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X-RAY STRUCTURAL STUDIES OF SUPRAMOLECULAR AND ORGANIC COMPOUNDS

BY

KARRI AIROLA

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Doctor of Philosophy

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In memory of my family of childhood,
Vieno, Ilmari and Heikki.
To my family of adulthood,
Terhi and Atso.

List of original publicaltions

This thesis is based on the following original publications, which are referred to in the text by their Roman numerals.

I Karri Airola, Stefan Bartram, Kari Rissanen, Helically Chiral Thia and Diselena Quinquephenylophanes, *J. Chem Soc. Perkin Trans. 1*, **1995** 895-899. https://doi.org/10.1039/P19950000895

II Thierry Gefflaut, Udo Bauer, Karri Airola, Ari M.P. Koskinen, Asymmetric 1,3-Dipolar Cycloaddition: Synthesis of N-protected (4S)-4-Hydroxy L-Glutamic Acid Ester, *Tetrahedron: Asymmetry*, **7** (1996) 3099-3102. https://doi.org/10.1016/0957-4166(96)00407-7

III Ralf Ehlenz, Karl-Heinz Dötz, Martin Nieger, Karri Airola, Sugar Acyl Iron Complexes: Synthesis and Conformational Studies in Solution and in the Solution State, *J. Carbohydrate Chem.*, **16** (1997) 1305-1318. https://doi.org/10.1080/07328309708005751

IV Karl-Heinz Dötz, Ralf Ehlenz, Wolfgang, Straub, J.C. Weber, Martin Nieger and Karri Airola, Organotransition Metal Modified Sugars 4: Carbene Complex Functionalized Acyclic Carbohydrates, *J. Organometal. Chem.*, **548** (1997) 91-98. https://doi.org/10.1016/S0022-328X(97)00335-5

V Karri Airola, Jari Ratilainen, Tommi Nyrönen, Kari Rissanen, A Linear Open-Chain Piperazine–pyridine Ligand and its *meso*-helical Co complex, *Inorg. Chim. Acta*, **277** (1998) 55-60. https://doi.org/10.1016/S0020-1693(97)06122-7

VI Hanadi Sleiman, Paul Baxter, Kari Rissanen, Karri Airola, Jean-Marie Lehn, Multicomponent Self-Assembly: The Construction of Rigid–Rack Multimetallic Complexes of Rotaxane-Type, *Inorg. Chem.*, **36** (1997) 4734-4742. https://doi.org/10.1021/ic9702227

VII Fritz Vögtle, Ingo Michel, Ralf Berscheid, Martin Nieger, Kari Rissanen, Sirpa Kotila, Karri Airola, Nicola Armaroli, Mauro Maestri,Vincenzo Balzani, Concave Macrobicycles: Absorption Spectra, Luminescence Properties and Endocavital Complexation of Neutral Organic Guests, *Liebigs Ann./Recueil,* **1996** 1697-1704. https://doi.org/10.1002/jlac.199619961102

VIII Karri Airola, Volker Böhmer, Erich Paulus, Kari Rissanen, Christian Schmidt, Iris Thondorf, Walter Vogt, Selective Derivatisation of Resorcarenes: 1. The Regioselective Formation of Tetra-Benzoxazine Derivatives, *Tetrahedron*, **53** (1997) 10709-10724. https://doi.org/10.1016/S0040-4020(97)00685-6

IX Christian Schmidt, Karri Airola, Volker Böhmer, Walter Vogt, Kari Rissanen, Selective Derivatisations of Resorcarenes: 3. Multiple Regioselective Ring Closure Reactions, *Tetrahedron*, **53** (1997) 17691-17698. https://doi.org/10.1016/S0040-4020(97)10236-8

PREFACE

The present study was carried out between the years 1993 and 1997 at the University of Joensuu, the University of Jyväskylä and at the Friedrich-Wilhelm University of Bonn.

First of all, I wish to express my deepest thanks to my supervisor, Professor Kari Rissanen, for providing years encouragement and continuous support in addition to the scientific network. I am also grateful to Professor Jussi Valkonen, head of the Inorganic and Analytical Chemistry Laboratory, for support in the field of crystallography.

For giving me the opportunity to learn about structurally interesting chemical phenomena I wish to thank the following Professors: Professor Jean-Marie Lehn at the University of Louis Pasteur, Strasbourg, France; Professor Fritz Vögtle at the University of Bonn; Professor Volker Böhmer at the University of Mainz, Professor Karl-Heinz Dötz at the University of Bonn, Germany; and Professor Ari Koskinen at the University of Oulu, Finland.

Most of all, I wish to express my deepest gratitude to my tutor, friend and colleague Docent Martin Nieger, University of Bonn, for the good and patient guidance he has provided through the years. I wish I could have had the opportunity to profit more of his advice.

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My special thanks go to following persons who have contributed to the work: Docent Roland Fröhlich, University of Münster; Docent Erkki Kolehmainen, University of Jyväskylä; Doctor Jari Ratilainen, University of Kuopio and Docent Salme Koskimies, my present superior, for the opportunity to complete this work. I wish to thank Michael Peacock for his careful revision of the language of this study.

The financial support of the Graduate School of Bio-organic Chemistry, the Finnish Academy, and the Neste foundation is gratefully acknowledged.

ABSTRACT

Altogether fourteen different organic, organometallic, metalloorganic and supramolecular structures, determined by X-ray crystallography, are reported on. The structures described in the study represent various crystallographic and structural problems such as the refinement of large data sets and interpretation of intra- and intermolecular interactions.

The structures studied in this work are divided into four classes. Firstly, pure organic compounds (original publications I-II, 3 structures), which typically contained some special topological or chiralilty problems to be solved. Secondly, organometallic sugar derivatives (publications III-IV, 4 structures). Thirdly, metal–containing organic or supramolecular compounds, in which the molecular design is partly utilised to generate selective binding (V-VI, 3 structures). In some of these complexes, helicity based on topology is created. The fourth class consists of supramolecular inclusion compounds which are mainly host-guest complexes, in which the neutral guests are encapsulated by host compounds with a specific topology and chemical interior (VII-IX, 4 structures). The encapsulation may be an accidental inclusion of the solvent molecules or a desired inclusion of guest molecules with matching shape and functionality.

Special attention is paid to the interpretation of non-covalent bonding patterns, the weak intra- and intermolecular forces that determine the behaviour of parent molecules in their ambient media. Solid state structures play a key role in demonstrations and predictions of molecular and supramolecular interactions. In publications I, III, VI, VIII and IX the multinuclear NMR was also used to interpret the conformations in solution.

The work shows the importance of molecular interactions in generating topological or regioisomers, and in generation of solid state clathrates. A short review of the literature on the terminology of supramolecular crystallography and in general supramolecular chemistry is presented in the Introduction.

CONTENTS

1. INTRODUCTION

1.1 Supramolecular chemistry

Supramolecular chemistry as a branch of chemistry is a relatively young area of science. The first findings, by Pedersen and Lehn in the late 60's, on the ability of crown ethers and cryptands to bind alkali metals, established the basis for the field of research.[1-2] The roots of supramolecular chemistry extend to organic chemistry and its synthetic procedures nowadays cover techniques in molecular construction, the coordination chemistry of ligands, and theoretical studies of molecular interactions.[3]

To make a difference between organic molecules and supramolecules one has to look at bonding in organic and supramolecular compounds. The elements in organic molecules are bound by covalent bond. In supramolecular compounds, actions such as self-organisation or supramolecular arrangement follow from weak bonding that defines the shape and the functions of supramolecular aggregates.[4]

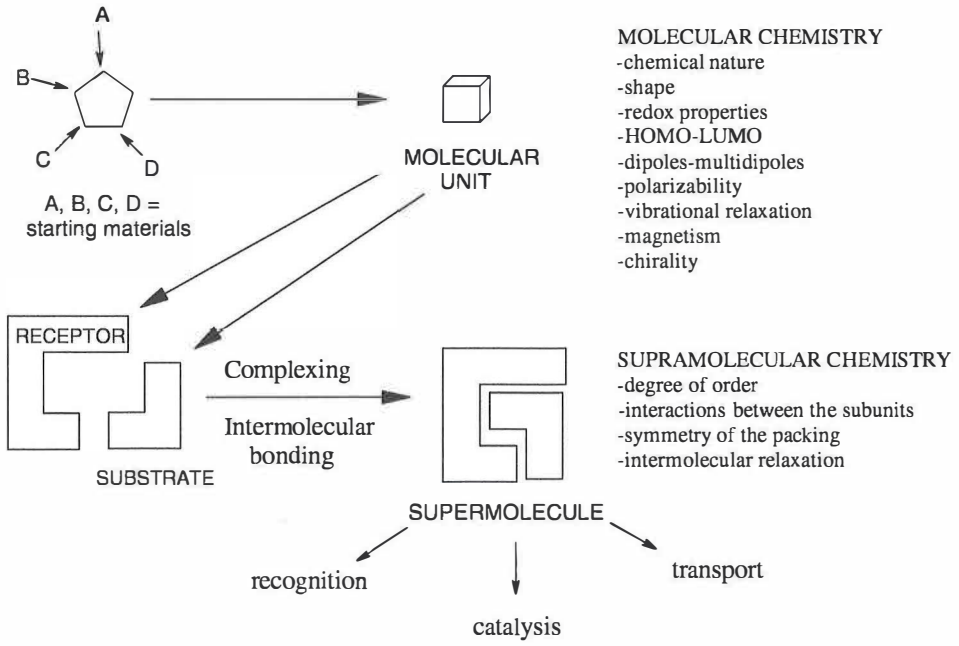


Figure 1. A general presentation of the relationships between supramolecular and molecular chemistry.[5]

Supramolecular chemistry is considered to be a chemistry of molecular assemblies and of the intermolecular bond, since much of the nature of supramolecular species is determined by non-covalent interactions.[6] These interactions, such as hydrogen bonding and π-stacking, play a dominating role when the supramolecular counterparts are formed into a supramolecular assembly. To synthetise these molecular subunits one can selectively use a large number of reactions and tools, such as the template effect, or self-organisation, to reduce the number of synthesis steps.[7] Nowadays, certain covalently assembled complexes, such as exotic metal-ligand systems, are also categorised as supramolecular chemistry.[8]

The goals in supramolecular chemistry are often to gain control over the intermolecular bond.[9] Simplified, supramolecular chemistry mimics the phenomena that typically take place in natural supramolecules, enzymes.

