Chiral Macrocyclic Schiff Bases: An Overview

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Abstract: Macrocyclic Schiff bases form an important class of macrocyclic host systems, which are formed by self condensation of a diamine with a diformyl compound. Chiral modification of macrocyclic Schiff bases with different central cavity sizes were recently developed and explored. This mini-review will discuss some of the synthetic strategies, solid state crystal structures, and recent applications of different [n+n] chiral macrocyclic Schiff bases.

Keywords: Chiral [n+n] macrocycles, schiff bases, diastereomers, ligands, enantioselective synthesis.

I. INTRODUCTION

In recent years, supramolecular chemistry has emerged as one of the actively pursued research fields of the chemical sciences. Its implication now reaches from the basis of molecular recognition in natural systems such as protein-substrate interactions to exciting new applications in chemical technology and materials science. The challenge for any supramolecular scientist is the identification of a host molecule or receptor that binds to a specific guest molecule with a high binding constant and with the required selectivity. Macrocyclic Schiff bases form an important class of macrocyclic host systems, which are formed by self condensation of a diamine with a diformyl compound. The appropriate choice of the reaction conditions together with the structure of the reacting components provides a facile condition for the construction of these macrocycles. Both cyclic and acyclic products can be synthesized and the synthesis of unsymmetrical macrocycles can be achieved using an acyclic Schiff base. Template methods are frequently employed for the synthesis of macrocyclic Schiff bases [1]. Metal ions like alkali and alkaline earth metals and lanthanide metals are particularly useful in the construction of macrocycles in high selectivity over the others. Apart from metal ions, non-metal templates like borate ions are also used for macrocycle synthesis. Many good reviews that provide an excellent analysis of the synthesis and properties of different kinds of macrocyclic Schiff bases are reported [2-10]. Chiral modification of macrocyclic Schiff bases with different central cavity sizes were recently developed and explored [11]. Considerable efforts have been made for developing metal-free methods for furnishing chiral macrocycles starting from various enantiopure diamines and dicarbonyl compounds. In this review, we collected for the first time the data dealing with the synthesis of enantiopure macrocyclic azomethines under metal-free conditions. The literature in this review is covered until November 2007. A brief collection of the applications and crystal structures of these chiral macrocycles are also described.

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II. CHIRAL [3+3] MACROCYCLIC SCHIFF BASES

Gawronski and coworkers, introduced a new preparative strategy for the synthesis of large poly-imine *meta*- and *para*- cyclophane type macrocycles using a [3+3] cyclocondensation strategy [12]. Triangular 30- and 27-membered hexaiminomacrocycles ((**1**) and (**2**), Fig. (**1**)) of D_3 and C_3 symmetry, respectively, are obtained by unprecedented [3+3] cyclocondensation of *trans*-(1*R*,2*R*)-diaminocyclohexane with terephthalaldehyde and isophthalaldehyde respectively. Molecular mechanics energy (MMX) calculations on the macrocycle (**1**) suggested that the course of the reaction, leading to macrocyclisation, is governed by conformational constraints imposed on the structural components of the intermediate products. The X-ray crystal structure of macrocycle (**1**) indicates the formation of an inclusion compound where a molecule of ethyl acetate partly penetrates the macrocyclic cavity and assumes an unsymmetrical position relative to the macrocycle.

Later, Chadim and coworkers, reported a non-templated synthesis of [3+3] cyclocondensed molecular triangles from enantiomeric and racemic forms of *trans*-1,2-diaminocyclohexane and terephthalaldehyde in quantitative yields [13]. Macrocycle (**1**) was formed in the case of enantiopure diamine and the X-ray structure of the macrocycle (**1**) grown from CH_3CN-CH_2Cl_2 differed markedly from that reported by Gawronski and coworkers. The crystal showed no inclusion compound but exhibited stacking of triangles in an eclipsed manner, giving rise to infinite microporous pillars. However, the reaction of racemic-*trans*-1,2-diaminocyclohexane produced diastereomeric pairs of macrocycles (**1**) and (**3**), as the products of condensation. The macrocycle (**3**) [(2*S*,3*S*,12*S*,13*S*,22*R*,23*R*) or (2*R*,3*R*,12*R*,13*R*,22*S*,23*S*)-**3**] contained both (*R*,*R*) and (*S*,*S*)-diaminocyclohexane units in the same molecular triangle. It was observed that the macrocycle (**3**) was also formed by co-crystallization of the 1:1 mixture of the (2*S*,3*S*,12*S*,13*S*,22*S*,23*S*)-**1** and (2*R*,3*R*,12*R*, 13*R*,22*R*,23*R*)-enantiomers of (**1**). The formation of diastereomer (**3**) during co-crystallization was attributed to the presence of 1,2-diaminocyclohexane, which was found to be an efficient catalyst that allows a reproducible rapid conversion.

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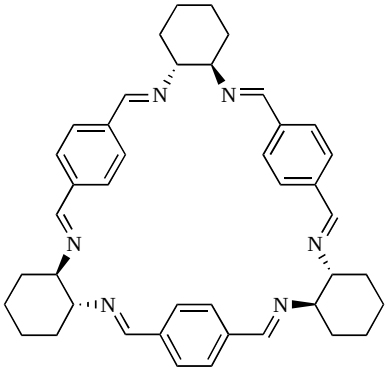
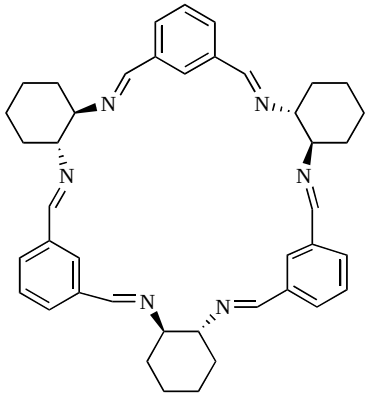
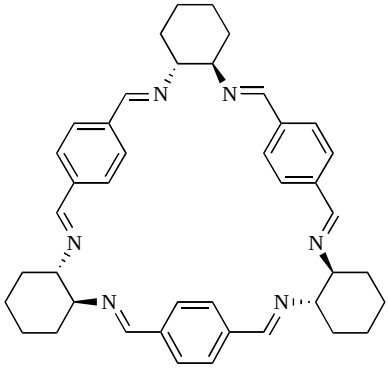


(2*R*,3*R*,12*R*,13*R*,22*R*,23*R*)-**1**

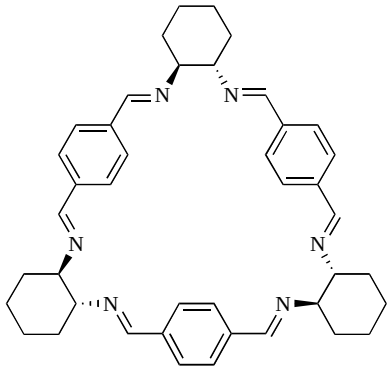


(2*R*,3*R*,11*R*,12*R*,20*R*,21*R*)-**2**

Fig. (1). Molecular structures of [3+3] macrocycles (**1**) and (**2**).



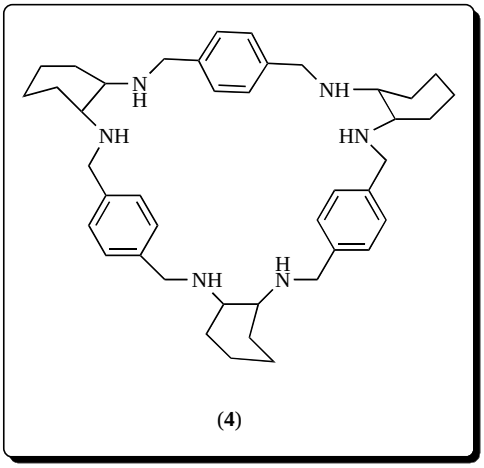
(2*S*,3*S*,12*S*,13*S*,22*R*,23*R*)-**3**



(2*R*,3*R*,12*R*,13*R*,22*S*,23*S*)-**3**

Kuhnert and Lopez-Periago, named this new class of [3+3] macrocycles as trianglimines and their reduced forms as trianglamines based on their unique triangular shape [14]. They also reported the synthesis of non-racemic [3+3] macrocycles formed from acyclic 1,2-diamine ((*R*,*R*)-stilbenediamine) and aromatic dialdehydes (terephthaldehyde and isophthaldehyde). Due to the increased conformational flexibility of the acyclic diamine, the yields for the macrocycles were reduced in comparison to those obtained with conformationally more restricted cyclic diamines. The trianglimine formed from acyclic diamine decomposed after 2 days in $CDCl_3$ to give linear oligomeric products, suggesting that the trianglimine was the kinetic product of the reaction. The [3+3] cyclocondensation strategy was extended using a series of aromatic dicarboxaldehydes and successfully synthesized macrocycles with (1*R*,2*R*)-diaminocyclo-hexane (at 0.1 M concentration in CH_2Cl_2) [15]. A series of methyl substituted 1,3-dialdehydes and fused ring 1,3-dialdehydes like 1,3-diformylazulene were examined for the formation of [3+3] macrocycles. In most of the cases trimeric products were formed in good yields along with some dimeric products. According to Kuhnert, in the case of 1,3-dicarboxaldehydes, the [3+3] cyclo-condensation products were formed under kinetic control and the [2+2] condensation products were formed under thermodynamic control using (1*R*,2*R*)-diaminocyclohexane. Ring contraction occurred under thermodynamic control and most of the [3+3] macrocycles could be transformed to the corresponding [2+2] macrocycle in quantitative yields by simple refluxing (12-72 h). Oxygen, nitrogen, and sulphur substituted aromatic heterocyclic dicarboxaldehydes were employed for the construction of [3+3] macrocycles with heteroatoms in excellent yields. Gao and Martell reported the synthesis of achiral trianglimine (**4**) formed from *cis*-diaminocyclohexane and terephthaldehyde [16]. The simple condensation procedure under high dilute reaction conditions produced a mixture of dimeric and trimeric Schiff base macrocycles. However, the trimeric macrocycle (**4**) free from [2+2] macrocycle was isolated in high yield by adopting a different one-pot procedure that involved reductive amination in the presence of diamine and dialdehyde.

