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One-step Access to Resorcinsalens – Solvent Dependent Synthesis, Tautomerism, Self-sorting and Supramolecular Architectures of Chiral Polyimine Analogues of Resorcinarene

Joanna Szymkowiak,[a,b] Beata Warżajtis,[a] Urszula Rychlewska,[a] and Marcin Kwit*[a,b]

Abstract: *The substituted 2,4- and 4,6-dihydroxyisopthalaldehydes were condensed with optically pure and racemic trans-1,2-diaminecyclohexane to form resorcinarene-like polyimine macrocycles (resorcinsalens) of the structure and stoichiometry controlled by the choice of the reaction medium. Particularly, the cyclocondensation reactions are driven by the solubility, tautomerisation or by social self-sorting. The resorcinsalens crystallize as inclusion compounds, where the guest molecules are situated either in channels or in voids. In the highly hydrated crystals of phase* ***I*** *of* ***3a*** *and chloroform solvated crystals of meso-****5a*** *the channels are interconnected, as in zeolites, enabling possible migration of loosely bound solvent molecules in three-dimensions. The association mode depends on the structural modification of the host molecule and the type of included solvent molecule(s).*

Controlled synthesis of functionalized chiral macrocycles by means of Dynamic Covalent Chemistry (DCC) concept is gaining popularity for the development of new supramolecular receptors, ligands and for designing of porous materials.[1,2] While most of the macrocyclisation reactions usually require special reaction conditions or laborious elongation of open-chain precursor prior macrocyclization,[1] application of the DCC allowed rational design of molecules, varied in shape and functionalities, from relatively simple building blocks.[2] The DCC-based, reversible cycloimination reaction emerges now as convenient template-free method providing shape-persistent, optically pure polyimine macrocycles from structurally predisposed substrates.[3] These polyazamacrocycles are further applied as chiral catalysts and ligands in stereoselective synthesis, as molecular receptors or organic porous materials.[4,5] The use of racemic substrates in cycloimination reactions often provides complex mixtures of diastereoisomers. Chiral self-sorting is achieved in those of DCC-based reactions whose products significantly differ in symmetry, therefore in rotational entropy.[6,7]

Due to the diequatorial position of amine groups and skeleton rigidity, *trans*-1,2-diaminecyclohexane (DACH, **1**) is the amine of choice for cycloimination. While the quantitative [3+3] cyclocondensations between **1** and various aromatic 1,4-dialdehydes provide triangular macrocycles (*trianglimines*) of symmetry and shape depending on the aldehyde structure,[8,9] the reactions utilizing 1,3-dialdehydes are less selective. However, the presence of hydroxyl group between two adjacent CHO groups drives the reaction to the vase-like [3+3] products (*calixsalens*) and significantly stabilizes their structure. Both, the size and electronic properties of a substituent at C5 position of the arene ring control the abilities to form calixsalen supramolecular architectures in all states of matter.[10]

To the best of our knowledge, to date there are no reports on chiral polyimine macrocycles that contain two imine and two hydroxyl groups in relative 1,3 positions within the same aromatic unit. These macrocycles, in principle, should exhibit molecular and supramolecular properties differrent from the compounds known so far, for instance reversible proton tautomerism – one of the most important processes in chemistry and biochemistry.[11] Recently, Lisowski *et al.* and Banerjee *et al.* indicated proton tautomerism as one of the decisive factors that caused unexpected formation of chiral and achiral [2+3] keto-enamine organic cages from 1,3,5-triformylphloroglucinol.[12] MacLachlan et al. proved strong preference of acyclic imines from 2,4-dihydroxyisopthalaldehyde to form keto-enamine tautomers (NH form), while imines derived from 4,6-dihydroxyisopthalaldehyde preserved the enol-imine form.[13]

Thus, it seemed desirable to expand the study into chiral polyimine resorcinarene-like systems, being 2,4-dihydroxyisopthalaldehyde or 4,6-dihydroxyisopthalaldehyde derivatives. The compounds considered as good candidates for the synthesis represent members of a new class of highly functionalized macrocycles (*resorcinsalens*). We intended to demonstrate, how the aldehyde structure, reaction conditions and/or the diamine enantiomeric purity affect the structure of the product(s). Hydroxyl groups present in the macrocycle skeleton will be capable of forming hydrogen bonds and controlling, in this way both, the molecular structure and the assembly in the solid state. The OH form is generally considered as the most stable form at room temperature. Consequently, hydroxylated polyimine chiral macrocycles exist as enol-imine tautomers. So far none of the macrocycles has been characterized as purely NH form by a single crystal X-ray diffraction method.[14] Meanwhile, we anticipated that some of the newly synthesized macrocycles may appear as the keto-enamine tautomeric forms.