1.2 Concepts in structural supramolecular chemistry

1.2.1. Host-Guest chemistry

A descriptive term, host-guest chemistry, brings together the importance of the shapes of the molecules and the coordination processes which follow from special shapes. Generally, host-guest chemistry covers all types of molecular interactions that follow from structural parameters; but more specifically it is concerned with inclusion compounds.[5] The formation of a host-guest complex requires molecular recognition,[10] a targeted construction of supramolecular complexes with variable sites for interactions arranged in conformationally defined ways.[11] Although supramolecular chemistry covers phenomena such as arrangement into liquid crystals,[12] in this work the focus is on the covalently and non-covalently bonded host and guest molecules.

Host molecules may represent various shapes: open, half open and closed hosts;[11] and they may bond to various types of molecules: cationic, anionic and neutral guests.[13]

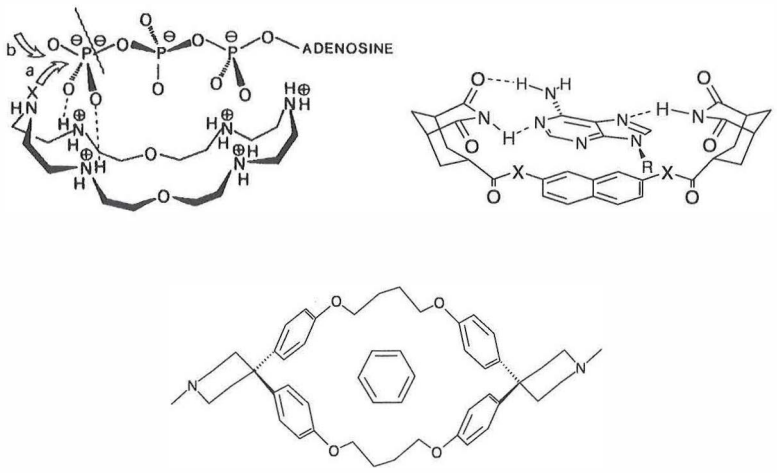


Figure 2. Examples of host-guest complexes. Top left: an open host binding an anionic guest.[14] Top right: a half-open cleft binding a neutral guest.[15] Below: a closed host binding a neutral guest (benzene molecule).[16]

In addition to the intramolecular encapsulation of a guest molecule, an intermolecular incorporation, a clathrate formation, may also take place.[17] The guest molecules are either incorporated into existing intermolecular cavities or they may induce, on crystallisation, structures of the host lattice with guest-specific spaces.[18]

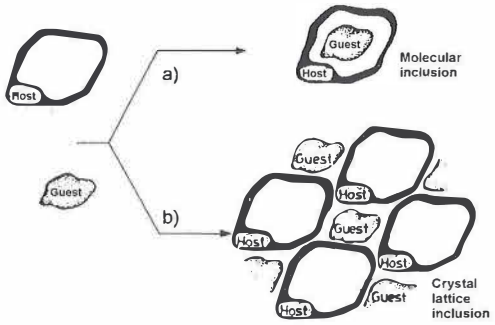


Figure 3. Alternative routes to inclusion complexes. a) intramolecular encapsulation to a Host-Guest compound. b) intermolecular encapsulation to a traditional clathrate.[18]

1.2.2. Self-organisation and template-effect

The aim in supramolecular design is to affect molecular structure, including specific binding sites. From the complementarity of molecular components arises recognition-induced spontaneous assembly to a supermolecule, self-organisation.[9]

The tendency of covalently bonding ligand to wrap around metal cations may be utilised in the design of helically–twisting ligands[19] and looping molecular strands,[20] and in other fascinating molecular arrays.[21] The application of the template effect is particularly versatile in catenane synthesis.[22]

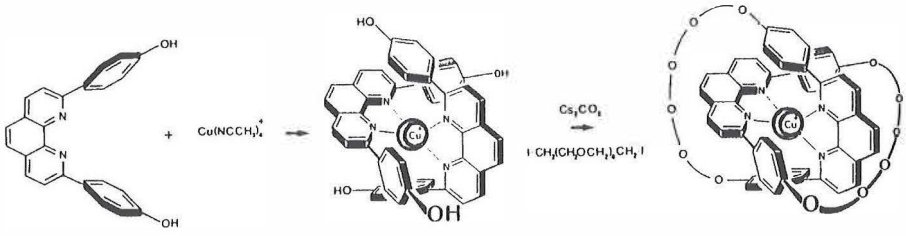


Figure 4. An example of template–aided catenane synthesis. Copper(I) ion assists the formation of a catenane.[22]

1.2.3. Conformational isomerism and topological chirality

In supramolecular structures, the Euclidian geometry that provides the basis for normal streochemistry is often insufficient to make differentiation between isomers. The concept of topology comes from mathematics. The molecules may be homomorphic, but bonding directs compounds to adopt different overall conformations.[23] At its simplest, a topological difference between conformational isomers may be helicity caused by substantial twisting of structural elements, as in multi-layered cyclophanes.[24] Another example is the regioisomorphism of calixarene–type compounds (see figure 5). The conformers may be interconvertible in solution, but when the temperature of solution is decreased in dynamic NMR experiment, different conformers are observed.[25]

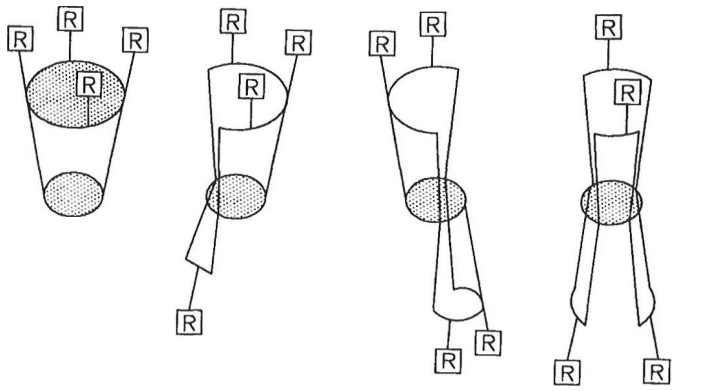


Figure 5. The conformational isomers of calix[4]arene. [26]

1.3 Crystallography in supramolecular chemistry

Despite of advanced molecular modeling tools and NMR-methods employing new and highly sophisticated pulsing techniques, which make it possible to study conformations in solution, these techniques can still not provide very detailed structural information. "A space-averaged photograph of a molecule" can only be obtained by X-ray crystallography. The crystallisation techniques which have been developed, used in conjugation with efficient data collection methods make possible the use of X-ray diffraction to resolve complicated structural problems. The criteria for the crystals have been brought down and the data quality improved by new techniques like improved radiation sources and area detectors.[27]

Crystallography in supramolecular chemistry for the most part faces the same challenges as in all its other application areas. The major difficulties arise from crystallisation, quality of crystal, quality of data set, structure solution and quality of result.[28] In supramolecular chemistry the most important element is the interpretation of results; finding the molecular interactions that determine the various structures.

Crystals are made up of molecules (receptor or substrate types), solvent (either encapsulated or clathrate type) and ions. The formation of crystals from molecules can be desrcibed in terms of two "non-crystallographic" levels of organisation. At the first level of organisation, atoms are connected to form a molecule which is a structurally asymmetric element. The second level of organisation reproduces the molecule, solvents and ions in three dimensions by means of symmetry operations.[29] The building–blocks of crystals are held together by non-covalent interactions which are: electrostatic interactions through hydrogen bonding, aromatic stacking, dipole-aromatic interactions, and hydrophilic interactions.[30] By studying these interactions and making estimations from the strength of interactions one can make progress in interpreting the diverse weak forces which direct the crystallisation of supramolecules.[31]

In the case of resolved topological enantiomers or simply chiral compounds like natural products, the assignment of right symmetry, *i.e.* the determination of absolute configuration, gives evidence as to the possible stereoselectivity in reactions and as to the spontaneous or induced resolution of enantiomers. Crystallographic literature describes several ways to determine absolute configuration based on the anomalous scattering of the reflections.[32] Today the most general method is a refinement of Flack's parameter. [33-34]

2. EXPERIMENTAL

In the experimental section the major results, and the findings which are responsible for the conclusions drawn with regard to crystallography and the associated structural problems are set down. Particular weight is given to those structures in the resolution of which the authors' own contribution is significant. The details of the synthetic and X-ray work are shown in the individual publications.

2.1 Aims of this work

The interactions that take place in molecular systems are several: e.g. selective metal cation complexation by designed ligands, weak interactions between supramolecular hosts and guests. Some of the interactions can be studied in solution, but detailed information about the structures, and supramolecular and organic compounds, are obtained from solid–state X-ray structures. The aim of the study was in part to prepare organic and supramolecular complexes; but more importantly to study their structures by means of X-ray crystallography.

In this work the detailed knowledge about structures was used to help the synthetic work, so that the molecules would, in addition to their tailored functions, be suitable to be solved as solid state structures too. For example, the ligands were modified so that they would prefer only one type of complexation and so provide uniform good quality crystals for crystallography. The detailed structural data available on solid–state structures was then used to design better and more selective target molecules. Of course, these methods may not always work, and the usual challenge in crystallography, to be able to solve and refine a difficult structure, remains.