In contrast to the formation of trianglimine as a sole product during condensation of 2,5-dithiocarboxaldehyde and *trans*-(1*R*,2*R*)-diaminocyclohexane, Gao and Martell reported that the trimer was formed along with dimer as a mixture under identical reaction conditions. The use of metal ion (Pb(II)) template improved the yield of trimeric macrocycle (~76 %) though the resulting product was a mixture of [2+2] and [3+3] macrocycles. Hong and coworkers, utilized the concept of [3+3] cyclocondensation for one-step synthe-

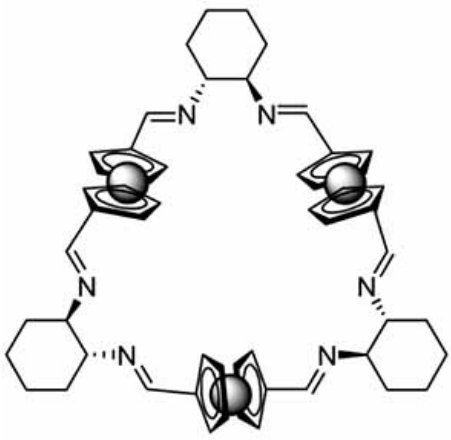


(**4**)

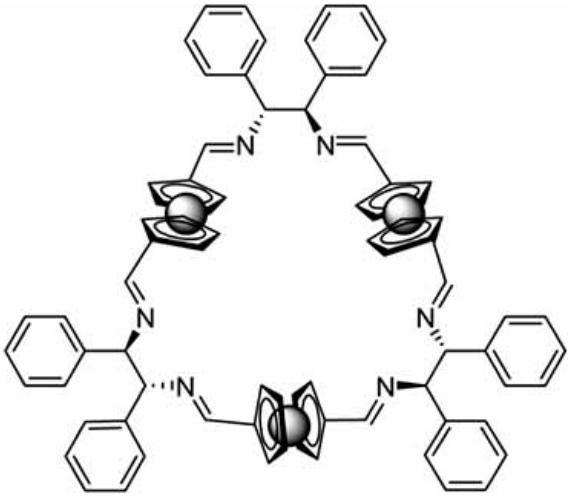
sis of chiral ferrocenyl triangles (Fig. (**2**)) [17]. The method involved treating 1,1′-ferrocenedicarboxaldehyde with (1*R*,2*R*)-diaminocyclohexane in CH_2Cl_2 in the presence of molecular sieves at room temperature for one day. The procedure afforded ferrocenyl-[3+3] macrocycle (**5**) in high yield. The strategy was extended using (1*R*,2*R*)-diphenylethylenediamine whose condensation with 1,1′-ferrocenedicarboxaldehyde afforded ferrocenyl-[3+3] macrocycle (**6**) in 76 % yield under similar reaction conditions. The synthesis of biaryl and terphenyl dicarboxaldehyde using Suzuki coupling were reported and explored for macrocyclisation reactions with (1*R*,2*R*)-diaminocyclohexane [18, 19]. The crude reaction mixtures were analyzed by ^{1}H-NMR spectro-scopy, FAB and ESI mass spectrometry after 12 and 48 h of reaction time in CH_2Cl_2 at room temperature, and determined the ratios of [2+2] and [3+3] cyclocondensation reaction products.

Diffusion NMR experiments were employed to assign minor and major products of the reaction. The macrocyclic polyimine compound displaying a smaller diffusion coefficient was assigned to the [3+3] cyclocondensation product, whereas the compound with the larger diffusion coefficient was assigned to the [2+2] cyclocondensation product. They observed that the ratio of products determined by integration of the crude ^{1}H-NMR spectra and the mass spectra differ greatly and that the mass spectrometry over estimated the formation of lower molecular weight product in all the cases. Among FAB and ESI-MS, FAB-MS was found to over estimate the amount of the lower molecular weight compound formed. The nature of cyclocondensation product depends strongly on the overall geometry of the dicarboxaldehyde building block. Dicarboxaldehydes with linear arrangement of carbonyl-biaryl axis afforded trianglimines exclusively, whereas dicarboxaldehydes with nonlinear carbonyl biaryl axes geometry afforded [2+2] condensation products. Dialdehydes derived from hydroquinone diethers containing similar O-alkylated groups (D_{2h} symmetry) and dicarboxaldehydes with reduced symmetry derived from hydroquinone methyl ether containing two different O-alkyl groups (C_{2v} symmetry) were utilized for the construction of oxygenated trianglimine macrocycles [20]. Trianglimines derived from such C_{2v} dialdehydes were expected to display two different binding sites, one above a plane formed by three imine nitrogens and one below a plane formed by three imine nitrogens, thus offering improved versatility in guest binding. In both the cases of dialdehydes, [3+3] macrocycles were formed as expected.

A series of *N*-alkylated trianglamine (Fig. (**3**)) formed by [3+3] cyclocondensation of (1*R*,2*R*)-diaminocyclohexane with terephthaldehyde followed by $NaBH_4$ reduction and alkylation was reported in good yields [21]. X-ray diffraction analysis and CD studies, in conjunction with molecular modeling and calculations of CD spectra, demonstrated that the molecular skeletons of these trianglamines can assume a variety of low-energy conformations. The crystal structures of hexamines differ significantly as a result of inclusion of various guests, solvent molecules and counter anions, and this could be ascribed to the facile formation of interpenetrated structures preventing formation of large cavities. The ability to include guest molecules in the crystal was strongly reduced in the case of *N*-alkylated derivatives (**7**-**17**) though trianglamine (**18**) was found to exhibit inclusion of guest molecules. Macrocycle (**1**) and hydroxy functionalized [3+3]



Ferrocenyl-[3+3] macrocycle **5**



Ferrocenyl-[3+3] macrocycle **6**

Fig. (2). Structures of chiral ferrocenyl trianglimines.

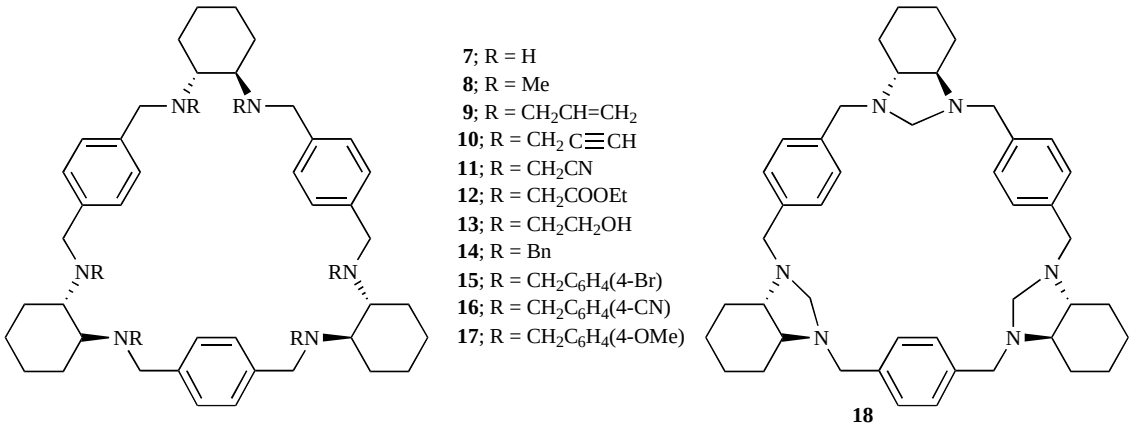


Fig. (3). Structures of *N*-alkylated trianglimines.

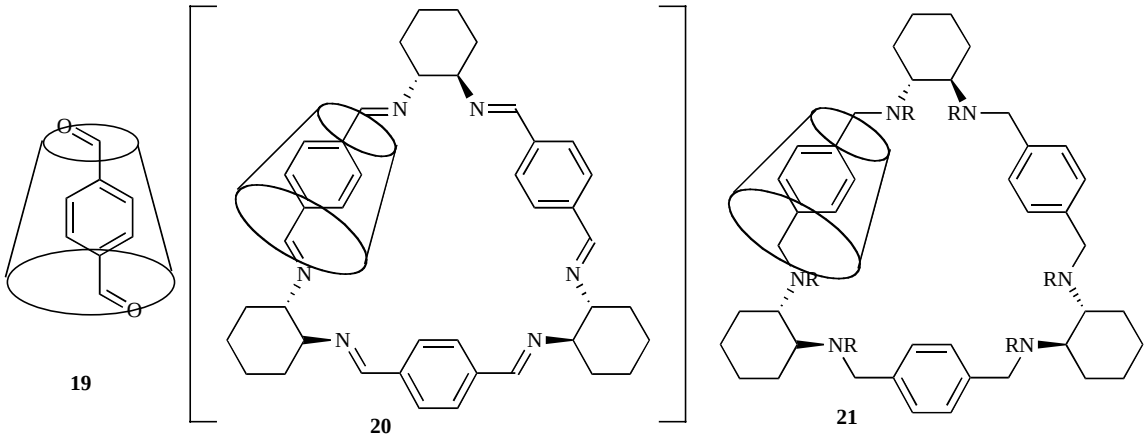


Fig. (4). Structure of trianglamine-β-cyclodextrin-[2]-catenanes (**21**).