To initiate the work, we synthesized 2,4-dihydroxy- (**2a**-**2c**) or 4,6-dihydroxyisopthalaldehydes (**2d**, **2e**) from respective, commercially available, resorcinols and through Duff formylation.[15] The aldehydes were obtained with yields ranging from 11% to 45% (after chromatography and crystallization) and were further subjected to reaction with (*R*,*R*)-**1** or *rac*-**1** (Scheme

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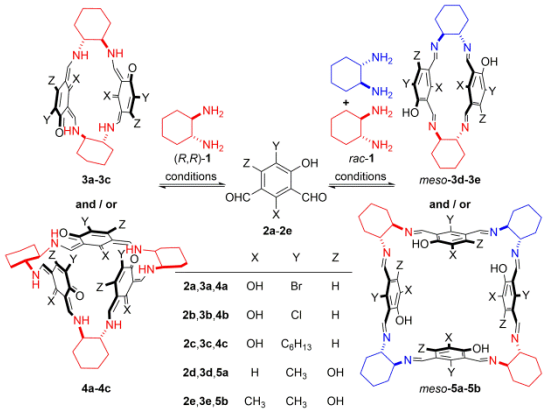
1). Due to the presence of OH groups at C2 and C4 positions in aldehydes **2a**-**2c**, we expected the same *s-trans* conformation of the imine bonds (see Scheme S1) as in known calixsalens[10c] and exclusive formation of [3+3] macrocycles **4a**-**4c**.

Indeed, reactions carried out in chloroform, at room temperature, provided orange colored macrocycles **4a**-**4c**, formation of which was confirmed by mass spectra. During the reaction, color of the mixture changed to green with precipitation of hardly soluble solids (apart from the quantitatively obtained **4c**).



Scheme 1. Reactions of **1** with **2a**-**2e** leading to *resorcinsalens* **3**-**5**.

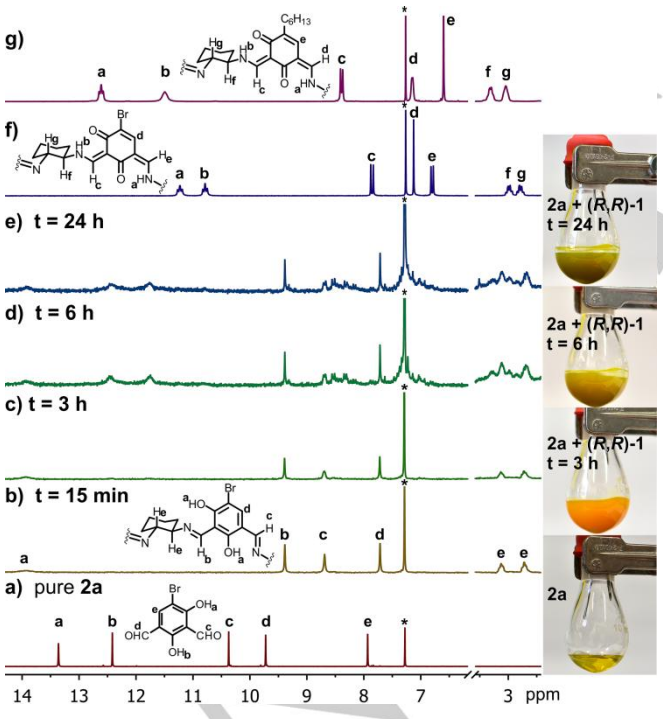


Figure 1. a-e) Parts of the ^{1}H NMR spectra [$CDCl_3$] measured during cycloimination reaction between (*R*,*R*)-**1** and **2a**. Diagnostic regions of ^{1}H NMR spectra [$CDCl_3$] of f) **3a** and g) **4c**. On the right are shown pictures taken during reaction between (*R*,*R*)-**1** and **2a**. Asterisks indicate trace solvent peaks.

