonitrile or methanol. Products **144** are formed in nearly quantitative yields.

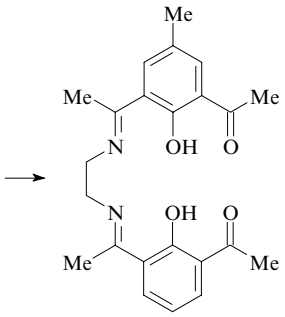


144

R = Cl, Me; X = $(CH_2)_n$ (n = 2, 3),[202] $(CH_2)_2NH(CH_2)_2$, $(CH_2)_2S(CH_2)_2$,[75] $CH_2(CH_2OCH_2)_2CH_2$,[202] $(CH_2)_2NHC(O)C(O)NH(CH_2)_2$,[79] NHC(S)NH.[88]

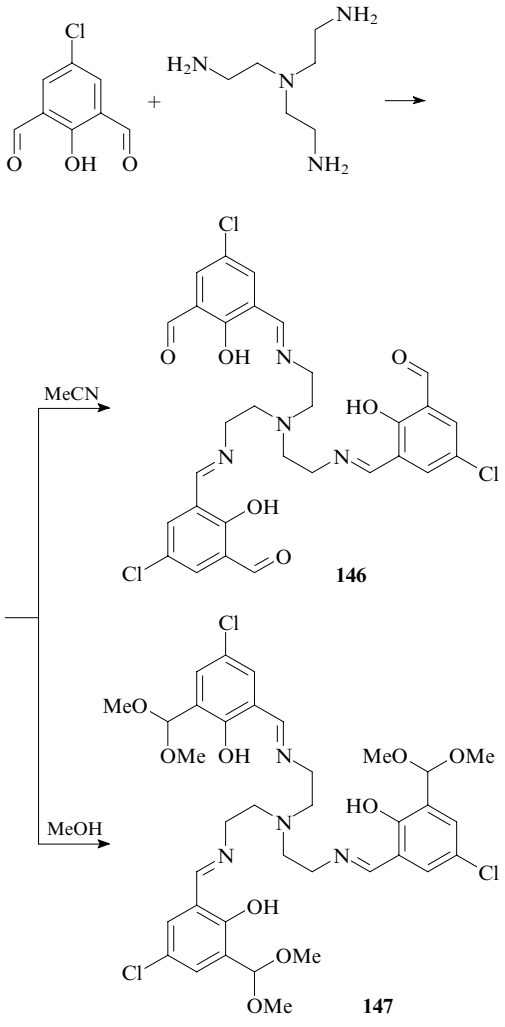
2,6-Diacetyl-4-methylphenol reacts analogously yielding azomethine **145**.[203]





145

The condensation of diformyl derivatives of phenols with tris(2-aminoethyl)amine in a ratio of 3 : 1 in anhydrous acetonitrile affords [3 + 1]-condensation product **146**.[147, 202, 204, 205] Acyclic condensation product **146** is formed only if the reactants are used in a stoichiometric ratio; otherwise, the macrocyclisation giving cryptands is the main reaction pathway (see Section II.4.e).

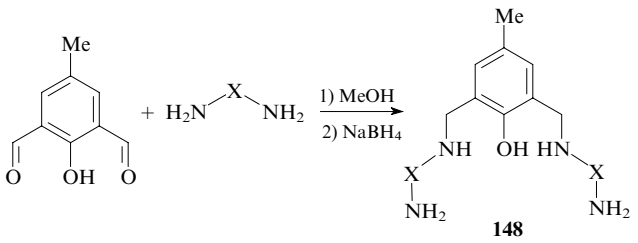


146

147

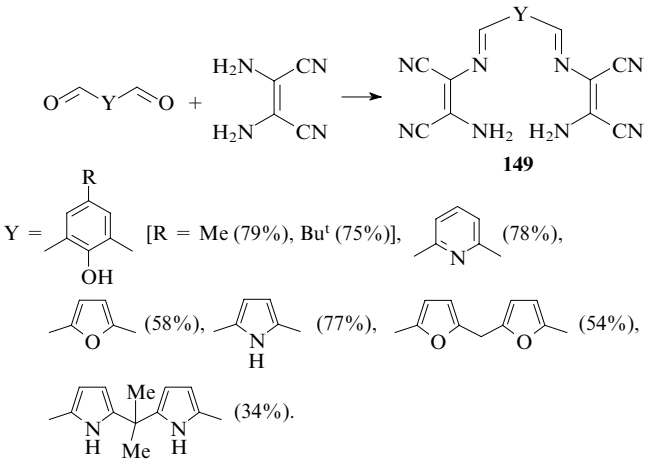
The reaction in methanol results not in the triformyl derivative but in its acetal **147**.[206]

All attempts to perform the stoichiometrically controlled [1 + 2] condensation of dicarbonyl compounds with two equivalents of aliphatic diamines failed. The reactions afford [1 + 2]-condensation products only in the presence of a 50 – 100-fold excess of diamines. However, attempts to isolate azomethines in the pure form were also unsuccessful because of hydrolytic instability of these compounds. The corresponding stable amines **148** are formed only after reduction of Schiff bases with sodium borohydride.