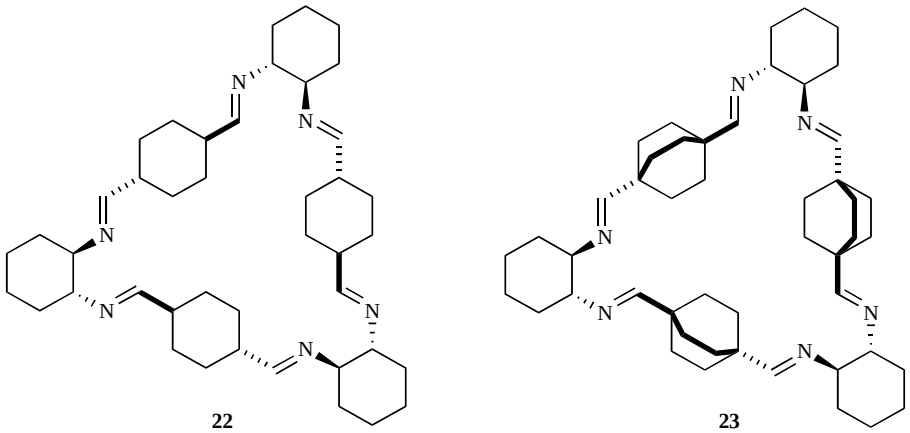


Fig. (5). Structures of aliphatic dialdehyde derived chiral [3+3] macrocycles.

macrocycles were synthesized in excellent yields in short reaction times under microwave irradiation. The reaction was carried out under aqueous reaction conditions using the salts of chiral diamines in contrast to the free diamines normally employed [22]. Terephthaldehyde was known to form inclusion complex (**19**) with β-cyclodextrin. This inclusion complex (**19**) was used for the construction of [2]-catenane-trianglimine with (1*R*,2*R*)-diaminocyclohexane [23]. The condensation was carried out with 1 equiv. of inclusion complex (**19**), 2 equiv. of terephthaldehyde and 3 equiv. of (1*R*,2*R*)-diaminocyclohexane in methanol for 48 h at room temperature which produced a mixture of macrocycle (**1**) (75%) along with 25 % catenane (**20**) as judged by crude ^{1}H-NMR spectrum and ESI mass spectrum (Fig. (**4**)). Though the hexaimine catenane (**20**) could not be isolated, its reduced product (**21**) formed by *in situ* reduction of the crude reaction mixture with $NaBH_4$ was isolated in 18 % yield.

Aliphatic dialdehydes with rigid structures were successfully applied for the construction of macrocycles by cyclo-condensation with enantiomerically pure *trans*-1,2-diamino-cyclohexane [24]. Under dilute reaction condition and inert atmosphere, aldehydes (**22**) and (**23**) afforded [3+3] macro-

cycles in 39-43% yields with *trans*-(1*R*,2*R*)-diaminocyclohexane (Fig. (**5**)). These aliphatic macrocyclic imines isolated as crystalline compounds that displayed high stability in contrast to the usual instability of aliphatic imines.

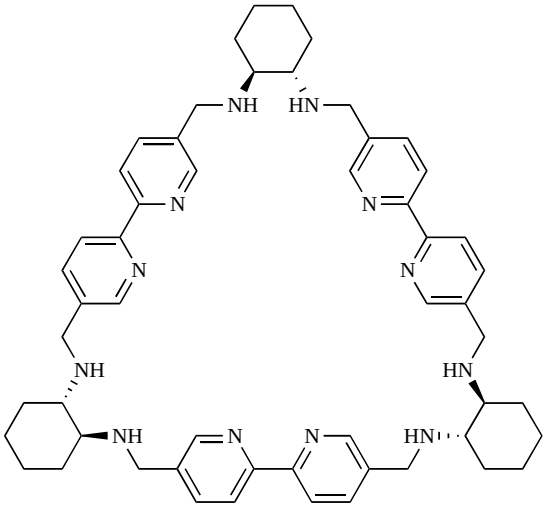
42-Membered [3+3] chiral polyaza macrocycle (**24**) was synthesized by cyclocondensation of both the enantiomers of *trans*-1,2-diaminocyclohexane and 2,2′-bipyridine-5,5′-dicarbaldehyde in 79-84 % yields (Fig. (**6**)) [25]. Similar yields of macrocycles were obtained by the use of tartrate salt of diamine and a base in the place of free diamine itself. Sodium borohydride reduction of (**24**) afforded the corresponding trianglamines in excellent yields (84-87 %).

III. CHIRAL [2+2] MACROCYCLIC SCHIFF BASES

Trianglimines derived from (1*R*,2*R*)-diaminocyclohexane and rigid linear aromatic dicarboxaldehydes like 1,4-aromatic dicarboxaldehydes (e.g. terephthaldehyde) were the thermodynamically favoured products and were formed as sole condensation products. On the other hand, [2+2] macrocycles were thermodynamically more favoured product in the condensation of 1,3-aromatic dicarboxaldehydes. Therefore, thermal equilibration of a mixture of products will lead to the formation of [2+2] macrocycles in high yields. In addition, tuning the overall geometry of the dicarboxaldehydes with aromatic dialdehydes of bent structure forms an excellent method for the synthesis of [2+2] macrocycles.

Achiral binuclear macrocyclic, Robson-type of complexes were studied in detail since 1970 because of their applications as models for biomolecules [26]. Typically, Robson-type macrocyclic complexes have been derived from the template condensation of achiral diamines such as ethylenediamine or diethylenetriamine and 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde. However, the use of chiral diamines such as (1*R*,2*R*)-diaminocyclohexane, (1*R*,2*R*)-diphenylethylenediamine, and (*R*)-1,1′-binaphthalenyl-2,2′-diamine in the construction of chiral Schiff base Robson-type macrocycles have received only limited study (Fig. (**7**)).

Wu *et al*., reported template-free and intramolecular hydrogen bond self-template synthesis of a series of chiral Robson-type macrocyclic ligands [27]. The reaction temperature was maintained at 50 ^{o}C and a slow addition of



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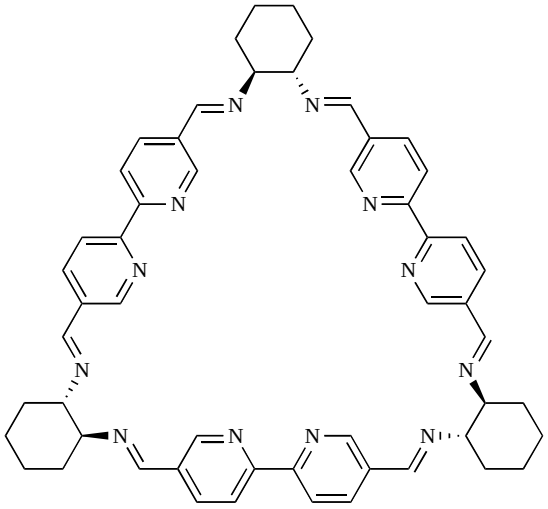

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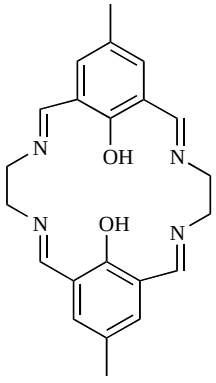
Fig. (6). Polyaza chiral macrocycle by [3+3] cyclocondensation.



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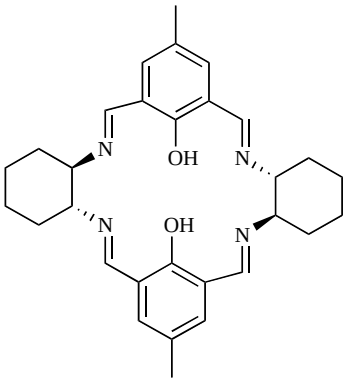

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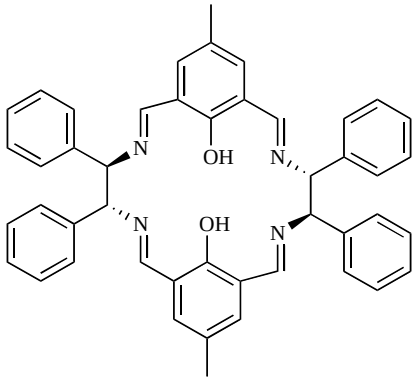

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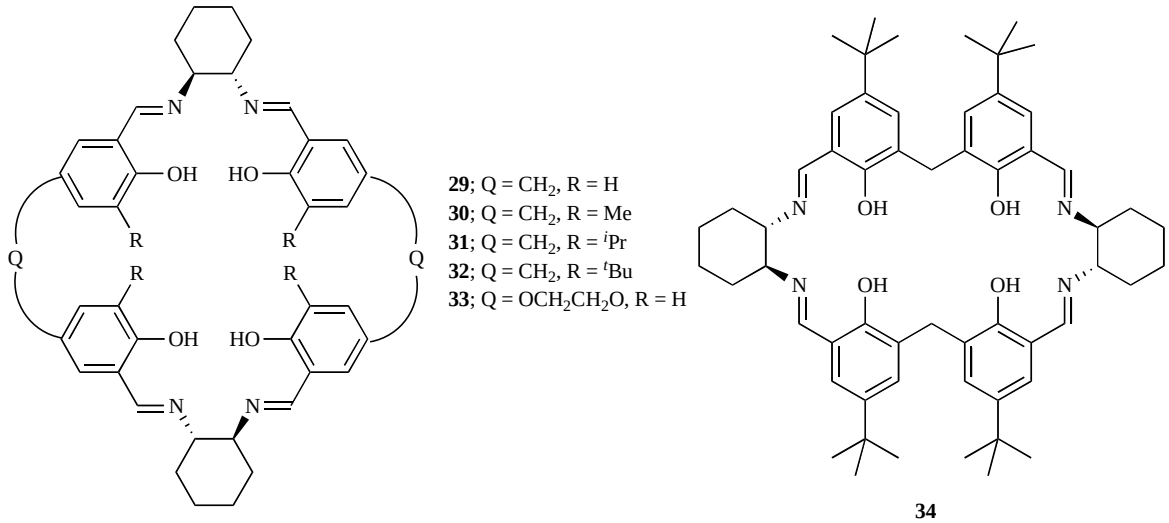
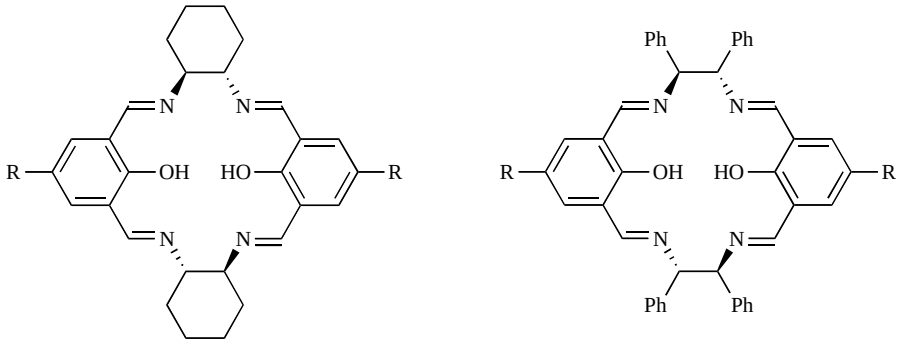
Fig. (7). Structures of Robson macrocycle (**26**) and its chiral variants (**27** and **28**).