The ^{1}H NMR and mass spectra recorded at the time intervals for the model reaction between (*R*,*R*)-**1** and **2a**, carried out in $CDCl_3$ (Figure 1), gave an insight into the course of the cycloimination reaction. Within 15 minutes almost immediate disappearance of the aldehyde and formation of C_3-symmetrical [3+3] product **4a** was observed. The diagnostic CH=N imine sharp singlets that appeared at δ = 9.39 and 7.72 ppm are typical for the OH form of the macrocycle. This particular form is stable in chloroform solution up to 3 hours. After that time, a step-wise decrease of the diagnostic signals intensity was observed with simultaneous appearance of new downfield broad signals at δ = 12.4 and 11.8 ppm, together with a set of signals in the region between 9÷8 ppm. The MS did not show any significant changes, which provided compelling evidence of the ongoing tautomerisation rather than contraction or expansion of the macrocycle ring. Since neither the appearance nor the disappearance of already present signals was complete, we assumed the presence of complex equilibrium involving number of possible tautomers.

In the UV spectra measured during the cycloimination reaction between (*R*,*R*)-**1** and **2a**, a shift (ca. 50 nm) of the absorption maxima of the pure aldehyde into lower energy region has been observed while the concentration of the cyclic product **4a** increased. The highest intensity absorption band appeared at 302 nm and its position did not change. However, as time passed, we observed gradual changes in the shape of the lower energy regions of the spectra. Well-formed band at around 400 nm was gradually covered by a wide absorption band in which characteristic peaks could not be distinguished. Note that spectrum measured for the [2+2] macrocycle **3a** has similar shape as those of **4a** (see Figures S1-S2).

Apart from **4c** (*vide infra*), we were unable to fully characterize the obtained products **4a** and **4b**, due to their insolubility. However, the appearance of enamine derived, broadened NH triplets at δ = 12.25 and 11.49 ppm and =CHN doublets at δ = 8.41 and 7.15 ppm indicated formation of pure NH form of **4c**. Note that the NH signals disappeared after addition of a drop of D_2O to the NMR test tube.

The same reactions carried out in boiling ethanol provided the contracted [2+2] products **3a** and **3b** with yields 87% and 45%, respectively. The number and the multiplicity of diagnostic signals observed in ^{1}H NMR spectra unequivocally confirmed the presence of **3a**-**3c** solely as the keto-enamine tautomer. However, the reaction route between (*R*,*R*)-**1** and the hydrophobic **2c** appeared to be more complex. We observed precipitation of **4c** (yield 40%), which was hardly soluble in polar solvents and was not subjected to further transformations. The major product **3c** was purified by several crystallizations from supernatant, which provided analytically pure sample with yield equal to 41%.

DFT calculations carried out for the model compounds being *N*-methylimine derivatives of **2a** (imine **6**) and **2c** (imine **7**) (Schemes S2-S3, Figures S3-S4) as well as for **3a**-**3c** and **4a**-**4c** confirmed the preference for the keto-enamine forms.[16] The calculated energy differences are primarily dependent on the environment, simulated by the solvent model. The type of the substituent attached to the aromatic ring had much smaller impact. The absolute values of energy gaps (in kcal mol^{-1}) between OH and NH forms of **6** (values for **7** are shown in

parentheses) increase from 4.4 (3.2) in the gas phase, through 8.9 (7.0) in $CHCl_3$, to 10.6 (8.5) calculated for the ethanol solvent model. An increase of the environment polarity was associated with a decrease of the energy barriers of proton transfers from the OH groups to the imine nitrogen atoms. To sum up these results, in ethanol, the enamine-imine equilibria reside almost completely on the side of the respective enamine (NH) tautomers.

Regardless of the macrocycle size, the imine or enamine groups adopt the *s-trans* orientation (see Scheme S1). This allows formation of intramolecular hydrogen bonds, each closing a six-membered ring, and thus significantly stabilizes the macrocycle structure.[10c] While the linkers in **4a**-**4c** are planar, the C=C(-N) bonds in **3a**-**3c** are placed out of the plane of the 1,3-quinone ring (Figure S3).