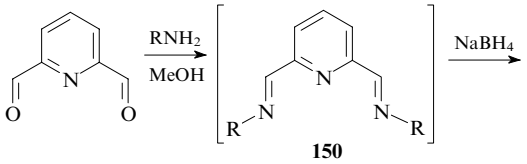
X = $(CH_2)_2$ (80%),[207] $(CH_2)_3$ (64%),[208, 209] $(CH_2)_2NH(CH_2)_2$.[210]

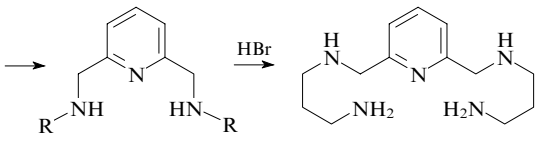
2,3-Diaminomaleonitrile existing (like *o*-phenylenediamine) in the enediamine form has low basicity and nucleophilicity due to the strong electron-withdrawing effect of two nitrile groups conjugated with the amino groups. The reactions of this compound with dicarbonyl compounds give [1 + 2]-condensation products **149** in high yields.[211, 212]



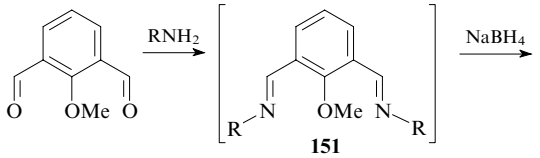
After completion of the reaction at the first amino group, the nucleophilicity of the second amino group decreases so that the process is terminated. Regardless of the nature of the dicarbonyl compound and the reactant ratio, diamines **149** were isolated as the only products.

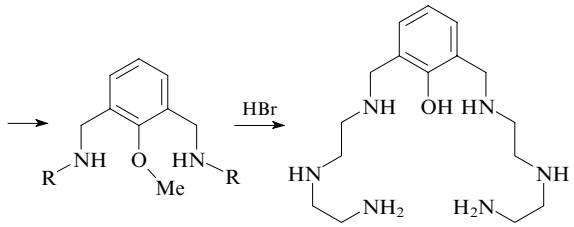
Special procedures were developed for the controlled synthesis of [1 + 2]-condensation products. In these procedures, one of two amino groups in diamines is preliminarily protected. After condensation and reduction of the imine function, the protecting group is removed. For example, the monoacetyl [199] derivative of 1,3-diaminopropane and the monobenzyloxycarbonyl [200] derivative of diethylenetriamine gave [1 + 2]-condensation products with diformylpyridine and diformylanisole, respectively, in high yields (the reactants were used in a stoichiometric ratio). The resulting Schiff bases **150** and **151** were immediately (without isolation) reduced to amines followed by deprotection. [213, 214]





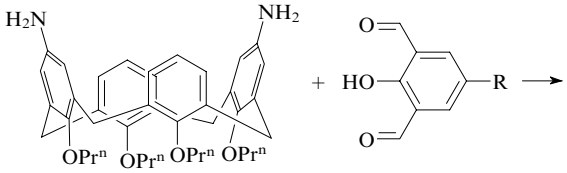
R = $(CH_2)_3NHAc$.

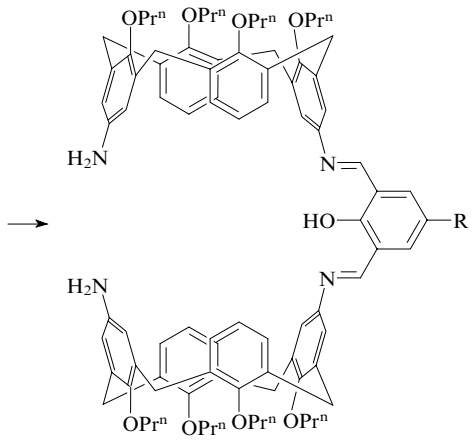




R = $(CH_2)_2NH(CH_2)_2NHCbz$ (Cbz is benzyloxycarbonyl).

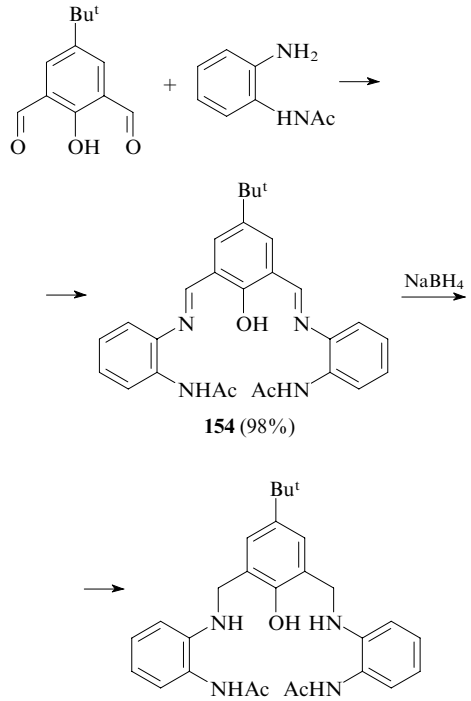
The reactions of 2,6-diformyl-4-R-phenols (R = H or Cl) with a twofold excess of the diamino derivative of calixarene **152** in methanol afford the stoichiometrically controlled [1 + 2]-condensation product **153**.[152] In this case, the aromatic diamine gives the [1 + 2]-condensation product without the formation of the corresponding macrocycle.





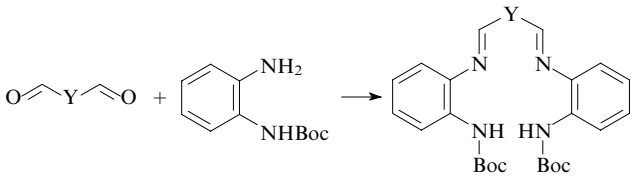
R = H, Cl.