29; Q = CH_2, R = H
30; Q = CH_2, R = Me
31; Q = CH_2, R = ^{i}Pr
32; Q = CH_2, R = ^{t}Bu
33; Q = OCH_2CH_2O, R = H

34

Fig. (8). Chiral [2+2] macrocycles containing two N_2O_2 binding sites prepared by metal-ion (**29-33**) and non-metal ion (**34**) template methods.



35; R = H
36; R = ^{t}Bu

37; R = H
38; R = ^{t}Bu

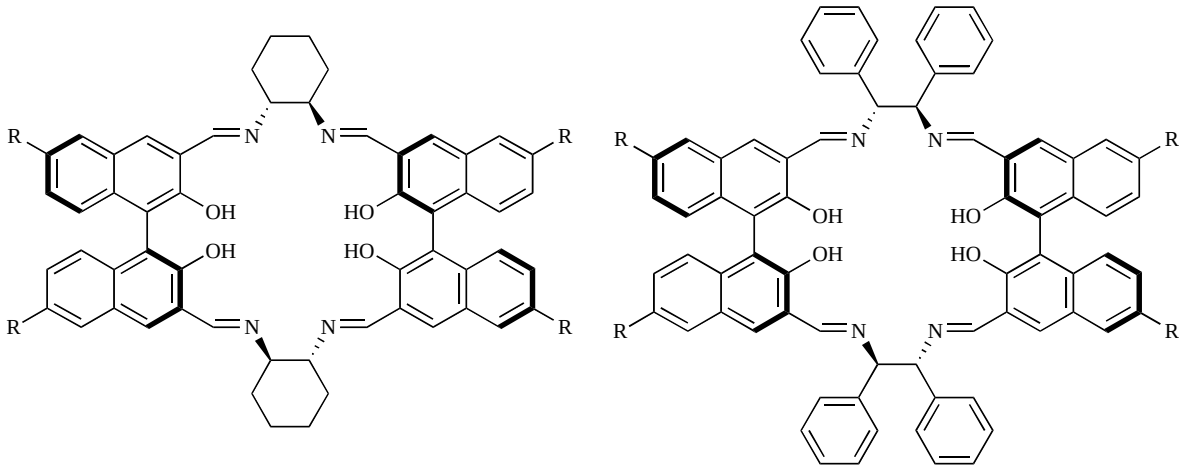
Fig. (9). Chiral [2+2] macrocyclic salen ligands.

diamine was employed and this condition maintained stable hydrogen bonding which directed macro-cyclisation. However, most other authors reported the formation of [3+3] Robson-type chiral macrocycles rather than the [2+2] macrocycles under template-free high dilute reaction conditions. Dutta *et al.*, reported an efficient proton templated synthesis of macrocycle (**27**) in high yield [28]. Gao *et al.*, reported the synthesis of macrocycles (**27**) and (**28**) in the presence of nickel ion template [29]. However, this template method could not be extended to the synthesis of [2+2] macrocycle involving (*R*)-1,1′-binaphthalenyl-2,2′-diamine. The failure of the reaction was attributed to the inability for the formation of a near planar four-coordination geometry of N_2O_2 with Ni^{2+} due to structural rigidity and axial chirality.

Jablonski reported Ba^{2+} ion templated synthesis of [2+2] macrocycles (**29**-**33**) from various *bis*(hydroxyaldehydes) and (1*R*,2*R*)-diaminocyclohexane (Fig. (**8**)) [30]. The method however produced mixture of macrocycles in most of the cases. They named this class of macrocycles as 'calixsalens' due to their close structural resemblance to calixarenes. Structurally related [2+2] macrocycle (**34**) containing two N_2O_2 binding sites was reported by Shimakoshi and coworkers [31]. The synthesis involved a boric ion as a template which produced the macrocycle in satisfactory purity. Neither the metal ion template methods nor the high-dilution methods were found to yield the desired product in high purity.

[2+2] Macrocyclic salen ligands (**35**-**38**) (Fig. (**9**)) for enantoselective epoxidation of olefins and enantioselective borohydride reduction of ketones, were formed exclusively from hydroxyl dialdehydes in good yields [32].

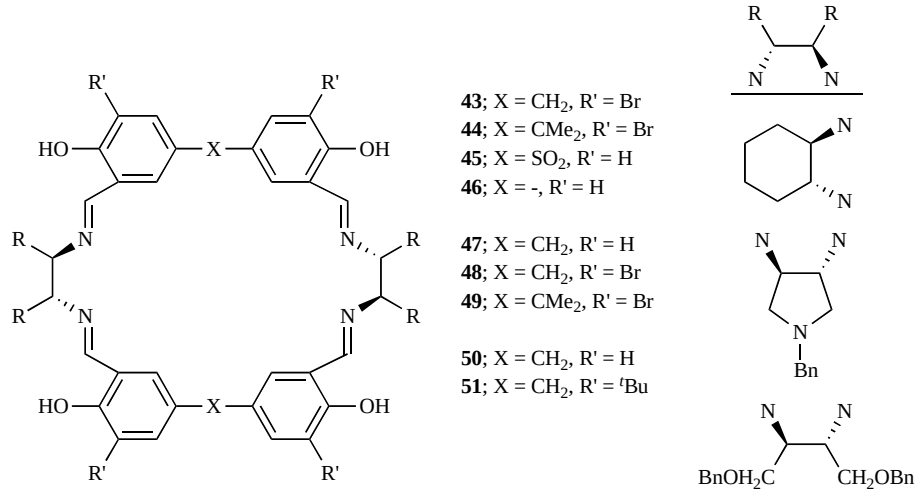
Bru *et al.*, used [2+2] cyclocondensation strategy for the synthesis of a series of chiral 32-membered ring peptidomimetic macrocycles [33]. The macrocycles were obtained in good yields from easily obtained synthons by one-pot two-step cyclisation procedure, based on reductive amination reactions. Biphenyl dicarboxaldehydes with two carbonyl groups at the 4,4′-positions invariably formed [3+3] macrocycles. On the other hand, the presence of two carbonyls either at the 3,3′- or 3,4′-positions leads to [2+2] macrocycles with chiral diamines. Kuhnert and coworkers reported the synthesis of [2+2] macrocycles in good yields using differently substituted biaryl dicarboxaldehydes [19]. In the case of terphenyl dicarboxaldehydes with a bent structure, the [2+2] macrocycles were formed as mixtures though in



39; R = H
40; R= 4-OEt-Ph

41; R = H
42; R= 4-OEt-Ph

Fig. (10). Chiral [2+2] macrocycles derived from (*S*)- 3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl.



43; X = CH_2, R' = Br
44; X = CMe_2, R' = Br
45; X = SO_2, R' = H
46; X = -, R' = H

47; X = CH_2, R' = H
48; X = CH_2, R' = Br
49; X = CMe_2, R' = Br

50; X = CH_2, R' = H
51; X = CH_2, R' = ^{t}Bu

Fig. (11). [2+2] Macrocycles formed under microwave irradiation.

higher yields. Gawronski and coworkers reported the synthesis of rhomb-shaped tetraimine macrocycles formed in the reaction of *trans*-(1*R*,2*R*)-diaminocyclohexane with a bent aromatic dialdehydes having an ether linkage [34]. They named these macrocycles rhombimines based on the rhomboidal nature of the cross section of the macrocycle. Brunner and Schiessling synthesized [2+2] macrocycles derived from a chiral dialdehyde [35]. (*S*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl formed [2+2] macrocycles (**39**) and (**41**) with (1*R*,2*R*)-diaminocyclohexane and (1*R*,2*R*)-diphenylethylenediamine in good yields (Fig. (**10**)). The cyclocondensation was found to depend on the chirality of both the reacting components and hence, (*R*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl did not produce any cyclocondensation product with these chiral diamines. Lin *et al.*, synthesized similar chiral macrocycle by condensing (*S*)-3,3′-diformyl-2,2′-dihydroxy-1,1′-binaphthyl and *o*-phenylenediamine in quantitative yield [36, 37].

Li *et al.*, synthesized the corresponding tetramines by $NaBH_4$ reduction of macrocycles (**39**, **40**) and (**41**, **42**) and applied them for catalysis and fluorescent recognition studies [37]. [2+2] Macrocycles (**43**-**51**) of different ring sizes and different functionality possessing two N_2O_2 binding sites and free from other macrocycles were synthesized in moderate to good yields under microwave irradiation (Fig. (**11**)). The microwave reaction however works well for stabilized (H-bonding) imine and hydroxyaldehydes (salicylaldehydes) [22].