The reactions between equimolar amounts of *rac*-**1** and respective aldehydes **2d** and **2e** carried out in chloroform led, at first, to the formation of the [2+2] products **3d**, **3e** that precipitated from the reaction mixtures. The [4+4] products **5a** and **5b**, which retained in their respective reaction mixtures, were purified by crystallization from the respective supernatants. While this procedure provided a pure sample of **5a** with yield equal to 40%, we were unable to obtain a pure sample of **5b** in the same way, despite many attempts. MS and NMR data confirmed formation of [2+2] and [4+4] macrocycles **3d**, **3e** and **5a**, respectively, as enol-imine tautomers. The number of diagnostic signals observed in ^{1}H NMR spectra corresponds to the C_{2h} symmetry of a given [2+2] macrocycle having two diamine subunits of the opposite helicity and to the S_4 symmetry of **5a**. The formation of *meso* diastereomers represents an example of social self-sorting, unusual for polyimine compounds. Similar self-sorting phenomenon has been reported to occur during the dynamic formation of a disulfide containing macrocyclic tetramer.[17]

The ^{1}H NMR and MS spectra measured at the time intervals for the model reaction between *rac*-**1** and **2d**, show complete disappearance of the aldehyde just within 15 minutes with formation of a mixture of [4+4], [3+3] and [2+2] products in 70:15:15 ratio as indicated by ^{1}H NMR (see Figure 2) and MS measurements. Prolongation of the reaction time up to 3 days did not alter the shape of the spectrum. Due to the same symmetry number (σ = 2) we did not expect any difference in rotational entropy between the [2+2] and [4+4] products. However, DFT calculations indicated non-symmetrical, heteorochiral [3+3] macrocycle as thermodynamically the most stable over all possible structures (Table S1, Figure S5). Thus, the formation of dominant [4+4] product can not be explained on the basis of the entropy of symmetry rule postulated for, *inter alia*, reversible, thermodynamically controlled cycloimination reactions.[18,19] On the other hand, the formation of [2+2] products is driven by their lower solubility in the reaction medium. As in the above mentioned case of **4c**, the precipitated products were not subjected to further transformations.

The single crystal X-ray diffraction study provided tangible structural evidence for keto-enamine or enol-imine tautomers of respective resorcinsalens. Resorcinsalens **3a**-**3b** crystallize as NH tautomers stabilized by intramolecular NH···O hydrogen bonds supplemented by intramolecular π-π stacking interactions (Figure 3a). The X-ray determined C=O bond lengths vary from 1.247(3) to 1.274(3) Å with the mean value of 1.258(4) Å for 24 observations (Table S4), in agreement with the mean value of 1.285(13) Å calculated for 107 fragments containing the keto-enamine tautomers of salicylimine deposited in CSD data base and with results of DFT calculations.[14]

Depending on crystallization conditions, **3a** forms two types of solvated crystals of space group symmetry *R*32 and $P6_5$, distinguished as phase **I** and **II,** respectively. The two phases differ *inter alia* in a number of ethanol and water molecules per one host molecule and in a molecular symmetry (C_2 *vs*. C_1, respectively). In the crystals of phase **I**, the basic supramolecular motif comprises a capsule formed by three macrocyclic molecules related by a three-fold symmetry axis and two water molecules entrapped inside the capsule (Figure 4a), and involved in 3-fold hydrogen bonding with the host molecules. The remaining highly disordered solvent molecules, *i.e.* ethanol and water, are located in large channels, bringing about an impression that the supramolecular aggregates are sailing in the 'sea' of solvent molecules, as picturesquely described by Cooper and co-workers.[20] The total volume of unit cell occupied by these molecules equals to 30% (probe radius of 1.4 Å)[21]. Meanwhile, out of 22 [2+2] imine macrocycles deposited in the CSD[14] only 10 are solvated and only one of them contains included water molecules. In these 10 crystal structures the volume of the voids occupied by solvent molecules ranges from 2% to 32% with the mean value of 18(9)%. Hence, the crystal structure of phase **I** of **3a** is exceptional in both the content of included guest molecules and the percentage of space available to them. The effect of inducing the aggregation of larger components by smaller components is known in the colloid science. The mechanism underlying this phenomenon is claimed to be entropic*, i.e*. the ordering of larger components allows for increasing disorder among the smaller components and ultimately in the entire system.[22]