To perform the target [1 + 2] condensation of dicarbonyl compounds with *o*-phenylenediamine, one of the amino groups is protected, as in the case of aliphatic diamines (see above). *N*-Acetyl-*o*-phenylenediamine reacts with 4-*tert*-butyl-2,6-diformylphenol in methanol at room temperature to form [1 + 2]-condensation product **154**, which is then reduced with $NaBH_4$ to yield the corresponding tetramine.[215]

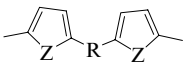
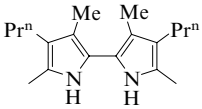


154 (98%)

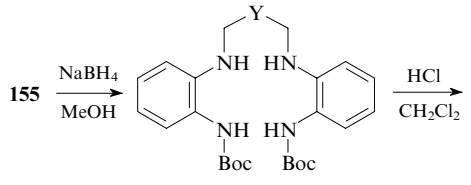
Under analogous conditions (methanol, room temperature), the reaction of *N*-(*tert*-butoxycarbonyl)-*o*-phenylenediamine produces [1 + 2]-Schiff bases **155**.



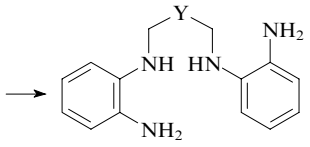
155

Y	Z	R	Yield (%)
	COH	Bu^t	70
	N	H	60
	O	–	71
	NH	–	75
	NH	CMe_2	69
	O	S	90
	–	–	10

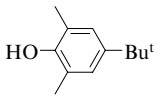
Reduction of the C=N bond in azomethines **155** with $NaBH_4$ followed by treatment of tetramines **156** with gaseous HCl in dichloromethane afforded salts of acyclic diamines **157**.[215]



156



157

Y	Yield of **156** (%)	Yield of **157** (%)
	98	90
	98	75
	95	80
	76	80

These condensations allow the synthesis of diamines and dicarbonyl derivatives containing additional functional groups of different nature. The resulting compounds can be used as building blocks for the construction of more complex macrocycles, which are of interest as polydentate ligands.

VI. Conclusion

The data summarised in the present review show that the condensation of dicarbonyl compounds with diamines under thermodynamic equilibrium conditions gives dynamic combinatorial libraries, which can contain numerous products, due to reversibility of all steps of series-parallel reactions involved in the condensation process. A careful choice of the conditions (the solvent, the concentration and the ratio of the reactants, the temperature and acid catalysis) allows the equilibrium to be shifted toward the target product, and free Schiff bases can be synthesised in good yields in the absence of metal cations, which are traditionally used as template agents. The most complex problem of the formation of unsymmetrical macrocycles can be successfully solved by performing fragment assembly from enlarged building blocks as precursors. In the final step of the synthesis, not only metal ions but also anions can be used as template agents. The latter are particularly efficient in the assembly of macrocycles containing a large number of proton-donor groups capable of hydrogen bonding inside the cavity. Such template condensations provide an approach to the design of artificial anionic and cationic receptors. Polydentate Schiff bases play an important role in coordination and supramolecular chemistry, organic synthesis and various biological and medical applications, resulting in the extensive development of this field of chemistry.

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References

1. V E Kuz'min, V P Lozitsky, G L Kamalov, R N Lozitskaya, A I Zheltvay, A S Fedtchouk, D N Kryzhanovsky *Acta Biochim. Polonica* **47** 867 (2000)
2. J Gao, F R Woolley, R A Zingaro *J. Med. Chem.* **48** 7192 (2005)