2.2 Types of structures

The structures examined in this study may be divided into four classes of compounds:

1) Organic compounds (original publications I-II).

Compounds where there are no special intaractions between the molecules except for some very weak interactions through crystallographic packing. Yet the compounds in this class may provide a number of special topological or chiralilty problems to be solved.

2) Organometallic compounds (III-IV).

Organometallic complexes of sugar derivatives. The sugar backbones are affected by acetoxy substitutions and carbene complexes. The solved structures represent pure enantiomers in which the chirality is known from the starting materials.

3) Metalloorganic supramolecular compounds. (V-VI)

Supramolecular ligands that bind metal cations (typically transition metals) in unexpected or in designed fashion to form a metalloorganic complex. Bonding is covalent, and the bonding patterns may also be used for template synthesis.

4) Supramolecular inclusion compounds. (VII-IX)

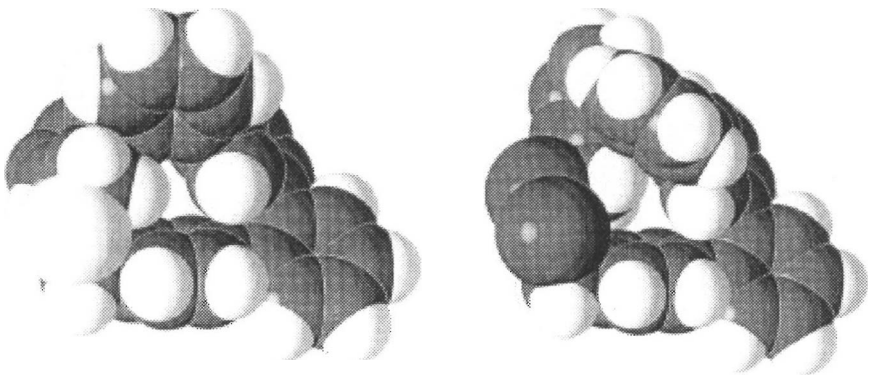
Host guest complexes, in which neutral guests are encapsulated by the host compounds having a specific topology and chemical interior for forming a supramolecule. The encapsulation may be either an accidental inclusion of solvent molecules or a designed inclusion of molecules with matching shape or functionality.

2.3 Structural studies

2.3.1 Helically chiral quinquephenylophanes[I]

Quinquephenylophanes **1** and **2** represent compounds in which the topological conformation causes chirality. In the synthesis the compounds are received as racemic mixtures but the chiral separation may be used to separate topological enantiomers.[35] In this study the compounds were designed to have a heavy atom (sulphur or selenium) to facilitate the determination of the absolute configuration of **1** and **2**.[I]

The eight-step synthesis path led to the target compounds thiaquinquephenylophane **1** and diselenaquiquephenylophane **2**.[I] As it is seen from the crystal stuctures of the phanes (figure 6), the compounds are very strained. Inverting the helicity of the enantiomers would require crossing a substantial energy barrier. The barriers in similar types of stucture have been calculated by Vögtle *et al* to be of such a magnitude that the interconversion between the enantiomers does not take place at room temperature.[36 37] The *P* (+) and *M* (-) isomers were separated with a chiral HPLC column ((+)-poly-triphenylmethacrylate resin),[35] and the CD-spectra of pure enationmers substantiated the existence of enantiomers of the same helically chiral molecule. Crystallization of the resolved enantiomers was also attempted, but in spite of the good success obtained with racemic crystals, the enantiomers did not form single crystals and thus the correlation between the absolute configuration and the corresponding CD-spectrum was left unresolved.



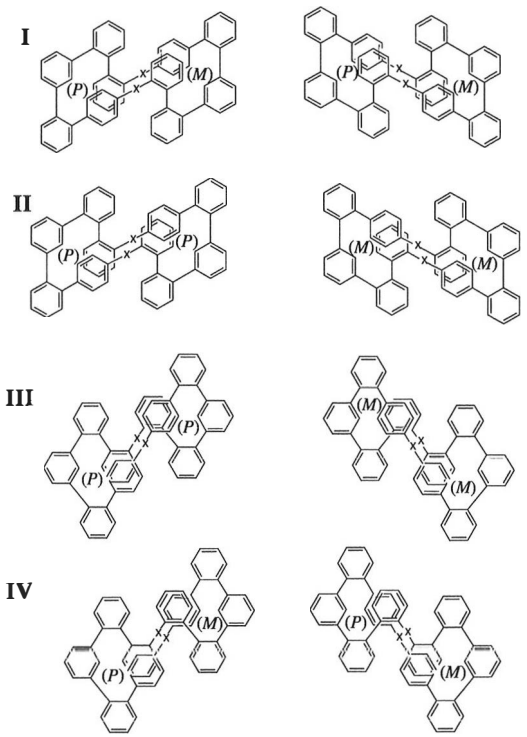
1 **2**

Figure 6. Crystal structures of thia- and diselenaquinquephenylophanes.[I]

Usually high-dilution reactions produce cyclic compounds of various sizes, depending on the molecular structure.[38] Separation and NMR-analysis of larger cycles, primarily the dimerics of the reacting components, revealed some interesting features. Usually the larger cycles are identified from the molecular peaks in FAB-MS or MALDI-TOF spectra, but they are not further characterized even if separated.[38] In this case the purification of fraction containing dimeric cycles offered the opportunity to study different diastereomers. Since the building block, bis(bromomethyl)quinquephenyl,[39] is

prehelical,[40] the number of possible dimeric enantiomers is a result of connective terminal coupling (*ortho* or *para*) and the prehelicity (*P* or *M*). Thus the number of diastereomeric pairs is four, two of the pairs being *meso*-helical (*P* or *M* and *o-p* coupled) and the other two pairs being enantiopairs (Scheme 1).

NMR cannot distinguish between the enatiomers, but the structural differences in diastereomers can cause variation in chemical shifts. In proton or carbon spectra the probable multiple overlapping signals cannot be interpreted, but in the case of the diselena compounds the NMR-active nucleus ^{77}Se could be used, since ^{77}Se-shifts are sensitive tochanges in the chemical environment.[41] And indeed, the number of Se-signals (1+1+2+2) match to the expected number of diastereomers. The mesohelical forms are responsible for two of the signals, and the two diastereopairs for the remaining four signals.



Scheme 1. The four possible diastereomeric pairs of selena–bridged coupled quinquephenyls. I: *o-p*, *o-p* coupled with different helicity of moieties; II: *o-p*, *o-p* coupled with same helicity of moieties; III: *p-p*, *o-o* coupled with same helicities; IV: *p-p*, *o-o* coupled with different helicities.

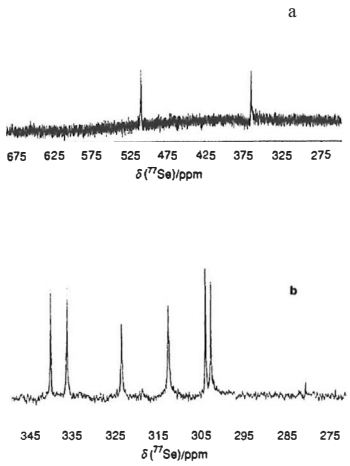
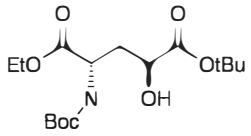


Figure 7. ^{77}Se spectra of quinquephenyl cycles. a) The spectrum of diselenaquinquephenylophane. b) Dimeric monoselena bridged quinquephenylophanes.[I]

2.3.2. Synthesis and structure of *N*-protected amino acid ester

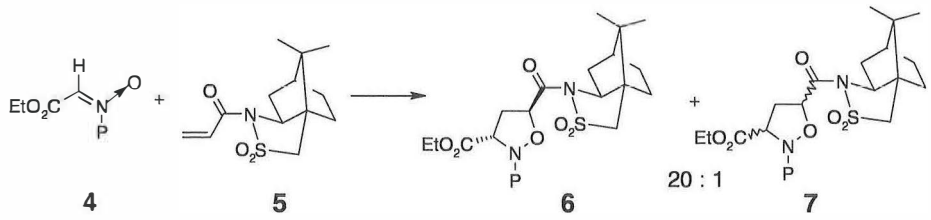
The crystal structure of a chiral N-protected (4*S*)-4-hydroxy L-glutamic acid diester confirms the result of the asymmetric synthesis. Isoxazoline ring formation proceeds stereoselectively with a suitable stereochemistry for the synthesis of N-protected (4*S*)-4-hydroxy L-glutamic acid diester **3**.[II]



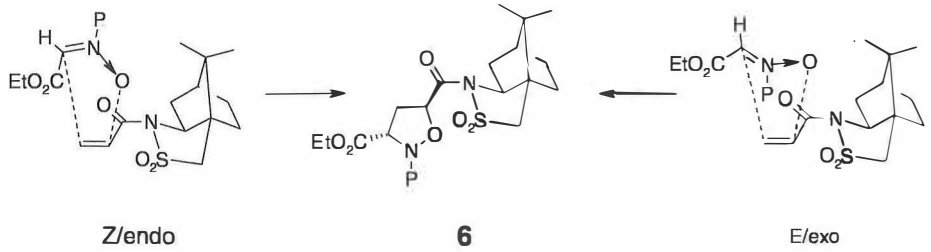
3

In the synthesis of enantiopure *N*-protected γ hydroxy L-glutamic acid diester **3**, an isoxazoline intermediate with suitable stereochemistry is needed.[42-46] A key feature in the synthetic work is the asymmetric 1,3-dipolar cycloaddition of nitrone **4** with acrylamide **5** derived from Oppolzer's chiral sultam. Because of the rigidity of the bicyclic framework of **5**, and consequent stereofacial discrimination in the transition states (scheme 3), the cycloaddition gives in practice a single diastereomer **6**.[47-48] The major diastereomer **6** was isolated in 82 % yield. The right strereochemistry of **6** was estabilised by X-ray crystallography; refining the complete data set required for the

determination of absolute configuration. The refinement of the Flack's parameter to 0.01 with good e.s.d. (0.05) ensures confidence as to the absolute configuration achived. From the X-ray structure the newly–generated C-3 and C-5 stereogenic centers of the isoxazolidine were both determined as *S* (figure 8).