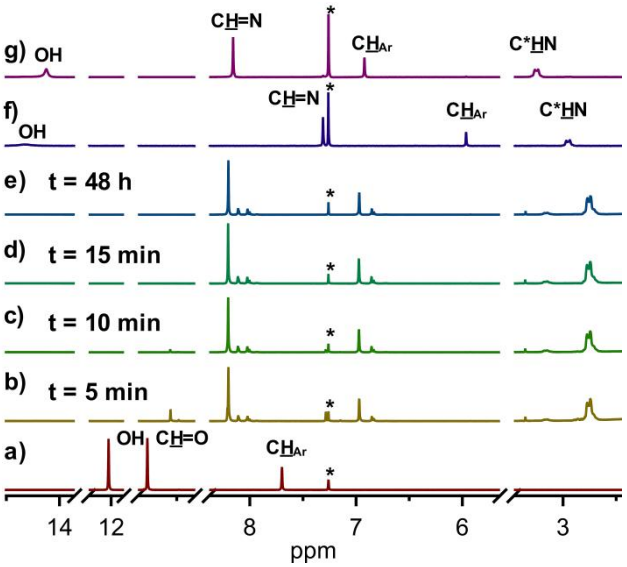


Figure 2. a) Traces of ^{1}H NMR spectra [$CDCl_3$] measured for the pure aldehyde **2d**. b-e) Traces of ^{1}H NMR spectra [$CDCl_3$] measured during reaction between **2d** and *rac*-**1**. f, g) Traces of ^{1}H NMR spectra [$CDCl_3$] measured for *meso*-**3d** and *meso*-**5a**. Asterisks indicate trace solvent peaks.

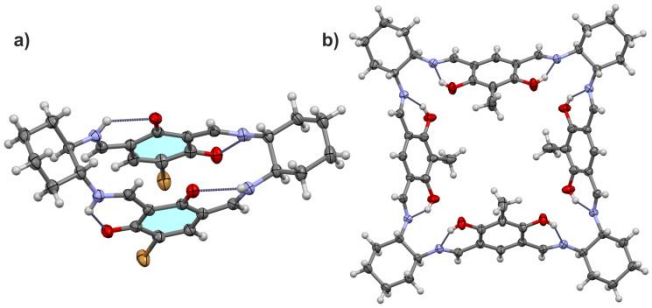


Figure 3. Perspective views of the molecules **3a** a) and **5a** b) as present in crystals at 130K. Displacement ellipsoids for non-H atoms are drawn at 40% probability. Intramolecular hydrogen bonds stabilizing the tautomeric forms are represented by dashed lines. Shaded areas mark π-π stacking interactions.

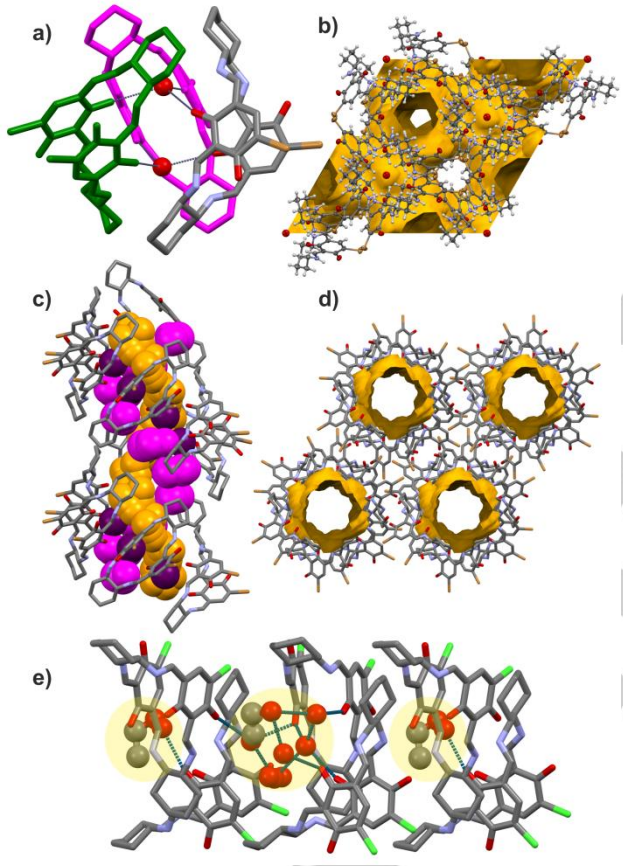


Figure 4. 3D, 1D and 0D solvent compartments in the crystal structures of **3a** and **3b**. Hydrogen atoms are omitted for clarity. a) Higher-order aggregate present in crystal phase **I** of **3a** having the water mediated hydrogen-bonded cyclic trimer as the basic supramolecular motif. The three units generated by a three-fold symmetry axis are distinguished by colors. b) Intersecting solvent channels in crystal phase **I** of **3a**. c) Side view of the helical arrangement of molecules **3a** (represented as sticks) around the 6_5 screw axis in crystal phase **II**. Solvent molecules entrapped inside the channel are represented as spheres of the van der Waals radii; d) top view of the same channels deprived of solvent molecules. e) Capsules (shaded in yellow) with included solvent molecules (space-fill representation) formed by molecules **3b** (represented as sticks). Green dashed lines indicate intermolecular hydrogen bonds.