3. D E Burton, K Clarke, G W Gray *J. Chem. Soc.* 438 (1965)
4. R Lozytska, D Kryzhanovsky, A Mazepa, V Gorodniuk, V Kuz'min, V Lozitsky, A Fedchuck, S Rybalko, S Diadiun, J J V Eynde *ARKIVOC* (xiv) 118 (2004)
5. S Brooker *Eur. J. Inorg. Chem.* 2535 (2002)
6. A E Martell, J Perutka, D Kong *Coord. Chem. Rev.* **216–217** 55 (2001)
7. S Di Bella *Chem. Soc. Rev.* **30** 355 (2001)
8. A J Gallant, J K-H Hui, F E Zahariev, Y A Wang, M J MacLachlan *J. Org. Chem.* **70** 7936 (2005)
9. J L Sessler, E Katayev, G D Pantos, Yu A Ustynyuk *Chem. Commun.* 1276 (2004)
10. H Schiff *Ann. Chem. Pharm.* **131** 118 (1864)
11. C Godoy-Alcántar, A K Yatsimirsky, J-M Lehn *J. Phys. Org. Chem.* **18** 979 (2005)
12. S M Nelson *Pure Appl. Chem.* **52** 2461 (1980)
13. W Radecka-Paryzek, V Patroniak, J Lisowski *Coord. Chem. Rev.* **249** 2156 (2005)
14. M C Thompson, D H Busch *Chem. Eng. News* **40** 57 (1962)
15. D H Busch, J A Burke, D C Jicha, M C Thompson, M L Morris *Advances in Chemistry* (Ed. R E Gould) (Washington, DC: American Chemical Society, 1963) Vol. 37, p. 125
16. G A Melson, D H Busch *Proc. Chem. Soc.* 223 (1963)
17. G A Melson, D H Busch *J. Am. Chem. Soc.* **87** 1706 (1965)
18. *Templates in Chemistry I (Topics in Current Chemistry)* Vol. 248 (Eds C A Schalley, F Vögtle, K H Dötz) (Berlin, Heidelberg: Springer, 2004)
19. *Templates in Chemistry II (Topics in Current Chemistry)* Vol. 249 (Eds C A Schalley, F Vögtle, K H Dötz) (Berlin, Heidelberg: Springer, 2005)
20. M D Lankshear, P D Beer *Coord. Chem. Rev.* **250** 3142 (2006)
21. N Gimeno, R Vilar *Coord. Chem. Rev.* **250** 3161 (2006)
22. P A Gale, R Quesada *Coord. Chem. Rev.* **250** 3219 (2006)
23. R Vilar *Angew. Chem., Int. Ed.* **42** 1460 (2003)
24. P D Beer, M R Sambrook, D Curiel *Chem. Commun.* 2105 (2006)
25. S R Collinson, D E Fenton *Coord. Chem. Rev.* **148** 19 (1996)
26. U Beckmann, S Brooker *Coord. Chem. Rev.* **245** 17 (2003)
27. S Brooker *Coord. Chem. Rev.* **222** 33 (2001)
28. S Brooker, T C Davidson, S J Hay, R J Kelly, D K Kennepohl, P G Plieger, B Moubaraki, K S Murray, E Bill, E Bothe *Coord. Chem. Rev.* **216–217** 3 (2001)
29. N V Gerbeleu, V B Arion, J Burgess *Template Synthesis of Macrocyclic Compounds* (Weinheim, New York, Chichester, Brisbane, Singapore, Toronto: Wiley-VCH, 1999)
30. P Guerriero, S Tamburini, P A Vigato *Coord. Chem. Rev.* **139** 17 (1995)
31. P A Vigato, S Tamburini *Coord. Chem. Rev.* **248** 1717 (2004)
32. W B Callaway, J M Veauthier, J L Sessler *J. Porphyrins Phthalocyanines* **8** 1 (2004)
33. N E Borisova, M D Reshetova, Yu A Ustynyuk *Chem. Rev.* **107** 46 (2007)
34. S Chandra, L K Gupta *Spectrochim. Acta, Part A* **60** 1751 (2004)
35. N M Shauib, A-Z A Elassar, A El-Dissouky *Spectrochim. Acta, Part A* **63** 714 (2006)
36. S Chandra, L K Gupta *Spectrochim. Acta, Part A* **62** 307 (2005)
37. M Shakir, S Khatoon, S Parveen, Y Azim *Transition Met. Chem.* **32** 42 (2007)
38. H Adams, N A Bailey, D E Fenton, S Moss, C O Rodriguez de Barbarin, G Jones *J. Chem. Soc., Dalton Trans.* 693 (1986)
39. Y Tian, J Tong, G Frenzen, J-Z Sun *J. Org. Chem.* **64** 1442 (1999)
40. A E Martell, R J Motekaitis, Q Lu, D A Nation *Polyhedron* **18** 3203 (1999)
41. R Gupta, R Mukherjee *Inorg. Chim. Acta* **263** 133 (1997)
42. H Fenniri, C Dallaire, D P Funeriu, J-M Lehn *J. Chem. Soc., Perkin Trans. 2* 2073 (1997)
43. D Chen, A E Martell *Tetrahedron* **47** 6895 (1991)
44. P Comba, A Fath, T W Hambley, A Vielfort *J. Chem. Soc., Dalton Trans.* 1691 (1997)