Gawronski and coworkers designed interesting macrocyclic structures utilizing the importance of predisposition of reactants (diamines) to form steric-free macrocyclic product in a reversible reaction [38]. A series of diamines (**52**) and (**53**) in which two diaminocyclohexane units were joined in such a way that the two connecting C-N bonds are colinear, were utilized for cyclocondensation. Both the diamines exist in two different conformations (*S* and *C* conformer, Fig. (**12**)) where disposition of two C-N bonds are either anti-parallel or projected at an angle of 60°. Cyclocondensation of terephthalaldehyde with diamine (**52**) unusually afforded [3+3] macrocycle whose NMR showed the presence of the *C*

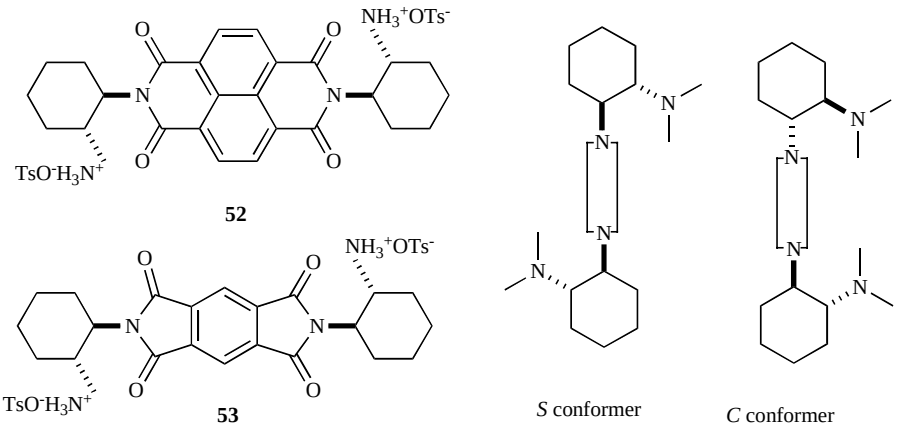


Fig. (12). Structure of conformers of diamines (**52**) and (**53**).

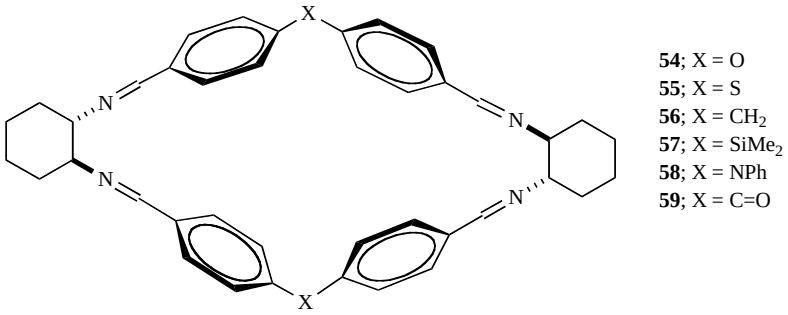


Fig. (13). [2+2] Macrocyclic rhombimines.

and *S* conformers in a 2:1 ratio. Theoretical calculation revealed that the lower energy structure of the molecule is loop-shaped (hence named as loopimines). Condensation of the isophthalaldehyde with diamines (**52**) and (**53**) as well as the condensation of terephthalaldehyde with (**53**) afforded [2+2] macrocycle of different ring sizes made of two *C* conformers of the diamine, in a rectangular shape (hence named rectanglimines).

Structurally predisposed aromatic dialdehydes with a bent structures connected by a one-atom bridge were used for the synthesis of [2+2] macrocycles with rhomboid shape (hence named rhombimines) (Fig. (**13**)). Different linkers were used to study the structural constraints for the macrocycle formation [39]. Accordingly, [2+2] macrocycles **54**-**59** were synthesized from the corresponding dialdehydes and *trans*-(*R*,*R*)-1,2-diaminocyclohexane. Experimental results and DFT calculations revealed that the dialdehydes with S, CH_2 and $SiMe_2$ bridges are more facile for the formation of rhombimine macrocyles. Less stable macrocycles are formed in the case of NPh and C=O bridges as a result of sp^2 hybridisation of the bridging atom.

Enantiomerically pure aliphatic dialdehyde, [7]-triangulane displayed match-mismatch effect upon reaction with enantiomers of *trans*-1,2-diaminocyclohexane. The (*R*, *R*) enantiomer however afforded the [2+2] macrocycle (**60**) in moderate yield (32 %) (Fig. (1**4**)). The X-ray diffraction studies of this stable and crystalline macrocycle indicated the molecule is cigar-shaped [24].

IV. CHIRAL [1+1] MACROCYCLIC SCHIFF BASES

Though there are many examples that describe the synthesis of [2+2] and [3+3] chiral macrocyclic Schiff bases,

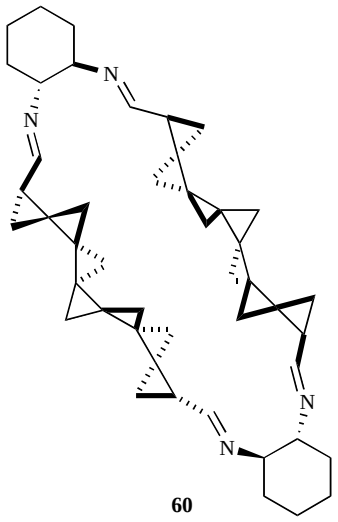
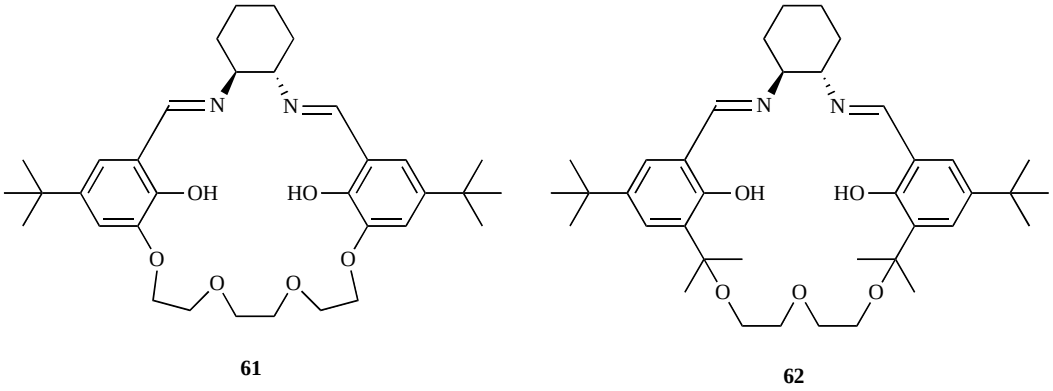


Fig. (14). [2+2] Macrocycle derived from [7]-triangulane.

there are only few papers involving the [1+1] macrocycles. The conformational bias offered by the dialdehydes forms a key factor in deciding the major macrocycle formed during the self condensation with chiral diamines. The dialdehyde therefore should adopt a conformation which favors the formation of [1+1] macrocycle over the higher order macrocycles. This requirement can be achieved by the use of dialdehydes containing a long tether between the aldehyde moieties. Martinez and coworkers utilized a dialdehyde containing long polyether tether for the construction of chiral [1+1] macrocycle (**61**) [40]. A second generation of the macrocycle (**62**) resembling Jacobsen's catalyst was synthesized by in-



61 **62**

Fig. (15). First (**61**) and second (**62**) generation [1+1] macrocyclic ligands.

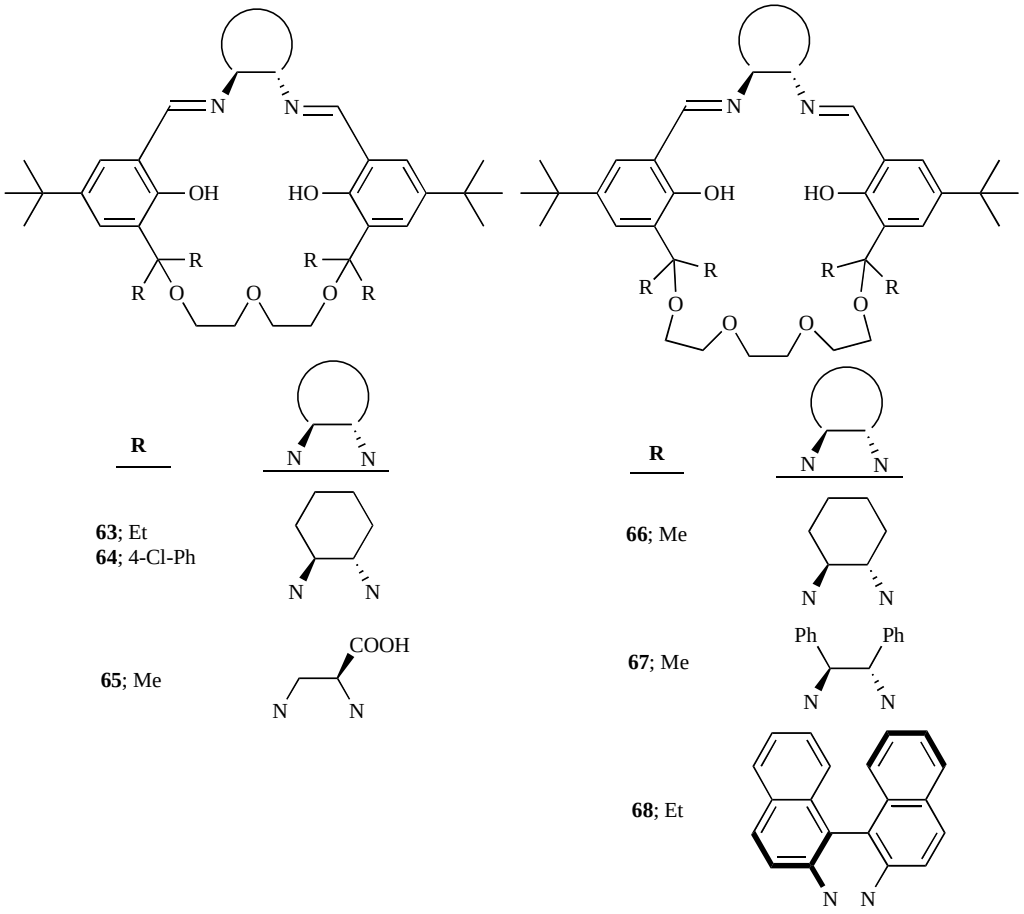


Fig. (16). Structures of [1+1] macrocycles of different ring sizes.

troducing methyl groups at the 3,3′-positions of the dialdehyde (Fig. (**15**)) [41].