Scheme 2. The reaction of sultam **5** with nitrone **4** to an isoxazoline derivative **6**.



Scheme 3. Diastereotopic transition states to **6**.

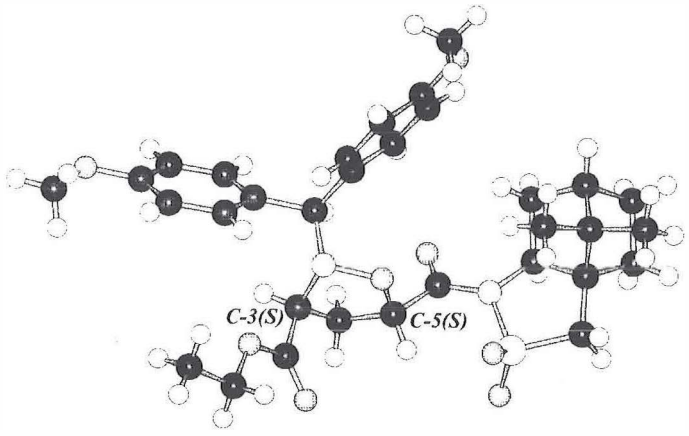
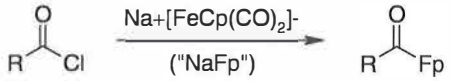


Figure 8. Crystal structure of *N*-protected intermediate **6**. Chiral centers labelled.

2.3.3 Sugar acyl Iron and Chromium carbene Complexes [III, IV]

Different acyclic sugar derivatives, namely acid chlorides of acetylated D-galactonic acid, D-gluconic acid, L-arabic acid and D-ribonic acid, were treated with a strong nucleophile. The addition of dicarbonyl cyclopentadienyl ferrate (NaFp) to acid chlorides is known to generate acyl iron compounds, which generally undergo alkylation by hard electrophiles to give cationic alkoxy iron carbenes (scheme 4).[49] Corresponding chromium compounds are received by reacting carbonyl chromates with sugar acid chlorides.[50]



Scheme 4. Synthesis of acyl iron complexes.[50]

The conformational changes caused by a bulky organometallic fragment at the C-1 terminus, were studied in solution and solid states. Generally acyclic sugars prefer a planar zigzag conformation unless *syn*-1,3-interactions enforce rotation of one or more C-C bonds to generate bent conformation.[51]

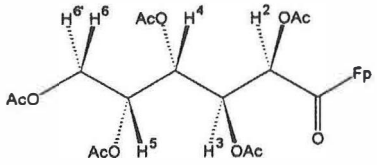


Figure 9. A planar conformation of D-galacto complex **8** in solution.[III]

NMR may be used in conformational studies in the solution state, since the vicinal coupling constants differ with *cis* and *trans* conformations. The NMR-study shows that the solution structure of the galactose compound **8** remains planar even at room temperature. Only the terminal (C-6) is easily switchable, indicated by the medium-sized coupling constant of $J_{5,6}$. The other coupling constants are in favour of the altering *cis-trans-cis* conformation from C-2 to C-5.[52] Comparative coupling constants are observed with the chromium compound **9** and with the methylated D-galacto acid **10**. In

the D-gluco compound **11** the planar zigzag structure would bring the 1,3-acetoyl substitutes too near to each other. This is avoided by rotating either C-2/C-3 or C-3/C-4 torsion (figure 10). This is observed as the medium-sized coupling constants of C-3 to C-5 protons. The low–temperature spectrum shows that the more favourable rotation is around C-3/C-4 torsion (table 1).

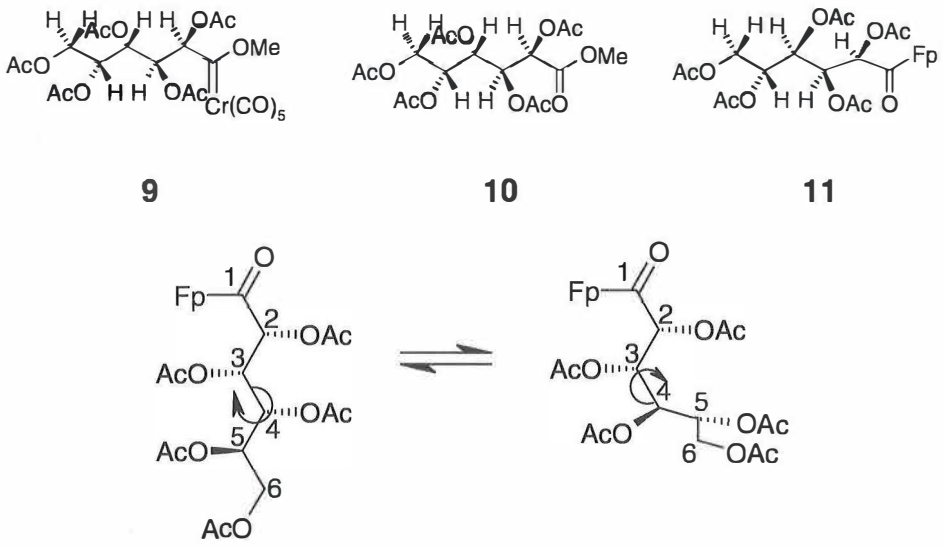
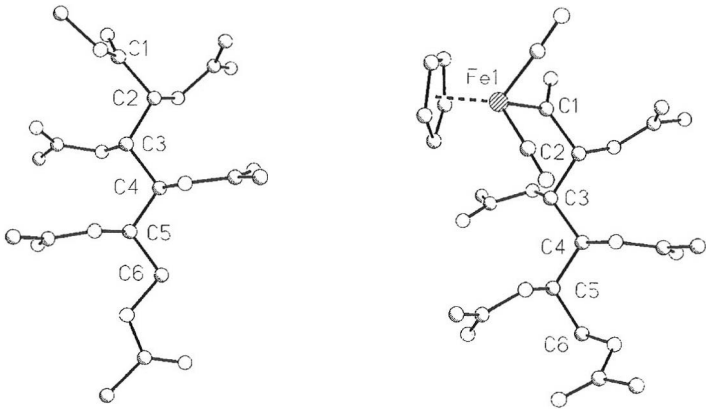


Figure 10. Conformational states of D-gluconic acid derivative **11**.

Table 1. Vicinal coupling constants of D-galacto compounds **8**, **9**, **10** and D-gluco compound **11** at variable temperatures.

sugar	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	conformation
D-galacto iron **8**	1.6	9.7	2.1	5.2	7.2	planar
D-galacto iron **8** (-50°C)	1.4	10.1	1.7	4.7	7.8	"
D-galacto chromium **9**	n.d.	10.2	n.d.	4.5	8.3	planar
D-galacto methyl **10**	1.6	10.1	1.9	5.2	7.4	planar
D-gluco iron **11**	3.5	5.4	6.0	3.2	6.3	rotated
D-gluco iron **11** (-50°C)	1.6	6.5	5.1	2.2	7.2	"



10 **8**

Figure 11. X-ray structures of D-galactonic acid derivatives **10** and **8** compared along the sugar backbone.

As depicted from solution state conformational studies, in solid state the galactose iron complex **8** as well as the ester derivative **10** adopt the planar conformation (figure 11). The precise stuctural information obtained from the X-ray structure shows that the sugar backbone of **8** is bent 20° from the ideal (180°) planar zigzag conformation along the C-3/C-4 axis because of the bulky Fp-substitute.

The solid–state structure of D-gluconic iron complex **11** presents a switched structure in which the torsion angle (C2)C3-C4(C5) is rotated (figure 12). The flexible C5-C6 axis is set to a 55° torsion angle to minimize the distortions of protecting groups at C5 and C6.

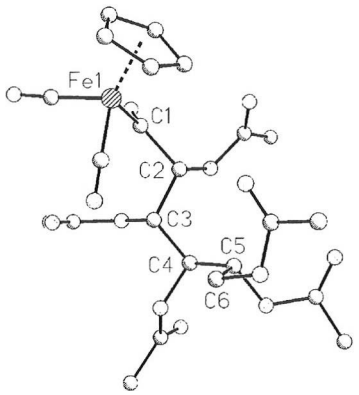


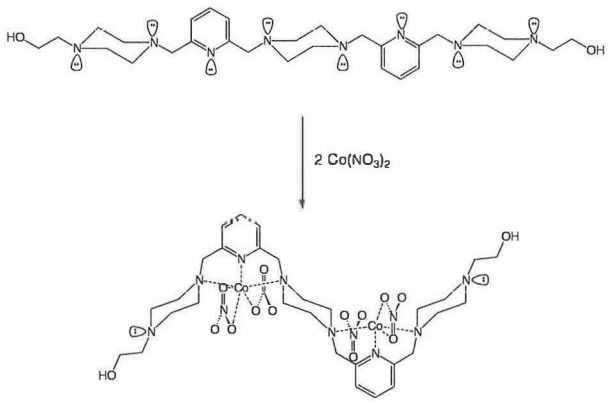
Figure 12. X-ray structure of D-gluconic iron complex **11.**

Although the chirality of the starting materials was known, data sets containing sufficient amounts of Friedel pairs were collected for **8**, **9** and **11** so that the Flack's parameter could be refined. The good esd's of Flack's parameters in all the structures showed that the solid state structures were enantiomerically pure. The Flack's parameter was also refined for **10**, but because of the poor refinement of the parameter and a poor e.s.d. [0.3(6)], no statement of the right enantiomer could be made from the crystallographic data.