45. G Wei, G A Lawrance, D T Richens, T W Hambley, P Turner *J. Chem. Soc., Dalton Trans.* 623 (1998)
46. M Allmendinger, P Zell, A Amin, U Thewalt, M Klinga, B Rieger *Heterocycles* **60** 1065 (2003)
47. J Gawronski, H Kolbon, M Kwit, A Katrusiak *J. Org. Chem.* **65** 5768 (2000)
48. N Kuhnert, G M Rossignolo, A Lopez-Periago *Org. Biomol. Chem.* **1** 1157 (2003)
49. N Kuhnert, A M Lopez-Periago *Tetrahedron Lett.* **43** 3329 (2002)
50. N Kuhnert, A M Lopez-Periago, G M Rossignolo *Org. Biomol. Chem.* **3** 524 (2005)
51. M Chadim, M Budesinský, J Hodacová, J Závada, P C Junk *Tetrahedron: Asymmetry* **12** 127 (2001)
52. N Kuhnert, N Burzlaff, C Patel, A Lopez-Periago *Org. Biomol. Chem.* **3** 1911 (2005)
53. N Kuhnert, C Patel, F Jami *Tetrahedron Lett.* **46** 7575 (2005)
54. M Kwit, P Skowronek, H Kolbon, J Gawroński *Chirality* **17** S93 (2005)
55. N Kuhnert, C Straßnig, A M Lopez-Periago *Tetrahedron: Asymmetry* **13** 123 (2002)
56. J Gawronski, M Brzostowska, M Kwit, A Plutecka, U Rychlewska *J. Org. Chem.* **70** 10147 (2005)
57. M Kwit, J Gawronski *Tetrahedron: Asymmetry* **14** 1303 (2003)
58. M Kaik, J Gawronski *Org. Lett.* **8** 2921 (2006)
59. J Gao, A E Martell *Org. Biomol. Chem.* **1** 2795 (2003)
60. D Utz, F W Heinemann, J Mukherjee, R Mukherjee, S Schindler *Z. Anorg. Allg. Chem.* **629** 2211 (2003)
61. S C Menon, A Panda, H B Singh, R P Patel, S K Kulshreshtha, W L Darby, R J Butcher *J. Organomet. Chem.* **689** 1452 (2004)
62. A Panda, S C Menon, H B Singh, C P Morley, R Bachman, T M Cocker, R J Butcher *Eur. J. Inorg. Chem.* 1114 (2005)
63. E A Kataev, M D Reshetova, Yu A Ustynyuk *Izv. Akad. Nauk, Ser. Khim.* 322 (2004) [a]
64. S Warzeska, R Krämer *Chem. Ber.* **128** 115 (1995)
65. Z Wang, J Reibenspies, A E Martell *Inorg. Chem.* **36** 629 (1997)
66. D A Plattner, A K Beck, M Neuburger *Helv. Chim. Acta* **85** 4000 (2002)
67. S W A Bligh, N Choi, W J Cummins, E G Evagorou, J D Kelly, M McPartlin *J. Chem. Soc., Dalton Trans.* 3369 (1994)
68. J Gregoliński, J Lisowski, T Lis *Org. Biomol. Chem.* **3** 3161 (2005)
69. R W Stotz, R C Stoufer *J. Chem. Soc. D* 1682 (1970)
70. F Benetollo, G Bombieri, L De Cola, A Polo, D L Smailes, L M Vallarino *Inorg. Chem.* **28** 3447 (1989)
71. A B Blake, E Sinn, A Yavari, B Moubaraki, K S Murray *Inorg. Chim. Acta* **229** 281 (1995)
72. *Svoistva Organicheskikh Soedinenii* (Properties of Organic Compounds) (Ed. A A Potekhin) (Leningrad: Khimiya, 1984)
73. W Schilf, B Kameński, B Kolodziej, E Grech, Z Rozwadowski, T Dziembowska *J. Mol. Struct.* **615** 141 (2002)
74. A Aguiari, E Bullita, P Casellato, S Tamburini, P A Vigato *Inorg. Chim. Acta* **202** 157 (1992)
75. U Casellato, D Fregona, S Sitran, S Tamburini, P A Vigato *Inorg. Chim. Acta* **110** 181 (1985)
76. A Aguiari, N Brianese, S Tamburini, P A Vigato *Inorg. Chim. Acta* **235** 233 (1995)
77. L Tei, A J Blake, F A Devillanova, A Garau, V Lippolis, C Wilson, M Schrlder *Chem. Commun.* 2582 (2001)
78. P Guerriero, P A Vigato, J-C G Bünzli, E Moret *J. Chem. Soc., Dalton Trans.* 647 (1990)
79. A Aguiari, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **256** 199 (1997)
80. C-Y Shen, M-F Hu, Q-H Luo, M-C Shen *J. Inorg. Biochem.* **68** 195 (1997)
81. B Kersting, G Steinfeld *Chem. Commun.* 1376 (2001)
82. A J Atkins, D Black, A J Blake, A Marin-Becerra, S Parsons, I Ruiz-Ramirez, M Schröder *Chem. Commun.* 457 (1996)
83. D Black, A J Blake, R L Finn, L F Lindoy, A Nezhadali, G Rougnaghi, P A Tasker, M Schröder *Chem. Commun.* 340 (2002)