The methodology was extended for the synthesis of a series of macrocycles (**63**-**68**) with different ring sizes and functionalized with different diamines and alkyl groups in good yields (Fig. (**16**)) [42].

A new type of chiral macrocyclic [1+1] ONNO-type ligand was synthesized by the interaction of 1,3-bis(2-formylphenoxy)-2-propanol with chiral 1,2-diaminocyclohexane (both enantiomers) and applied as ligands for enantioselective transfer hydrogenation [43]. [1+1] Chiral macrocyclic 'aza-crown' ethers of varying ring size were synthesized by a Schiff base condensation of ether linked dialdehydes of varying chain length and (1*R*,2*R*)-(–)-1,2-diaminocyclo-hexane under mild conditions, which are subsequently reduced to yield the diamino analogues [44]. Chiral tetraaza [1+1] macrocyclic nickel(II) and palladium(II) complexes, containing one or two (*R*,*R*)-(-)-1,2-cyclohexanediyl bridges, were also synthesized by template condensation reactions [45]. A series of new chiral [1+1] macrocyclic Schiff bases (**69**-**80**) have been synthesized in high yields and short reaction times from cyclocondensation of dialdehydes with long tethers and chiral diamines. The

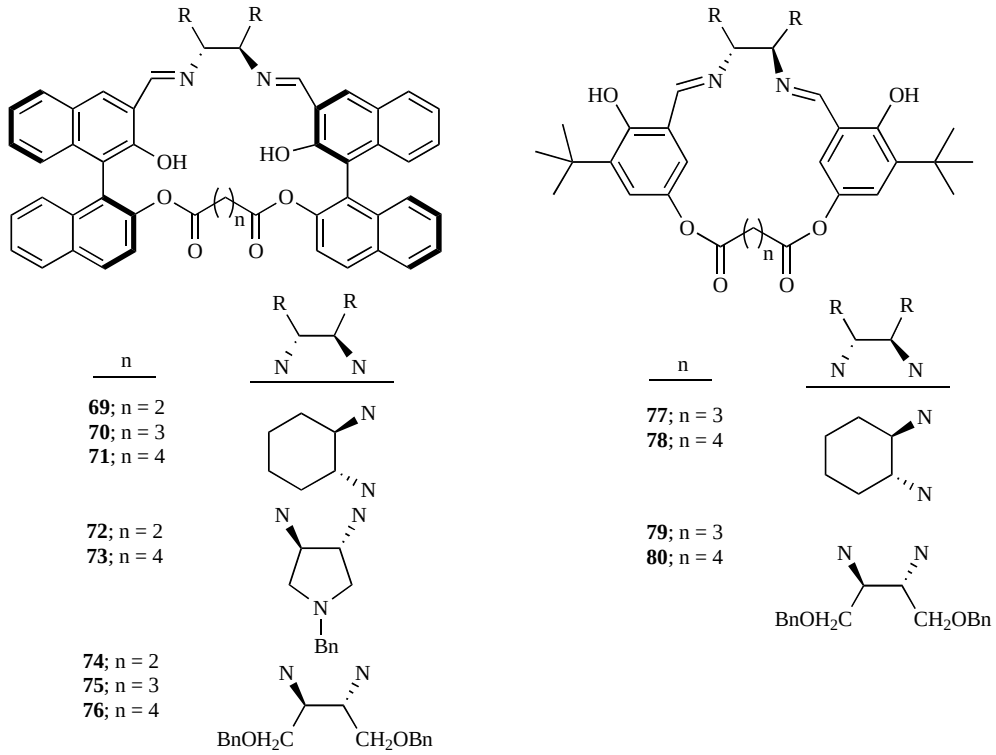


Fig. (17). Chiral [1+1] macrocyclic Schiff bases formed under microwave irradiation.

yields of the macrocycles were higher when the dialdehyde component is also chiral (**69**-**76**) (Fig. (**17**)) [46]. The macrocyclisation was performed under microwave irradiation and aqueous reaction conditions employing salts of the chiral diamine. BINOL based [1+1] macrocycle possessing a ether based tether was also prepared in good yield [47].

V. LARGE RING CHIRAL MACROCYCLIC SCHIFF BASES

Macrocyclic Schiff bases are formed under thermodynamic control and hence depending on the type of dialdehydes employed, the strategy can be extended for the synthesis of macrocycles with larger central cavities. However, chiral macrocyclic Schiff bases with a large central cavity formed by [3+3] cyclocondensation of long chain dialdehydes displayed poor solubility in organic solvents [48, 49]. The other strategy for the construction of large ring macrocycles involves a higher order [n+n] macrocyclisation. Though a few examples of chiral [4+4] macrocycles are known [50, 51, 52], there are no available reports on large ring chiral macrocyclic Schiff bases higher than [4+4] macrocycles. However, an appropriate choice of dialdehyde can provide a facile conformational bias for the construction of large ring macrocyclic Schiff bases. MacLachlan and coworkers reported the synthesis of achiral [6+6] macrocyclic Schiff bases using a series of dialdehydes of related structures [53]. These macrocycles however displayed limited solubility in common organic solvents. It was observed by us that 5,5'-bis-salicylaldehyde unusually formed [6+6] macrocycle (**81**) and (**82**) during condensation with chiral diamines [54] in good yields (Fig. (**18**)).

Both the [6+6] macrocycles displayed high solubility in common organic solvents ($CHCl_3$, DMSO, Acetone, EtOAc, etc.) facilitating their spectral characterization. NMR studies revealed that these macrocycles exist as a pair (1:1) of diastereoisomers as a result of restricted rotation of biphenyls and ESI-MS studies confirmed the absence of other small ring macrocycles during the reaction.

VI. CRYSTAL STRUCTURES OF MACROCYCLIC SCHIFF BASES

Apart from spectral characterization of the macrocycles, a few macrocycles have been characterized by their single-crystal X-ray structures. These macrocycles are expected to exhibit interesting structures due to their structural features like central cavity and multi-phenolic groups. Most of the macrocycles failed to form single crystals under a variety of crystallization conditions and in a few cases air stable crystals were obtained. Similarly, macrocycles with diamines other than *trans*-diaminocyclohexane failed to form stable crystals.

Gawronski *et al.*, reported that the reaction of *trans*-(1*R*,2*R*)-diaminocyclohexane and isophthaldehyde produced a [3+3] cyclocondensation product whose structure, according to spectroscopic data and molecular modelling studies, was vase-like [12]. In this structure the upper rim was formed by the imine-substituted benzene ring fragments and the cyclohexane rings whereas the lower rim was made up from methyl-substituted parts of the benzene rings. Applying molecular modeling studies (PM3 calculations) on [3+3] macrocycles derived from hydroxydialdehydes revealed that cyclic trimeric salens have vase-like structure, and hence are

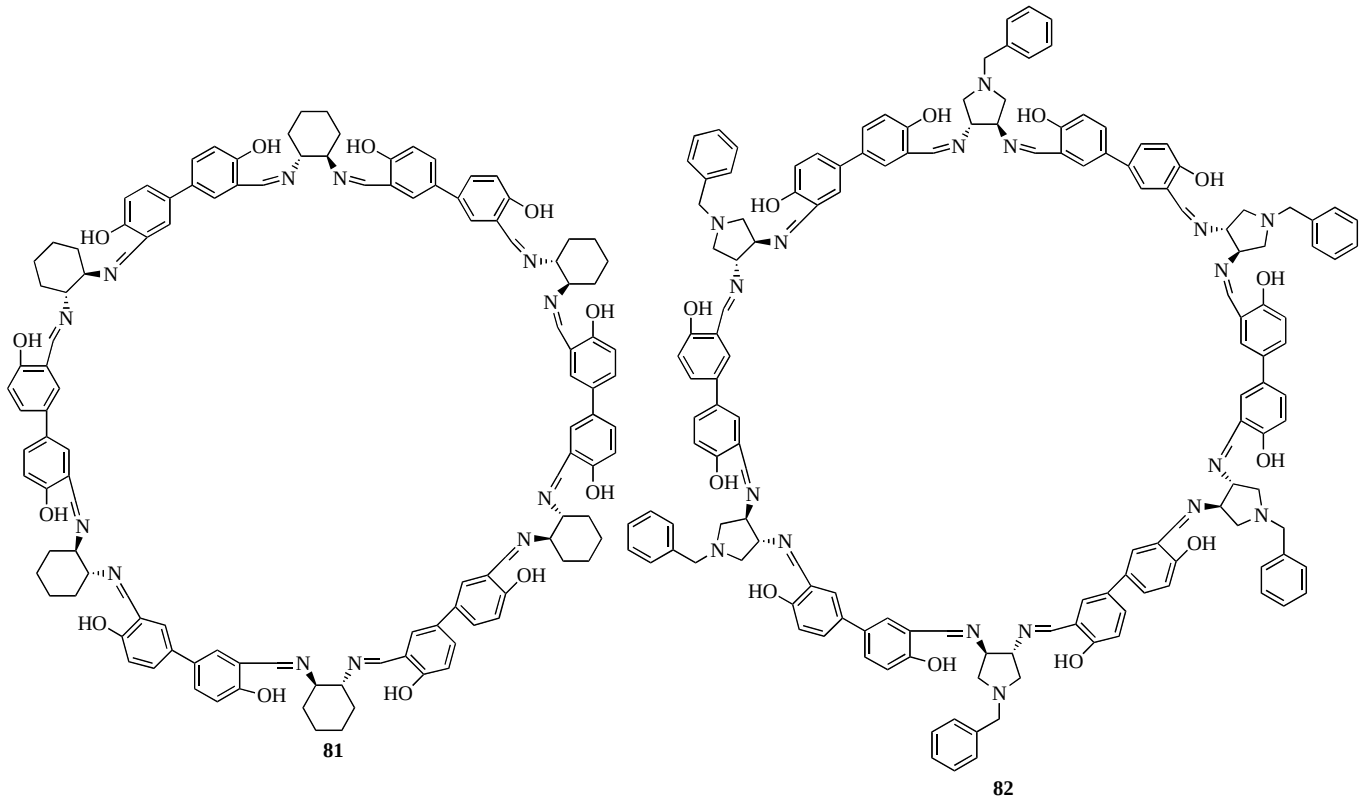


Fig. (18). Structures of 72-membered [6+6] chiral macrocyclic Schiff bases.