2.3.4. Piperazine-Pyridine ligand and its Co^{2+}-complex[V]

An octadentate piperazine-pyridine ligand **12** was designed and synthethised in order to study the molecular topology of its complex. By using transition metal ions with a proper coordination tendency the ligand was expected to wrap around metal cation in a helical single or double-stranded manner. From the literature it is known, that by tailoring suitable coordination sites for the metal cations, it is possible to create double or even triple helical structures.[53] However, the structure derived from single-crystal X-ray diffraction revealed the geometry of the *bis*(Cobalt) complex **13** not to be helical. Instead, the *meso*-helical form of ligand was formed. The conformation, and a possible favouring of zigzag–shaped structures was also supported by the molecular modelling studies.[V]

12



13

Scheme 5. Complexation of Co^{2+} with ligand **12** to a *meso*-helical complex **13**.

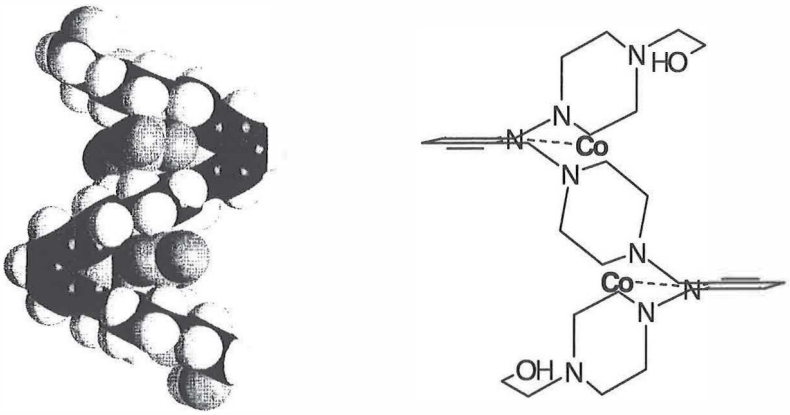


Figure 13. Side and top views of *bis*(Cobalt)-complex **13**. Top view as a schematic presentation derived from the X-ray structure.

Some interesting features of the complex can be noted: only six out of the eight possible nitrogen–free electron pairs are used for coordination. The octahedral coordination sphere is saturated with the available NO_3^- anions, creating a neutral complex. The Co^{2+}-octahedron is severely distorted due to the rigid ligand. The adaptation of the ligand around the cation causes a flipping of the piperazines from one side to the other. This is in principle starting–point for topological chirality; but the alternating flipping annuls the chirality of molecule, making it *meso*-helical and a crystallographically centrosymmetric structure.[54]

2.3.5 Multicomponent self-assembly to rigid-rack pseudorotaxane[VI]

A principle of the spontaneous assembly of a given set of components[55] is applied in a sophisticated way in the generation of rigid-rack pseudorotaxanes.[VI] In order to self-assemble a rack-type multimetallic compound, one needs to design the system in such a way that only stuctures arising from the mutual recognition are formed. Various systems where the metal-ion directed self-assembly reaction brings together two identical ligand types have been documented.[8] However, examples where non-identical components are brought together by metal binding are less numerous.[56-58]

A variety of intermolecular attractive forces have been applied in connecting a rotaxane axle and the loops together. In this example the template effect of metal-ion is the strongest but the weaker π-stacking interactions also play an important role.[59-60] In addition, solvophobic interactions may be used; as in threading cyclodextrin onto a variety of compounds.[61] In these compounds the cyclic phenyl-phenantroline crown-ether ligands **14** thread spontaneously onto linear pyridine-pyrazine ligand **15** encapsulating two copper ions which fix the structure to pseudorotaxanes with their tetraedric coordination (scheme 6).

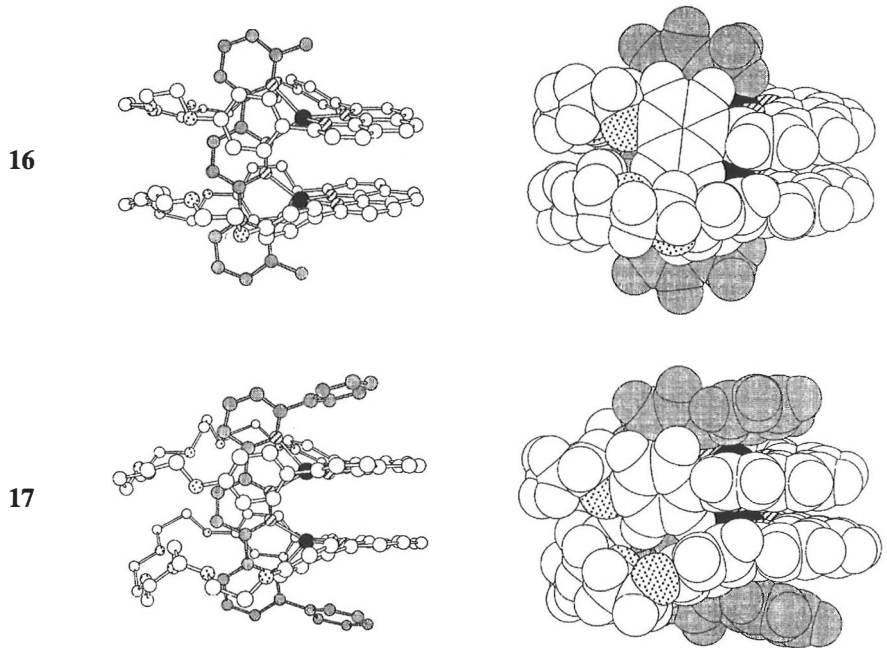
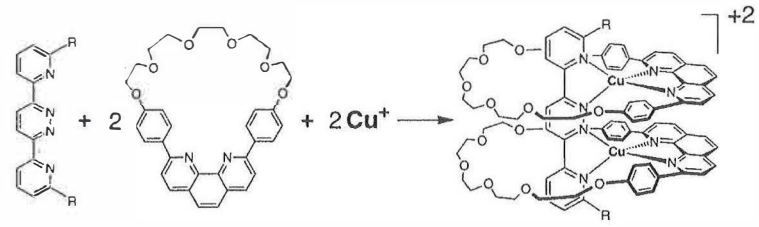


Figure 14. X-ray structures of two rigid-rack pseudorotaxanes **16** and **17**.

It is noteworthy in all the complexations that mixing Copper(I) ions with two different ligand types leads to the exclusive self-assembly of heteroligand inorganic architectures. The process is, however, more the mutual selection of the ligands on the copper ion than a real self-recognition.



14 **15** **16**: R=Me

17: R=Ph

Scheme 6. Threading of phenantroline-crown ether ligands **15** on a pyridine-pyrazine rod **14**.

The positioning of cyclic phenantroline ligands **15** relative to each others may be followed by NMR in the solution state. The close proximity of ligand strands causes several interferences on aromatic protons. Firstly, the complexed structure exhibits a remarkable (≈0.8 ppm) upfield shift for *p*-phenyl protons compared to free ligand. This is because of altering to ring current of 2,2'-*bipy* units of ligand **14**. Secondly, the *cisoid* and *transoid* conformations are differentiated with a general net shift of ca. 0.3 ppm. The face-to-face arrangement in *cisoid* form causes an upfield shift for all the macrocycle ligand **15** protons. Thirdly, the degree of freedom of the ligand **15** *p*-phenyl unit can be studied by observing the *ortho* and *meta* protons as averaged singlet or well defined coupled signals.

In solid state structures complexes **16** and **17** may be studied in more detail. A tendency to fit together the most conceivable and economical spatial arrangement of a set of ligands around the Copper(I) ion, and a tendency to fill the coordination sphere around Cu(I) efficiently give rise to several distortions from ideal tetrahedral geometry. Some general features of the structures may be listed: 1) The cyclic ligands are oriented so that the *p*-phenyl units are not badly interfered or distorted by other skeleton. 2) The ligands **15** are eclipsed, in other words, they display a substantial twist relative to one another, 24° in complex **16** and 42° in complex **17**. 3) The linear ligand is inclined at an angle of approximately 65° from the ideal 90° angle of rigid rack. This is supposedly to assist the comfortable saturation of the coordination centre.

Chirality of solid state structures

The eclipsing of phenantroline cycles causes overall twisting of a rigid-rack system to clock or counter-clockwise. This is in principle enough to create topological enantiomorphism in all structures. The fast changes that take place between the enantiomers in the solution state and the tendency of crystallograpic structures to search for the highest symmetry often inhibts such enantiomorphism.

The symmetry is distorted by disaligned phenantroline units of ligand **15** and by different orientations of phenyl "stoppers" at ligand **14**. These facts make compound **17** non-superimposable on its mirror image.

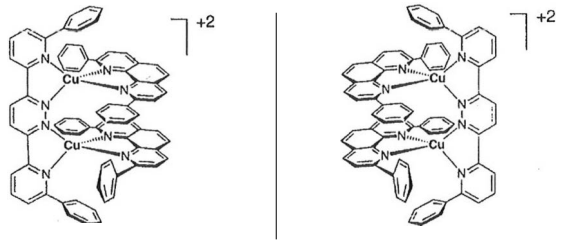


Figure 15. Non-superimposable mirror images of **17**. Oxa-bridges are omitted for clarity.