84. B Dutta, P Bag, B Adhikary, U Flörke, K Nag *J. Org. Chem.* **69** 5419 (2004)
85. A J Atkins, A J Blake, M Schröder *J. Chem Soc., Chem. Commun.* 353 (1993)
86. S S Tandon, V McKee *J. Chem. Soc., Dalton Trans.* 19 (1989)
87. M Bell, A J Edwards, B F Hoskins, E H Kachab, R Robson *J. Am. Chem. Soc.* **111** 3603 (1989)
88. A D Naik, S M Annigeri, U B Gangadharmath, V K Revankar, V B Mahale *J. Inclusion Phenom. Macrocycl. Chem.* **43** 291 (2002)
89. J Gao, J H Reibenspies, R A Zingaro, F R Woolley, A E Martell, A Clearfield *Inorg. Chem.* **44** 232 (2005)
90. G-J Kim, D-W Park, Y-S Tak *Catal. Lett.* **65** 127 (2000)
91. S R Korupoju, N Mangayarkarasi, S Ameerunisha, E J Valente, P S Zacharias *J. Chem. Soc., Dalton Trans.* 2845 (2000)
92. S R Korupoju, P S Zacharias *Chem. Commun.* 1267 (1998)
93. Yu A Ustynyuk, N E Borisova, V M Nosova, M D Reshetova, S S Talismanov, S E Nefedov, G G Aleksandrov, I L Eremenko, I I Moiseev *Izv. Akad. Nauk, Ser. Khim.* 454 (2002) [a]
94. N E Borisova, Yu A Ustynyuk, M D Reshetova *Izv. Akad. Nauk, Ser. Khim.* 174 (2004) [a]
95. D S Kumar, V Alexander *Inorg. Chim. Acta* **238** 63 (1995)
96. B Srinivas, N Aruslamy, P S Zacharias *Polyhedron* **10** 731 (1991)
97. H Houjou, S-K Lee, Y Hishikawa, Y Nagawa, K Hiratani *Chem. Commun.* 2197 (2000)
98. H Shimakoshi, T Kai, I Aritome, Y Hisaeda *Tetrahedron Lett.* **43** 8261 (2002)
99. S Abe, J Mochizuki, T Sone *Anal. Chim. Acta* **319** 387 (1996)
100. S Srimurugan, B Viswanathan, T K Varadarajan, B Varghese *Tetrahedron Lett.* **46** 3151 (2005)
101. H Houjou, Y Nagawa, K Hiratani *Tetrahedron Lett.* **42** 3861 (2001)
102. M A Perez, J M Bermejo *J. Org. Chem.* **58** 2628 (1993)
103. E J Corey, R Imwinkelried, S Pikul, Y B Xiang *J. Am. Chem. Soc.* **111** 5493 (1989)
104. K Saigo, N Kubota, S Takebayashi, M Hasegawa *Bull. Chem. Soc. Jpn.* **59** 931 (1986)
105. H Brunner, H Schiessling *Angew. Chem., Int. Ed. Engl.* **33** 125 (1994)
106. S Akine, T Taniguchi, T Nabeshima *Tetrahedron Lett.* **42** 8861 (2001)
107. A J Gallant, M J MacLachlan *Angew. Chem., Int. Ed.* **42** 5307 (2003)
108. C T L Ma, M J MacLachlan *Angew. Chem., Int. Ed.* **44** 4178 (2005)
109. S Akine, D Hashimoto, T Saiki, T Nabeshima *Tetrahedron Lett.* **45** 4225 (2004)
110. A J Gallant, B O Patrick, M J MacLachlan *J. Org. Chem.* **69** 8739 (2004)
111. A J Gallant, M Yun, M Sauer, C S Yeung, M J MacLachlan *Org. Lett.* **7** 4827 (2005)
112. J K-H Hui, M J MacLachlan *Chem. Commun.* 2480 (2006)
113. D E Fenton, R Moody *J. Chem. Soc., Dalton Trans.* 219 (1987)
114. N A Bailey, M M Eddy, D E Fenton, S Moss, A Mukhopadhyay, G Jones *J. Chem. Soc., Dalton Trans.* 2281 (1984)
115. H Adams, N A Bailey, S R Collinson, D E Fenton, J C Hawley, S J Kitchen *J. Organomet. Chem.* **550** 20 (1998)
116. H Adams, N A Bailey, P Bertrand, S R Collinson, D E Fenton, S J Kitchen *Inorg. Chim. Acta* **250** 139 (1996)
117. A Lavery, S M Nelson, M G B Drew *J. Chem. Soc., Dalton Trans.* 2975 (1987)
118. N A Bailey, M M Eddy, D E Fenton, G Jones, S Moss, A Mukhopadhyay *J. Chem Soc., Chem. Commun.* 628 (1981)
119. J Gao, A E Martell *Org. Biomol. Chem.* **1** 2801 (2003)
120. R A Jones, G Quintanilla-Lopes, O Ozturk, S A N Taheri, G B Karatepe, R O Jones *J. Chem. Res.* 309 (2001)
121. S A N Taheri, R A Jones, S S Badesha, M M Hania *Tetrahedron* **45** 7717 (1989)
122. J L Sessler, W Callaway, S P Dudek, R W Date, V Lynch, D W Bruce *Chem. Commun.* 2422 (2003)