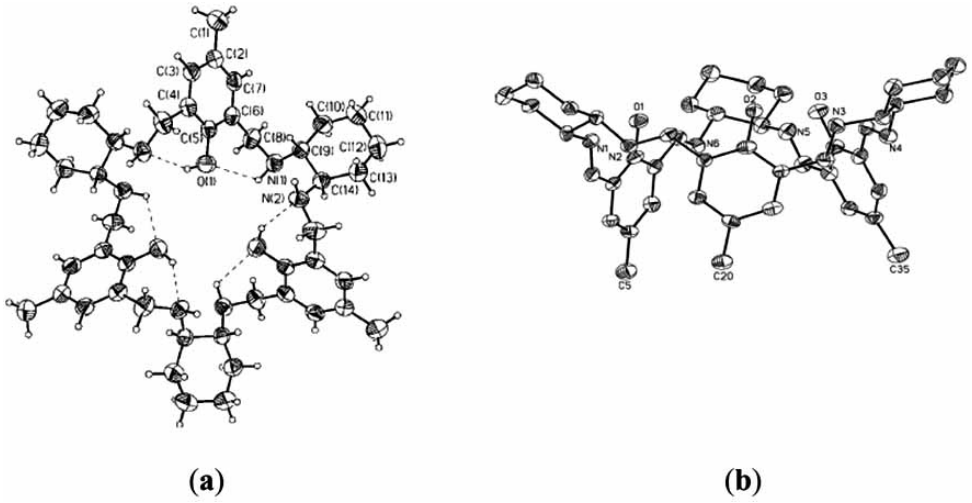


Fig. (19). Crystal structure of (a) hexamine (**2**) and (b) hexaimine (**1**) (cone conformation) derived from 2,6-diformyl-4-methylphenol.

described as calixsalens. As with calixarenes, the hydroxy groups in the calixsalen point in the direction of the upper rim, a remarkable feature that should be useful in future applications. Though the crystal structure of the hexaimine (**2**) is unknown, the crystal structure of the corresponding hexamine was earlier reported by Korupoju and Zacharias (Fig. (**19a**)) [54].

Later Paluch *et al.*, reported the crystal structure determination of [3+3] macrocycles derived from *trans*-(1*R*,2*R*)-diaminocyclohexane and 1,3-dialdehydes (crystal structure of **1**) [55]. The structure of (**1**) differs markedly from that of the amine analogue (Fig. (**19b**)). While the latter macrocycle of D_3 symmetry is relatively flat, and both cyclohexane and phenol rings are extended in one plane, (**1**) is of approximate C_3 symmetry and the aromatic rings form a cone-like cavity resembling calixarenes. The phenolic hydroxyl groups are positioned at the narrower rim of the cavity, while the methyl groups form the broader rim. In that respect the structure is different from the structure obtained from PM3 calculations that predicted a vase-shape molecule with methyl groups positioned on the narrower rim and smaller diameter of the cavity. The crystal structure of (**1**) confirms the predicted *S-trans* conformation of the diimine fragment. The crystal structure of hydroxy functionalised [3+3] macrocycle

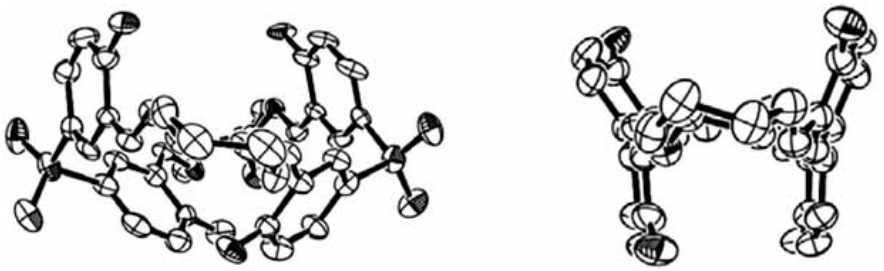


Fig. (20). Lateral view of [2+2] macrocycles (**45**) and (**46**).

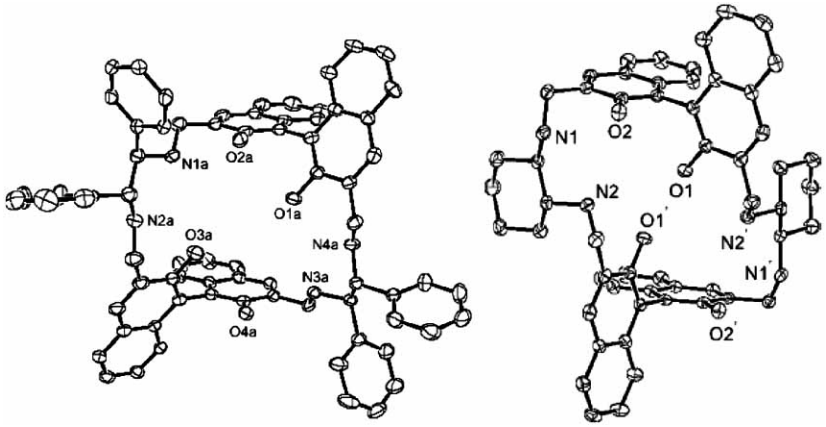


Fig. (21). ORTEP drawing of macrocycles ((*S*)-**41**) and ((*R*)-**39**).

derived from a 1,4-dialdehyde displayed a similar structural aspect as that of 1,3-dialdehydes discussed above.

Unlike trianglimines and trianglamines with aromatic spacers, trianglimines with aliphatic spacers (**22**) and (**23**) do not exhibit any inclusion properties [24]. Both the [3+3] macrocycles are very similar in shape and dimensions. Although very similar in molecular topology, the two trianglimines display very different crystal architectures. The molecules pack either in parallel layers or form a grid-like crystal. [3+3] macrocycle derived from 2,5-dihydroxy-terephthaldehyde is triangular in shape displaying strong intermolecular hydrogen bondings between hydroxy group of the macrocycle and the *N*-atom of the imines [22]. The crystal structure of the macrocycle also showed the presence of solvent molecules like CH_3CN (between the molecules) and ethanol (in the central cavity).

The crystal structure of [2+2] macrocycle (**29**) derived from bis(hydroxyaldehydes) was found to adopt a 1,3-dialternate conformation with a striking calixarene-like structure [30]. Structurally related [2+2] macrocycle (**45**) derived from 5,5′-disulfonyl-*bis*-salicylaldehyde displayed a strong intramolecular hydrogen bonding network [56]. However, no hydrogen bonding was observed from the oxygen atoms of the -SO_2- groups. There are one and half molecules in the crystallographic asymmetric unit with a C_2 space group and the two molecules are conformationally different.

The conformational difference can be seen by the presence of different S-S distances in the two molecules. For the ideally symmetric molecule, the dimensions of the cavity are 9.46 × 12.64 Å whereas for the other molecule the dimensions are 8.79 × 13.11 Å. Macrocycle (**46**) derived from 5,5′-bis-salicylaldehyde has an elongated structure with a central cavity dimension of 4.71 × 13.04 Å which was lesser than the macrocycle (**45**) with SO_2 spacer. The lateral view of both the [2+2] macrocycles (**46**) and (**46**) have a basket like structure with two alternate phenolic groups pointing in one direction while the other two phenolic groups directed towards the other direction. The overall conformation resembles the 1,3-alternate conformation of calixarene (Fig. (**20**)).

Two independent molecules of slightly different conformation were found to exist in the unit cell of the [2+2] macrocycle ((*S*)-**41**) [57] (one molecule was found in the case of cyclohexyldiamine derived ((*R*)-**39**) [47]) (Fig. (**21**)). The central cavity of the macrocycle is flanked on two opposite sides by almost exactly parallel naphthol moieties separated by 7.65 Å (8.13 Å in the case of ((*R*)-**39**)). The long axes of the two groups are mutually perpendicular. All of the O atoms of the naphthol units are on the same side of the macrocycle. The macrocyle rings are stabilized by intramolecular O-H···N bonds.

Similarly the crystal structure of the [2+2] macrocyclic tetraimines (**60**) crystallized as two independent molecules in the unit cell and consists of two helical chains composed of seven spiroannelated cyclopropane rings (*M* (minus) helicity) as the sides and cyclohexane fragments as the apexes (Fig. (**22a**)) [24]. The cigar shaped macrocycles are arranged in the crystal lattice in a double helical manner with a supramolecular helicity sense opposite to that of the individual macrocycles.

The crystal structure of manganese complex of [1+1] macrocycle (**60**) showed the presence of two identical molecules in the asymmetric unit (Fig. (**22b**)) [40]. The complex adopts a square-pyramidal geometry with the manganese center located only slightly above the basal plane (0.24 Å).