The interconversion of enantiomers is expected to happen easily in solution. An interesting feature is that when the complex crystallizes, it does not crystallize as a mixture of enanatiomers but as a single enantiomer, left-handed, as determined from the twisting of phenyl stoppers when viewed from the top. A crucial role in this spontaneous resolution of the enantiomers is probably played by the toluene molecule, which is captured in the crystal lattice between two pseudorotaxanes. The form of complex **17** and the packing of the crystal offers a suitable niche for toluene. Thus the clathrate–type inclusion of toluene seems to be a reason for homochiral crystals. One may suppose that when the first molecule of toluene is captured in the niche provided by the ligands, the direction of axial twisting of the entire complex is chosen. The packing then follows the handedness of the "seed". Several crystals were not picked up for crystallographic studies in order to see if both enantiomers had been present. Thus it is not certain whether the phenyl stoppers always direct the twisting in the same, in this case left-handed, direction.

2.3.6 Concave macrobicycles[VII]

In addition to recognition of neutral molecules via H-bonding,[62] the other or alternative forces in binding neutral guests may be different attractive forces between the aromatic π-bonds and π-σ interactions. In addition, solvophobic effects may cause the escape of guest molecules into the more favourable interior of the host.[11] Diyne bridging of aromatic "three-armed spacers" enables the shaping of macrobicyclic cavities to more rigid cages which are able to encapsulate sterically–fitted neutral guests. Thus, originated from π-clouds of triple bonds the macrocycle offers additional binding sites for the aromatic interactions.

An important circumstance in tailoring the host molecule is the optimum sterical fit for the desired types of guest molecules. It has been suggested that the ideal distance between two aromatic spacers for complexation of a flat aromatic guest would be 684 pm (6.8 Å).[63] This distance then allows the maximum forces in π-π interactions to come into play. These concave macrobicycles linked with alkyne bridges are not best suited to that principle, but are rather cavities for spherically shaped molecules which may form some weak interations with the interior of macrocycles. Moreover the spacers are easily pushed apart that height in alkyne bridged macrocycles varies from 800 to 1000 pm.

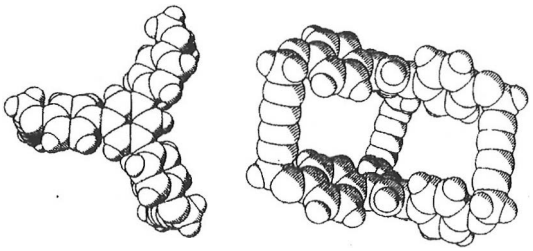


Figure 16. An example of a flat macrobicycle, in which the interior is more an ellipsoid than a sphere.

The crystal structure of macrocycle **18** shows that solvent molecules like DMSO are suitable for supramolecular inclusion. One DMSO molecule is takes on two different orientations in the solid state. By crystallographic means it is disordered. On average DMSO occupies a spherical space inside the cavity. Besides the included DMSO, the

two other DMSO molecules are clathrated in a crystal lattice and some ethanol has been trapped by weak hydrogen bonding.

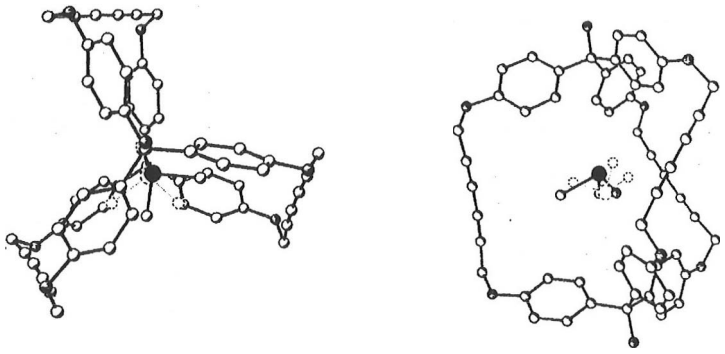


Figure 17. Macrobicycle **18** and a disordered DMSO molecule in the spherical cavity.

From the crystal structure of **18** it was predicted that macrocycle **19** would be more suitable for smaller solvents which may equally well reserve a spherical room. This was discovered from a study of the crystal structure of **19**, in which an acetone molecule occupies the center of the cavity.

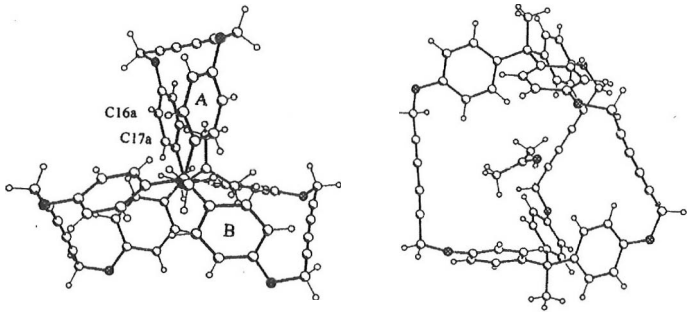


Figure 18. Macrobicycle **19** encapsulating acetone.

Although the supporting alkyne bridges have π-electrons to assist binding, no interactions between the guests and diyne bridges were observed. However the synthesis of similar type of structures may be applied in designing bigger neutral cavities for small cryptands or other spherically shaped–molecules.

2.3.7 Selective derivatisation of resorcarenes[VIII, IX]

A class of calixarenes, resorcarenes, readily available in all-cis form by the condensation of resorcinol with aldehyde, provide a good starting point for different further reactions. Both the phenolic hydroxyl groups and the 2-position of resorcinol units may be altered to chemical modifications. Basket shaped cavitands are formed by connecting adjacent oxygens by bifunctional reagents. [64-67] Reactions that may take place at 2-position are for instance electrophilic substitution such as bromination,[68] coupling with diazonium salts,[69] and aminomethylation.[70] With primary amines and formaldehyde the condensation leads to the formation of benzoxazine ring in a regioselective way.[71] By using aliphatic diamines of suitable length the additional bridging between adjcent benzoxazine rings is achieved. Adjusting the reaction conditions to more diluted, fairly good yields of macrocycles are obtained. By expanding the ring system the cavity is enlarged and further functionalities are thus added. The closure of the oxazine ring may occur to both directions of the adjacent resorcinols. Thus four different regioisomers may be formed.

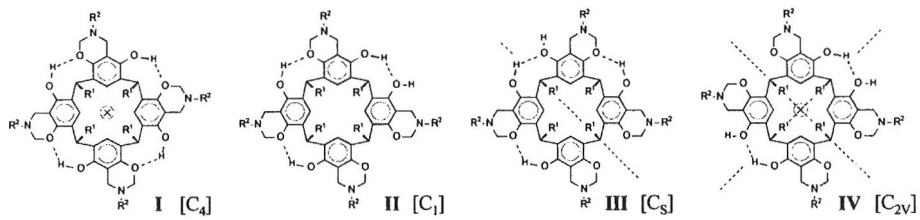


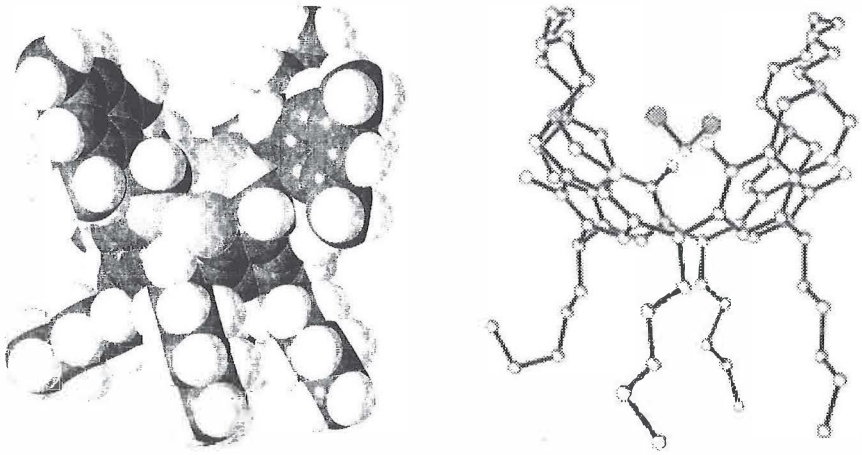
Figure 19. Four different regioisomers of oxazoline bridged resorcarene **20**.

The regioisomer I is expected to result as a major product since the product would be stablilized by four H-bonds and its calculated energy is the lowest.[VIII]

Acetaldehyde, hexanal and dodecanal were used as condensing aldehydes to receive corresponding substituted resorcarenes. The resulting products were further treated with several primary amines, varying from methacryl amine to phenethyl amine.

Conformations of derivatised resorcarenes were studied both in solution and in solid state. The existence of only one triplet for vicinally coupled methine proton (Ar-CHR'-Ar) in ^{1}H-NMR gives reason to assume that only the regioisomer I is present in solution. Further evidence is obtained from ^{13}C-NMR, which also exhibits only one signal for methine carbon, assigned by the DEPT experiment.

The crystal structures of the derivatised resorcarenes prove that the structures represent a single regioisomer. All the oxazine rings are in out-configuration, and the amine substitutes point axially downwards from the heterocycle nitrogen. The alkyl subsitutes are expected to take the lowest energy conformation: "all-trans"; but obviously the packing of molecules seems to allow different orientations and a slight disorder for the arms. Resorcarene's bowl–shaped cavity tends to encapsulate sterically fitting guest molecules. In the X-ray structure of **20**, the dicloromethane molecule is deeply embedded in the cavity. A sterical fit directs the chlorines upwards in the bowl and the 2,4,6-trimethylphenyl subsitutes partly close the cavity (figure 20). The dimensions of the cavity measured from diagonal distances of the amino-N are 9.68 Å and 12.77 Å in **20**.



20 **21**

Figure 20. The crystal structures of the resorcarene derivatives.