123. M R Johnson, C Slebodnick, J A Ibers *J. Porphyrins Phthalocyanines* **1** 87 (1997)
124. J L Sessler, T D Mody, V Lynch *Inorg. Chem.* **31** 529 (1992)
125. J L Sessler, T D Mody, V Lynch *J. Am. Chem. Soc.* **115** 3346 (1993)
126. C Givaja, A J Blake, C Wilson, M Schröder, J B Love *Chem. Commun.* 2508 (2003)
127. J M Veauthier, W -S Cho, V M Lynch, J L Sessler *Inorg. Chem.* **43** 1220 (2004)
128. S Meyer, B Andrioletti, J L Sessler, V Lynch *J. Org. Chem.* **63** 6752 (1998)
129. J L Sessler, W-S Cho, S P Dudek, L Hicks, V M Lynch, M T Huggins *J. Porphyrins Phthalocyanines* **7** 97 (2003)
130. J L Sessler, H Maeda, T Mizuno, V M Lynch, H Furuta *J. Am. Chem. Soc.* **124** 13474 (2002)
131. A Yu Chernyad'ev, Yu A Ustynyuk, O V Yazev, E A Kataev, M D Reshetova, A A Sidorov, G G Aleksandrov, V M Novotortsev, V N Ikorskii, S E Nefedov, I L Eremenko, I I Moiseev *Izv. Akad. Nauk, Ser. Khim.* 2334 (2001) [a]
132. M Kumar, V S N Bhalla, V Kumar, M Singh, G Singh *J. Inclusion Phenom. Macrocycl. Chem.* **39** 241 (2001)
133. V J Aran, M Kumar, J Molina, L Lamarque, P Navarro, E Garcia-Espana, J A Ramirez, S V Luis, B Escuder *J. Org. Chem.* **64** 6135 (1999)
134. L Lamarque, P Navarro, C Miranda, V J Aran, C Ochoa, F Escarti, E Garcia-Espana, J Latorre, S V Luis, J F Miravet *J. Am. Chem. Soc.* **123** 10560 (2001)
135. S Aime, M Botta, U Casellato, S Tamburini, P A Vigato *Inorg. Chem.* **34** 5825 (1995)
136. J Liu, Y Masuda, E Sekido *Bull. Chem. Soc. Jpn.* **63** 2516 (1990)
137. H Adams, N A Bailey, P Bertrand, S R Collinson, D E Fenton, S J Kitchen *J. Chem. Soc., Dalton Trans.* 1181 (1996)
138. S M Nelson, F S Esho, M G B Drew *J. Chem. Soc., Dalton Trans.* 407 (1982)
139. E Bullita, U Casellato, F Ossola, P Tomasin, P A Vigato, U Russo *Inorg. Chim. Acta* **287** 117 (1999)
140. Z H Chohan, K M Khan, C T Supuran *Appl. Organomet. Chem.* **18** 305 (2004)
141. M J L Tendero, A Benito, J M Lloris, R Martinez-Manez, J Soto, J Payá, A J Edwards, P R Raithby *Inorg. Chim. Acta* **247** 139 (1996)
142. O D Fox, T D Rolls, M G B Drew, P D Beer *Chem. Commun.* 1632 (2001)
143. K E Krakowiak, A V Bordunov, J S Bradshaw *J. Heterocycl. Chem.* **35** 169 (1998)
144. Q Lu, J-M Latour, C J Harding, N Martin, D J Marrs, V McKee, J Nelson *J. Chem. Soc., Dalton Trans.* 1471 (1994)
145. D McDowell, J Nelson *Tetrahedron Lett.* **29** 385 (1988)
146. J-J Zhang, W Zhang, Q-H Luo, Y-H Mei *Polyhedron* **18** 3637 (1999)
147. F Avecilla, R Bastida, A de Blas, D E Fenton, A Macias, A Rodriguez, T Rodriguez-Blas, S Garsia-Granada, R Corzo-Suárez *J. Chem. Soc., Dalton Trans.* 409 (1997)
148. M Kumar, V Sharma, J N Babu *J. Inclusion Phenom. Macrocycl. Chem.* **42** 247 (2002)
149. M Kumar, V J Arán, P Navarro *Tetrahedron Lett.* **36** 2161 (1995)
150. L Lamarque, C Miranda, P Navarro, F Escarti, E Garcia-España, J Latorre, J A Ramirez *Chem. Commun.* 1337 (2000)
151. S Brooker, J D Ewing, J Nelson *Inorg. Chim. Acta* **317** 53 (2001)
152. S Tamburini, P Tomasin, P A Vigato, A Casnati, L Domiano *Inorg. Chim. Acta* **254** 209 (1997)
153. J Jazwinski, J-M Lehn, D Lilienbaum, R Ziessel, J Guilhem, C Pascard *J. Chem. Soc., Chem. Commun.* 1691 (1987)
154. D McDowell, J Nelson, V McKee *Polyhedron* **8** 1143 (1989)
155. V McKee, W T Robinson, D McDowell, J Nelson *Tetrahedron Lett.* **30** 7453 (1989)
156. M G B Drew, V Felix, V McKee, G Morgan, J Nelson *Supramol. Chem.* **5** 281 (1995)
157. M G B Drew, D Marrs, J Hunter, J Nelson *J. Chem. Soc., Dalton Trans.* 11 (1992)