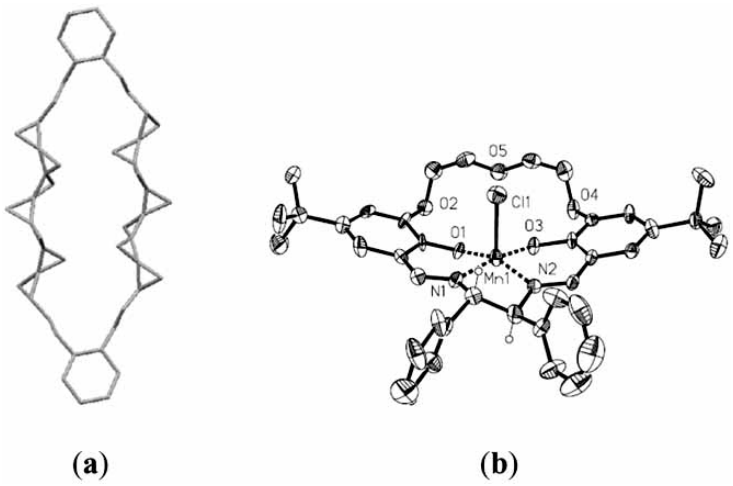


Fig. (22). Crystal structure of (a) [2+2] macrocycle (**60**) and (b) manganese complex of [1+1] macrocycle (**61**).

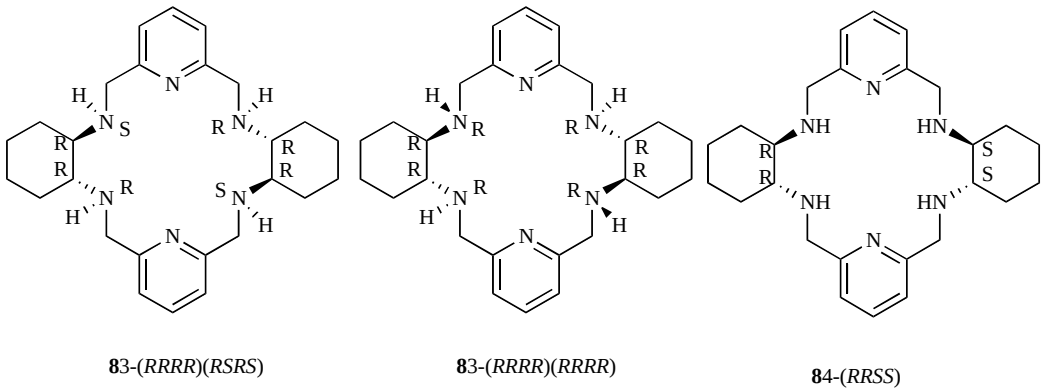


Fig. (23). Structures of the two isomers – chiral macrocycle (**83**) and *meso*-macrocycle (**84**).

Lanthanide(III) complexes of the enantiopure chiral hexaaza tetraamine macrocycle (**83**), as well as of its meso-type macrocycle (**84**), have been synthesized and characterized by spectroscopic methods (Fig. (**23**)) [58]. The complexes have C_2 symmetry in case of the [Ln**83**]$^{3+}$ and *Cs* symmetry in the case of [Ln**84**]$^{3+}$ complexes. The crystal structures of Pr, Dy, Yb and Eu complexes have been determined and for each type of complex, the conformation of the macrocycle and the axial ligation are different. The [Yb**83**]$^{3+}$ complex in particular exists in two stable forms corresponding to two diastereomers of ligand (**83**), which differ in the sense of the helical twist and the configuration at the stereogenic amine nitrogen atoms. In one of the stereoisomers, the macrocycle (**83**) of (*RRRR*) configuration at the stereogenic cyclohexane carbon atoms adopts the (*RSRS*) configuration at the amine nitrogen atoms, while in the other stereoisomer, the macrocycle (**83**) of (*RRRR*) configuration at the stereogenic cyclohexane carbon atoms adopts the (*SSSS*) configuration at the amine nitrogen atoms. The (*RRRR*)(*RSRS*) isomer is quantitatively converting to the (*RRRR*)(*SSSS*) isomer in water solution, while the reverse process is observed for an acetonitrile solution, thus representing the rare case of helicity inversion controlled by the solvent. Similar effects were also observed in the case of hexaimine macrocycles [59].

VII. APPLICATIONS OF CHIRAL MACROCYCLIC SCHIFF BASES

Korupoju *et al*., explored the second-order non-linear optical (NLO) properties of chiral Robson-type [2+2] macrocycle and its metal complexes [52]. It was observed that the complex exhibited modest efficiencies compared to that of the free macrocycle. Gao and Martell used various protonated forms of trianglamine (**7**) as a Lewis base catalyst for the asymmetric aldol reaction of 4-nitrobenzaldehyde and acetone [16]. It was observed that the enantioselectivities of the product increased with increasing deprotonation of hexabromide. However, addition of an excess amount of Et_3N after the total deprotonation did not change the enantioselectivity of the product. The result was explained as due to the strong basicity of the macrocyclic ligand and the stereoselection was considered to be controlled by a host-guest intercavity interaction. They also used the corresponding trimeric zinc complex to study the effect of Lewis acidity on the yield and enantioselectivity of the reaction. The trinuclear complex system displayed substantial improvements in enantioselectivity relative to the mono- and dinuclear analogues and the free ligand, with kinetic behavior consistent with cooperative reactivity within the macrocycle framework. Gao and Martell also explored the possible ap-

plication of [2+2] and [3+3] macrocyclic amines formed from *trans*-(1*R*,2*R*)-diamino-cyclohexane, 2,5-thiophenedicarboxaldehyde and $NaBH_4$ as ligands in asymmetric catalysis and molecular recognition. From various experiments conducted, it was observed that the tetramine [2+2] macrocycle and its tetra-alkylated [2+2] macrocycle showed strong selectivity towards Ag^+ ions among other metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Ca^{2+}). This strong selectivity for Ag^+ ions was attributed to the well-documented affinity for soft donors such as thioether sulfur. The [3+3] macrocyclic amine containing thiophene units was found to be an efficient catalyst over the [2+2] macrocycle in the presence of 3 eq. of $Zn(Et)_2$ for the asymmetric Henry (nitroaldol) reaction. The kinetic behavior coincided well with the cooperative reactivity within the macrocyclic framework.

Hong *et al*., obtained crystal structures of (*R*)-ferrocenyl-[3+3] macrocycle (**5**) by co-crystallisation with (*R*)-1,1′-binaphthol (BINOL) [17]. Such 1:1 co-crystals were not observed when (*R*)-ferrocenyl-[3+3] macrocycle (**5**) was co-crystallised with (*S*)-1,1′-binaphthol. They extended this enantioselective enclathration of the macrocycle for the optical resolution of racemic BINOL. In the presence of racemate, (*R*)-ferrocenyl-[3+3] macrocycle (**5**) selectively formed crystals only with (*R*)-BINOL and the enantioselectivity of the resolved BINOL was found to be over 99 % (HPLC analysis) in 86 % yield.

Hodacova and coworkers reported shape-complementarity in the recognition of tricarboxylic acids by [3+3] polyazacyclophane receptor (**7**) [60]. The interaction of isomeric tricarboxylic acids 1,3,5-benzenetricarboxylic acid (BTC), 1,2,4-BTC, 1,2,3-BTC and 1,3,5-benzenetriacetic acid (BTA) with trianglamine (**7**) was studied using potentiometry and NMR analysis. The isomer 1,3,5-BTC showed the highest interaction over the other isomers due to a perfect fitting between its shape and the macrocyclic structure. In the case of 1,3,5-BTA, the acid had to adopt a disposition in the cavity more distorted and cannot match as well the complementary binding sites of the receptors. In contrary, Gawronski and coworkers were not able to obtain any crystalline inclusion complexes by co-crystallization of (**7**) with numerous aromatic carboxylic acid guest molecules, including 1,3,5-BTC [21]. They concluded that the inner cavity of the trianglamine (**7**) was not large enough to accommodate any trisubstituted benzene derivatives.

Binuclear chiral macrocyclic Mn(III) calixsalen complexes were applied as dimeric variant of Jacobsen's catalyst for asymmetric epoxidation of unfunctionalised olefins [30]. In the case of epoxidation of styrene, the catalysts gave results comparable with that obtained with monomeric Jacobsen's catalyst. However, unlike monomeric catalysts, the enantioselectivity of the macrocyclic Mn(III) calixsalen systems were unrelated to the steric requirements of the R groups on the *ortho* position of phenol in the salen frame. It was therefore concluded that the observed enantioselectivity was controlled by the host-guest intercavity interactions. Manganese complexes derived from a variety of chiral [1+1] macrocyclic Schiff bases displayed enhanced reactivity and selectivity towards enantioselective epoxidation of prochiral olefins. It was found that the most efficient catalyst, in terms of stereoinduction (ee value, 96%), contains a diiminocyclohexyl moiety, ethyl groups in positions 3 and 3', and a short polyether junction arm [42].

Li and Pu observed a high enantioselective fluorescent enhancements of macrocyclic bisbinaphthyls in the presence of chiral α-hydroxycarboxylic acids and *N*-protected-α-amino acids [61]. In comparison to the acyclic analogues, the macrocycles showed greater enantioselectivity in the substrate recognition.

Recently, chiral Robson-type macrocyclic complexes of manganese and cobalt were successfully applied as catalysts for asymmetric cyclopropanation of styrene with diazoacetate. The binuclear Co(II) and Co(III) catalysts displayed cooperativity in the catalytic action with high degree of enantioselectivity [62]. Trianglamine **7** and similar [3+3] macrocycle derived from 4, 4′-diformylbiphenyl were reported as useful chiral shift reagents for determining of enantiomeric purity of different kinds of secondary alcohols, cyanohydrins and propargyl alcohols. It was found that the host forms a 1:1 inclusion complex with the former macrocyclic guest and a 2:1 complex with the latter one [63].

VIII. CONCLUSIONS

In conclusion, the review presents an overview of the reversible formation of different macrocyclic Schiff bases using various chiral macrocyclic derivatives of different ring sizes under metal-free conditions. This review also describes the formation of interesting self-assembled supramolecular structures of these multifunctionalised chiral macrocycles and their crystal structures. Furthermore, various applications of metallo complexes of these chiral macrocyclic Schiff bases have been reported.

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