The effect of regioselectivity is amplified in the syntesis of N-bridged resorcarenes. In principle, seven different regioisomers result from the connection of oxazine cycles with diamines. But as predicted on the basis of the previous resorcarene conformations and their NMR-spectra, all four oxazine rings point in the same direction, and the pairs of adjacent oxazine rings are connected by 3,6-dioxa-octan chains (first conformation with C_2-symmetry in figure 21). A molecular cleft is enlarged by the crown ether bridges, and in the cleft of resorcarene one molecule of dichloromethane is deeply embedded. Position and orientation are very similar to compound **20**, but the resorcarene is slightly more flattened, so that the cleft dimensions are 9.81 Å and 11.93 Å in **21**.

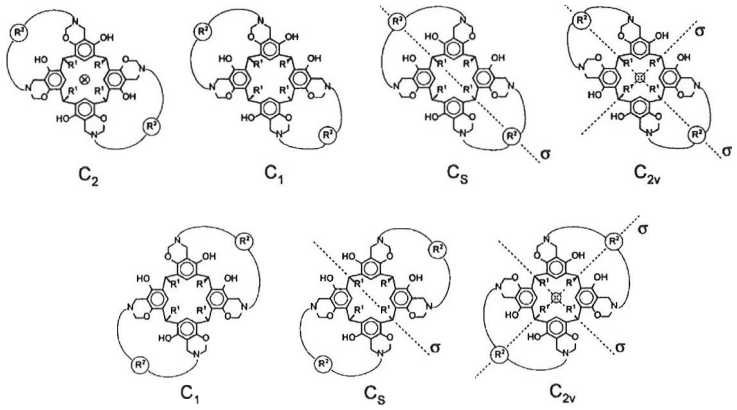


Figure 21. Seven different regioisomers of crown ether bridged resorcarene **21**.

The selectivity in the derivatisation of resorcarene result in multiple regioselective ring closure. However, when the most critical step, the identical orientation of the benzoxazine ring, creates *C2*-symmetry, the result in terms of further bridging can only be one.

3. SUMMARY AND CONCLUSIONS

In this study, various structural problems were solved and interpreted by means of X-ray crystallography. The significance of solid state structures was emphasized as a support for solution state studies; and the importance of crystal structures as a source of explanations in the interpretation of intra- and intermolecular interactions was demonstrated by several examples. Interesting structural "add-on –features" were revealed by solid state structures. As an example, there is the generation and resolution of topological isomers.[VI]

In publication I, the versatility of the various combinations of prehelical structural elements was further illustrated by ^{77}Se-NMR in the solution state. Normally the larger macrocycles are only observed from the molecular peaks in FAB-MS or MALDI-TOF spectra, but they cannot be further characterized even if separated. The higher species of a separated macrocyclic fraction was shown to represent four pairs of diastrereomers.

The determination of absolute configuration in publications II, III and VI had slightly different objectives. While the determination of chiral centers was not necessary in the case of sugar derivatives, since the starting materials were pure enantiomers,[III, IV] in the case of a natural intermediate product, *N* protected glutamic acid ester,[II] the information about the correct chirality and the enantiopure synthesis product was essential. In publication VI the diffraction studies revealed the rigid-rack pseudorotaxane **17** crystallizing in a chiral space group. The X-ray structure determination and the interpretation of the results lead to the conclusion that a spontaneous resolution of enantiomers upon crystallisation had occured, and that the resolution was a consequence of a clathrate formation with toluene.

X-ray crystallography was used as final evidence in cases where a considerable amount of conformational information had already been obtained from solution studies. In publications III, IV, VI, VIII and IX, solid–state structures had an important role in proving the assumptions made from NMR-spectra, and in better understanding the molecular interactions.

In supramolecular inclusion complexes, accurate structural determination is vital for estimating different intra- and intermolecular interactions between hosts and guests. In concave macrobicycles the size and the inclusion capabilities of the cavities were studied on the basis of the X-ray structures of macrocyclic hosts **18** and **19**. In resorcarenes **20** and **21** structural elucidation clarified the inclusion properties of the bowl–shaped cavities, in addition to providing a solution of regioisomers created by derivatisation of the parent resorcarenes.

In all, the importance of accurate "molecular photographs" is demonstrated by multiple examples. The versatility of X-ray crystallography is also employed in designing synthesis, so that the resulting compounds will be better able to perform their programmed functions.

4. REFERENCES

I Karri Airola, Stefan Bartram, Kari Rissanen, Helically Chiral Thia and Diselena Quinquephenylophanes, *J. Chem Soc. Perkin Trans. 1*, **1995** 895-899.

II Thierry Gefflaut, Udo Bauer, Karri Airola, Ari M.P. Koskinen, Asymmetric 1,3-Dipolar Cycloaddition: Synthesis of N-protected (4S)-4-Hydroxy L-Glutamic Acid Ester, *Tetrahedron: Asymmetry*, **7** (1996) 3099-3102.

III Ralf Ehlenz, Karl-Heinz Dötz, Martin Nieger, Karri Airola, Sugar Acyl Iron Complexes: Synthesis and Conformational Studies in Solution and in the Solution State, *J. Carbohydrate Chem.*, **16** (1997) 1305-1318.

IV Karl-Heinz Dötz, Ralf Ehlenz, Wolfgang, Straub, J.C. Weber, Martin Nieger and Karri Airola, Organotransition Metal Modified Sugars 4: Carbene Complex Functionalized Acyclic Carbohydrates, *J. Organometal. Chem.*, **548** (1997) 91-98.

V Karri Airola, Jari Ratilainen, Tommi Nyrönen, Kari Rissanen, A Linear Open-Chain Piperazine–pyridine Ligand and its *meso*-helical Co complex, *Inorg. Chim. Acta*, **277** (1998) 55-60.

VI Hanadi Sleiman, Paul Baxter, Kari Rissanen, Karri Airola, Jean-Marie Lehn, Multicomponent Self-Assembly: The Construction of Rigid–Rack Multimetallic Complexes of Rotaxane-Type, *Inorg. Chem.*, **36** (1997) 4734-4742.

VII Fritz Vögtle, Ingo Michel, Ralf Berscheid, Martin Nieger, Kari Rissanen, Sirpa Kotila, Karri Airola, Nicola Armaroli, Mauro Maestri,Vincenzo Balzani, Concave Macrobicycles: Absorption Spectra, Luminescence Properties and Endocavital Complexation of Neutral Organic Guests, *Liebigs Ann./Recueil,* **1996** 1697-1704.

VIII Karri Airola, Volker Böhmer, Erich Paulus, Kari Rissanen, Christian Schmidt, Iris Thondorf, Walter Vogt, Selective Derivatisation of Resorcarenes: 1. The Regioselective Formation of Tetra-Benzoxazine Derivatives, *Tetrahedron*, **53** (1997) 10709-10724.

IX Christian Schmidt, Karri Airola, Volker Böhmer, Walter Vogt, Kari Rissanen, Selective Derivatisations of Resorcarenes: 3. Multiple Regioselective Ring Closure Reactions, *Tetrahedron*, **53** (1997) 17691-17698.

1. Pedersen, C.J., *J. Am. Chem. Soc.*, **89** (1967) 7017-7036.
2. Diedrich, B., Lehn, J.-M., Sauvage, J.-P., *Tetrahedron Lett.*, **1969**, 2885-2888, 2889-2892.
3. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, Ch. 1.

4. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, Ch. 2.1.
5. Vögtle, F., *Supramolecular Chemistry*, Wiley, 1991, Surrey, U.K.
6. Weber, E., Vögtle, F., *Chemie in uns. Zeit* **23** (1989) 210-212.
7. Vögtle, F. (Ed.), *Host Guest Complex Chemistry, Topics in Current Chemistry*, Vol. **98**, Springer, Berlin, Heidelberg, New York, 1981.
8. Constable, E. C., In *Comprehensive Supramolecular Chemistry*, Pergamon, Exeter, U.K., 1996, Vol. 9, pp. 213-252.
9. Lehn, J.-M., *Angew. Chem. Int. Ed. Engl.*, **29** (1990) 1304-1319.
10. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, p. 11.
11. Schneider, H.-J., *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 1417-1436.
12. Vögtle, F., *Supramolecular Chemistry*, Wiley, 1991, Surrey, U.K., Ch. 8.
13. Vögtle, F., *Supramolecular Chemistry*, Wiley, 1991, Surrey, U.K., Ch. 2.
14. Hosseini, M. W., Lehn, J.-M., Mertes, M. P., *Helv. Chim. Acta* **66** (1983) 2454-2466.
15. Wolfe, J., Nemeth, D., Costero, A., Rebek Jr., J., *J. Am. Chem. Soc.* **110** (1988) 983-984.
16. Krieger, C., Diedrich, F., *Chem. Ber.* **118** (1985) 3620-3631.
17. Powell, H. M., *J. Chem. Soc.* **1948**, 61-73.
18. Vögtle, F., *Supramolecular Chemistry*, Wiley, 1991, Surrey, U.K., Ch. 5.
19. Constable, E. C., *Tetrahedron* **48** (1992) 10013-10059.
20. Beer, P. D., Wheeler, J. W., Moore, C. P., *J. Chem. Soc. Dalton Trans.*, **1992** 2667-2673.
21. Sleiman, H., Baxter, P. N. W., Lehn, J.-M., Rissanen, K., *J. Chem. Soc. Chem. Commun.*, **1995** 715-716.
22. Dietrich-Buchecker, C. O., Sauvage, J.-P., Kern, J.-M., *J. Am. Chem. Soc.* **106** (1984) 3043-3045.
23. Vögtle, F., *Supramolecular Chemistry*, Wiley, 1991, Surrey, U.K., p. 117.
24. Nakazaki, M., Yamamoto, K., Tanaka, S., *J. Org. Chem.* **41** (1976) 4081-4086.
25. Kämmerer, H., Happel, G., Caesar, F., *Makromol. Chemie* **162** (1972) 179-197.
26. Vögtle, F., *Cyclophane Chemistry*, Wiley, Surrey, U.K., 1993, p. 347.
27. Monaco, H. L., in *Fundamentals of Crystallography* (Ed. Giacovazzo, C.), Oxford University Press, Avon, U.K., 1992.