158. A Grohmann, H Lanig, W Bauer, S Schmidt, F W Heinemann *J. Mol. Model*. **6** 119 (2000)
159. S Schmidt, W Bauer, F W Hienemann, H Lanig, A Grohmann *Angew. Chem., Int. Ed.* **39** 913 (2000)
160. Yu A Ustynuyk, O V Yazev, I P Gloriozov, D N Laikov *Proceedings of Humboldtian Conference on Biomedical Science, Moscow, 2001* P. 7
161. H Okawa, H Furutachi, D E Fenton *Coord. Chem. Rev*. **174** 51 (1998)
162. M Vicente, R Bastida, A Macias, L Valencia, C F G C Geraldes, C D Brondino *Inorg. Chim. Acta* **358** 1141 (2005)
163. W H Correa, J L Scott *Molecules* **9** 513 (2004)
164. N Brianese, U Casellato, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **293** 178 (1999)
165. U Casellato, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **357** 4191 (2004)
166. U Casellato, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **341** 118 (2002)
167. U Casellato, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **262** 117 (1997)
168. D-H Won, C-H Lee *Tetrahedron Lett*. **42** 1969 (2001)
169. C-H Lee, K-T Oh *Tetrahedron Lett*. **40** 1921 (1999)
170. C-H Lee, J-W Ka, D-H Won *Tetrahedron Lett*. **40** 6799 (1999)
171. E Bértolo, R Bastida, A de Blas, D E Fenton, C Lodeiro, A Macias, A Rodriguez, T Rodriguez-Blas *J. Inclusion Phenom. Macrocycl. Chem*. **35** 191 (1999)
172. A H M Elwahy *Tetrahedron* **56** 897 (2000)
173. R Seangprasertkij, Z Asfari, F Arnaud, J Vicens *J. Org. Chem*. **59** 1741 (1994)
174. C Lodeiro, R Bastida, A de Blas, D E Fenton, A Macias, A Rodriguez, T Rodriguez-Blas *Inorg. Chim. Acta* **267** 55 (1998)
175. O Struck, L A J Chrisstoffels, R J W Lugtenberg, W Verboom, G J van Hummel, S Harkema, D N Reinhoudt *J. Org. Chem*. **62** 2487 (1997)
176. D Armspach, D Matt, F Peruch, P Lutz *Eur. J. Inorg. Chem*. 805 (2003)
177. E A Kataev, G D Pantos, J L Sessler, M D Reshetova, Yu A Ustynyuk *Izv. Akad. Nauk, Ser. Khim*. 161 (2005) [a]
178. V V Roznyatovskii, N E Borisova, M D Reshetova, A G Buyanovskaya, Yu A Ustynyuk *Izv. Akad. Nauk, Ser. Khim*. 2152 (2005) [a]
179. A A Abbas *Tetrahedron* **60** 1541 (2004)
180. K Gunst, S Seggewies, E Breitmaier *Synthesis* 1856 (2001)
181. S Meyer, M C Hoehner, V Lynch, J L Sessler *J. Porphyrins Phthalocyanines* **3** 148 (1999)
182. S Seggewies, T Schönemeier, E Breitmaier *Synthesis* 565 (1999)
183. J L Sessler, A E V Gorden, D Seidel, S Hannah, V Lynch, P L Gordon, R J Donohoe, C D Tait, D W Keogh *Inorg. Chim. Acta* **341** 54 (2002)
184. A Drews, T Schönemeier, S Seggewies, E Breitmaier *Synthesis* 749 (1998)
185. A Jasat, D Dolphin *Chem. Rev*. **97** 2267 (1997)
186. J L Sessler, R M Dávila, V Král *Tetrahedron Lett*. **37** 6469 (1996)
187. S Katsiaouni, S Dechert, C Brückner, F Meyer *Chem. Commun*. 951 (2007)
188. J L Sessler, V Roznyatovskiy, G D Pantos, N E Borisova, M D Reshetova, V M Lynch, V N Khrustalev, Yu A Ustynyuk *Org. Lett*. **7** 5277 (2005)
189. E J Corey, B-C Pan, D H Hua, D R Deardorff *J. Am. Chem. Soc*. **104** 6816 (1982)
190. W Moneta, P Baret, J-L Pierre *J. Chem. Soc., Chem. Commun*. 899 (1985)
191. L Salmon, P Thuery, E Riviere, S Miyamoto, T Yamato, M Ephritikhine *New J. Chem*. **30** 1220 (2006)
192. H Shimakoshi, H Takemoto, I Aritome, Y Hisaeda *Tetrahedron Lett*. **43** 4809 (2002)
193. H Höpfl, M Sanchez, V Barba, N Farfán, S Rojas, R Santillan *Inorg. Chem*. **37** 1679 (1998)
194. H Höpfl, N Farfán *J. Organomet. Chem*. **547** 71 (1997)
195. V Barba, H Höpfl, N Farfán, R Santillan, H I Beltran, L S Zamudio-Rivera *Chem. Commun*. 2834 (2004)
196. V Barba, R Villamil, R Luna, C Godoy-Alcantar, H Höpfl, H I Beltran, L S Zamudio-Rivera, R Santillan, N Farfan *Inorg. Chem*. **45** 2553 (2006)
197. V Barba, E Gallegos, R Santillan, N Farfán *J. Organomet. Chem*. **622** 259 (2001)
198. J L Sessler, E A Katayev, D G Pantos, P Scherbakov, M D Reshetova, V N Khrustalev, V M Lynch, Yu A Ustynyuk *J. Am. Chem. Soc*. **127** 11442 (2005)
199. P T Corbett, S Otto, J K M Sanders *Chem. – Eur. J*. **10** 3139 (2004)
200. E A Katayev, G D Pantos, M D Reshetova, V N Khrustalev, V M Lynch, Yu A Ustynyuk, J L Sessler *Angew. Chem., Int. Ed*. **44** 7386 (2005)
201. S Brooker, G S Dunbar, T Weyhermuller *Supramol. Chem*. **13** 601 (2001)
202. N Brianese, U Casellato, S Tamburini, P Tomasin, P A Vigato *Inorg. Chim. Acta* **272** 235 (1998)
203. X Chen, S Zhan, C Hu, Q Meng, J Shun *Inorg. Chim. Acta* **260** 95 (1997)
204. M D Timken, W A Marritt, D N Hendrickson, R A Gagne, E Sinn *Inorg. Chem*. **24** 4202 (1985)
205. U Casellato, S Tamburini, P Tomasin, P A Vigato, M Botta *Inorg. Chim. Acta* **247** 143 (1996)
206. S J Archibald, A J Blake, S Parsons, M Schröder, R E P Winpenny *J. Chem. Soc., Dalton Trans*. 173 (1997)
207. I E Dickson, R Robson *Inorg. Chem*. **13** 1301 (1974)
208. S Brooker, P D Croucher, T C Davidson, P D Smith *Polyhedron* **19** 1887 (2000)
209. S Brooker, P D Croucher *J. Chem. Soc., Chem. Commun*. 2075 (1995)
210. S Brooker, P D Croucher *J. Chem. Soc., Chem. Commun*. 1278 (1993)
211. N E Borisova, Yu A Ustynyuk, M D Reshetova, G G Aleksandrov, I L Eremenko, I I Moiseev *Mendeleev Commun*. 202 (2003)
212. N E Borisova, V V Roznyatovskii, M D Reshetova, Yu A Ustynyuk *Zh. Org. Khim*. **41** 1028 (2005) [b]
213. S Brooker, T J Simpson *J. Chem. Soc., Dalton Trans*. 1151 (1998)
214. G Ambrosi, M Formica, V Fusi, L Giorgi, A Guerri, M Micheloni, R Pontellini, P Rossi *Polyhedron* **22** 1135 (2003)
215. N E Borisova, M D Reshetova, M V Kuznetsov, Yu A Ustynyuk *Synthesis* 1169 (2007)

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[b] — *Russ. J. Org. Chem. (Engl. Transl.)*