28. Atwood, J. L. in *Crystallography of Supramolecular Compounds*, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1996, Article 1.
29. Pascard, C., in *Crystallography of Supramolecular Compounds*, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1996, Article 8.
30. Ratilainen, J., Ph.D Thesis, Department of Chemistry, University of Jyväskylä, Research Report no. 58, Jyväskylä, 1997, pp. 7-9.
31. Allen, F., in *Crystallography of Supramolecular Compounds*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996, Article 5.
32. Kivikoski, J. Ph. D. Thesis, Department of Chemistry,, University of Jyväskylä, Annales Academiæ Scientiarum Fennicæ, Series A, II. Chemica 244, Helsinki, 1993.
33. Bernardinelli, G., Flack, H. D., *Acta Cryst.* A**41** (1987) 500-511.
34. Berdardinelli, G., Flack, H. D., *Acta Cryst.* A**43** (1987) 75-78.
35. Yuki, H., Okamoto, Y, Okamoto, I., *J. Am. Chem. Soc.* **102** (1980) 6356-6358.
36. Hammerschmidt, E., Vögtle, F., *Chem. Ber.* **113** (1980) 1125-1129.
37. Hammerschmidt, E., Vögtle, F., *Chem. Ber.* **113** (1980) 3550-3556.
38. Ratilainen, J., Airola, K., Nieger, M., Böhme, M., Huuskonen, J., Rissanen, K., *Chem. Eur. J.* **3** (1997) 749-754.
39. Hammerschmidt, E., Vögtle, F., *Chem. Ber.*, **122** (1979) 1785-1790.
40. Hanan, G.S., Lehn, J.-M., Krytsakas, N., Fischer, J., *J. Chem. Soc. Chem. Commun*. **1995**, 765-766.
41. Harris, R.K., Mann, R.K. (eds.), *NMR and Periodic Table*, Academic Press, London, 1979.
42. Benoiton, L., Winitz, M., Birbaum, S. M., Greenstein, J. P., *J. Am. Chem. Soc.* **79** (1959) 6192-6198.
43. Kusumi, T., Kakisawa, H., Suzuki, S., Harada, K., Kashima, C., *Bull. Chem. Soc. Jpn.* **51** (1978) 1261 1262.
44. Kristensen, E. P., Larsen, L. M., Olsen, O., Sørensen, H., *Acta Chim. Scand.* **34** (1980) 497-504.
45. Passerat, N., Bolte, J., *Tetrahedron* **28** (1987) 1277-1280.
46. Hanessian, S., Nanasse, B., *Can. J. Chem.* **71** (1993) 1401-1406.
47. Kim, B. H., Curran, D. P., *Tetrahedron* **49** (1993), 293-318.

48. Kim, K. S., Kim, B. H., Park, W. M., Cho, S. J., Mhin, B. J., *J. Am. Chem. Soc.* **115** (1993) 7472-7477.

49. Brookhart, M., Studbaker, W. B., Humphrey, M. B., *Organometallics* **8** (1989) 132-140.

50. Preparation of carbonyl chromates: Schwindt, M. A., Lejon, T., Hegedus, L. S., *Organometallics* **9** (1990) 2814-2819.

51. Horton, D., Wander, J. D., *J. Org. Chem.* **39** (1974) 1859-1863.

52. Blanc-Muesser, M., Defaye, J., Horton, D., *J. Org. Chem.* **43** (1978) 3053-3055.

53. Examples on helical complexes: Krämer, R., Lehn, J.-M., DeCian, A., Fischer, J., *Angew. Chem. Int. Ed. Engl.* **32** (1993) 703-706; Constable, E. C., Hannon, M. J., Martin, A., Raithby, P. R., *Polyhedron* **11** (1992) 2967-2971; Lehn, J.-M., Sauvage, J.-P., Simon, J., Ziessel, R., *New. J. Chem.*, **7** (1983) 413-420; Potts, K.T., Keshararaz-K, M., Tharn, F.S., Abruña, H.D., Arana, C.R., *Inorg. Chem.* **32** (1993) 4422-4435.

54. Albrect, M., Kotila, S., *Angew. Chem. Int. Ed. Engl.* **34** (1995) 2134-2136.

55. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995. pp. 139-197.

56. Hasenknopf, B., Lehn, J.-M., Baum, G., Fenske, D., *Proc. Natl. Acad. Sci. U.S.A.* **93** (1996) 1397-1400.

57. Baxter, P., Hanan, G.S., Lehn, J.-M., *J. Chem. Soc. Chem. Commun.* **1996**, 2019-2020.

58. Baxter, P., Lehn, J.-M., DeCian, A., Fischer, J., *Angew. Chem. Int. Ed. Engl.* **32** (1993) 69-72.

59. Amabilino, D., Raymond, F., Stoddart, J., in *Comprehensive Supramolecular Chemistry*, Elsevier Science Ltd, Amsterdam, 1996, Vol. 9, Chapter 4.

60. Amabilino, D., Stoddart, J., *Chem. Rev.* **95** (1995) 2725-2828.

61. Ogino, H., *J. Am. Chem. Soc.* **103** (1981) 1303-1305.

62. Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995. p. 29.

63. Whitlock, B. J., Whitlock, H. W., *J. Am. Chem. Soc.* **116** (1994) 2301-2311.

64. Moran, J. R., Karbach, S., Cram, D.J., *J. Am. Chem. Soc.* **104** (1982) 5826-5828.

65. Robbins, T. A., Knoble, C. B., Bellew, D. R., Cram, D. J., *J. Am. Chem. Soc.*, **116** (1994) 111-122.

66. Helgeson, R. C., Paek, K., Maverick, E. F., Cram, D. J., *J. Am. Chem. Soc.*, **118** (1996) 5590-5604.

67. Yoon, J., Cram, D. J., *J. Chem. Soc. Chem. Commun.* **1997**, 497-498.

68. Sherman, J. C., Knobler, C. B, Cram, D. J., *J. Am. Chem. Soc.*, **113** (1991) 2194-2204.

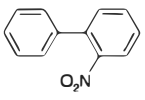
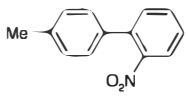
69. Manabe, O., Asakura, K., Nishi, T., Shinkai, S., *Chem. Lett.* **1990**, 1219-1222.

70. Schneider, U., Schneider, H.-J., *Chem. Ber.* **127** (1994) 2455-2469.

71. Arnecke, R., Böhmer, V., Paulus, E. F., Vogt, W., *J. Am. Chem. Soc.* **117** (1995) 3286-3287.

Errata

PAPER I

p. 896, Scheme 1. Compound **3**:  , should be: 

p. 896, in text and in Scheme 2. [3.3]quinquephenylophane, should be [3.3]decaphenylophane.

PAPER IV

p. 94, Table 3. Crystal system of **15**: triclinic, should be orthorhombic

PAPER VI

p. 4736, Table 1. Absolute structure parameter should be for 3f (not 3e)

PAPER VIII

p. 10723, X-ray structural analysis (chapter 4, line 4): diffracometer, should be diffractometer

PAPER I

https://doi.org/10.1039/P19950000895

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PAPER II

https://doi.org/10.1016/0957-4166(96)00407-7

(Reprinted from *Tetrahedron: Asymmetry*, **7**, Thierry Gefflaut, Udo Bauer, Karri Airola, Ari M.P. Koskinen, Asymmetric 1,3-Dipolar Cycloaddition: Synthesis of N-protected (4S)-4-Hydroxy L-Glutamic Acid Ester, 3099-3102, (1996) with permission from *Elsevier Science*)

PAPER III

https://doi.org/10.1080/07328309708005751

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PAPER IV

https://doi.org/10.1016/S0022-328X(97)00335-5

(Reprinted from *Journal of Organometalic Chemistry*, **548**, Karl-Heinz Dötz, Ralf Ehlenz, Wolfgang, Straub, J.C. Weber, Martin Nieger and Karri Airola, Organotransition Metal Modified Sugars 4: Carbene Complex Functionalized Acyclic Carbohydrates, 91-98, (1997) with permission from *Elsevier Science*)

PAPER V

https://doi.org/10.1016/S0020-1693(97)06122-7

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PAPER VI

https://doi.org/10.1021/ic9702227

PAPER VII

https://doi.org/10.1002/jlac.199619961102

(Reprinted from *Liebigs Annalen/Recueil*, **1996**, Fritz Vögtle, Ingo Michel, Ralf Berscheid, Martin Nieger, Kari Rissanen, Sirpa Kotila, Karri Airola, Nicola Armaroli, Mauro Maestri,Vincenzo Balzani, Concave Macrobicycles: Absorption Spectra, Luminescence Properties and Endocavital Complexation of Neutral Organic Guests, 1697-1704 with permission from *VCH Verlagsgesellschaft mbH*)

PAPER VIII

https://doi.org/10.1016/S0040-4020(97)00685-6

(Reprinted from *Tetrahedron*, **53**, Karri Airola, Volker Böhmer, Erich Paulus, Kari Rissanen, Christian Schmidt, Iris Thondorf, Walter Vogt, Selective Derivatisation of Resorcarenes: 1. The Regioselective Formation of Tetra-Benzoxazine Derivatives, 10709-10724, (1997) with permission from *Elsevier Science)*

PAPER IX

https://doi.org/10.1016/S0040-4020(97)10236-8

(Reprinted from *Tetrahedron*, **53**, Christian Schmidt, Karri Airola, Volker Böhmer, Walter Vogt, Kari Rissanen, Selective Derivatisations of Resorcarenes: 2. Multiple Regioselective Ring Closure Reactions, 17691-17698, (1997) with permission from *Elsevier Science*)