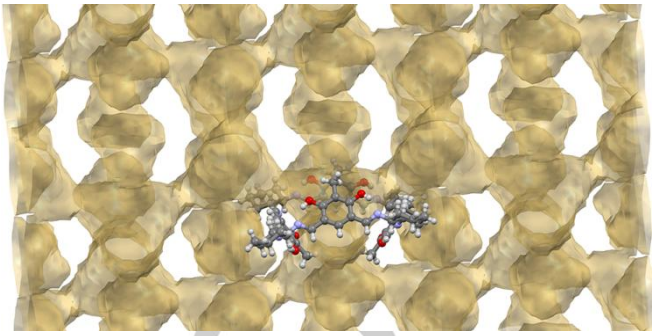


Figure 5. 3D system of interconnecting channels forming possible migration paths for guest molecules in the crystal of *meso*-**5a**.

In crystals of phase **II**, the molecules situated around the 6_5 screw axis form a helical channel (Figure 4c) with water and ethanol molecules all entrapped inside it. The percentage of the unit cell volume occupied by the solvent molecules is lower than in phase **I** and amounts to 20% (Figure 4d).

Close similarity of macrocycles **3a** and **3b** contrasts with their packing arrangements. Macrocycle **3b** crystallizes with four symmetry independent, but structurally very similar molecules in a triclinic unit cell. The structure contains two types of isolated 0D voids (Figure 4e) occupied by solvent molecules and the contribution of these voids to the unit cell volume equals to only 9%.

In the accessible volume of 267.8 Å^3 there are two molecules of ethanol and six and a half molecules of water involved in multiple hydrogen bonds, so the packing of solvent molecules is much more compact than in the two crystal phases of **3a** as well as in the crystal structure of *meso*-**5a**. Unlike **3a** and **3b**, the molecules of *meso*-**5a** preserve in the crystal the enol-imine form (Figure 3b). The mean value of the X-ray determined C–OH bond length amounts to 1.339(2) Å, (Table S4), in agreement with the mean value of 1.345(10) Å calculated for 1194 salicylimine fragments being the OH tautomers deposited in CSD data base.[14] The *meso*-**5a** crystallizes as chloroform solvate in space group $I4_1/a$. Like in the crystals of phase **I** of **3a**, solvent molecules occupy channels of varying cross-sections that extend in three dimensions. The set of interconnecting channels (compare Figs. 4b and 5) forms possible 3D migration paths for entrapped solvent molecules. The volume of unit cell occupied by these channels in the crystals of *meso*-**5a** equals to 30%. For comparison, in the three crystal structures of [4+4] imine macrocycles available in the CSD the contribution of voids to the unit cell volume does not exceed 16%.

In summary, in a single step we have successfully synthesized representative members of new class of highly functionalized macrocycles. The control of the structure and stoichiometry was achieved by the proper choice of reaction conditions, propensity of reaction products for tautomerisation and their solubility. Formation of *meso* heterochiral diastereomers by hydroxylated polyimine macrocycles has not been previously reported. Such macrocycles constitute examples of social self-sorting, unique for this type of compounds. Due to the stability of *meso*-**5a** crystals as

compared to the crystals of other resorcinsalens, this and related compounds give a chance for obtaining new organic, potentially porous materials. The work is currently under progress in our laboratory.

Experimental Section

For synthetic procedures, full characterization of all new compounds, calculation details and X-ray diffraction experiments details see the Supporting Information. CCDC 1588862-1588865 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: macrocycles • structure elucidation • tautomerism • imine • inclusion compounds

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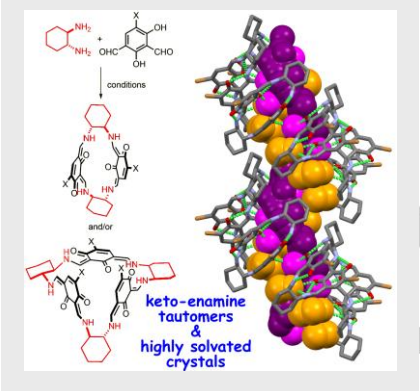
Layout 1:

COMMUNICATION

A combination of $^{1}H/^{13}C$ NMR and MS spectra as well as SCXRD and DFT studies provided compelling evidence for a one step synthesis of a new class of highly functionalized polyimine macrocycles**.** Selectivity in macrocyclization reactions was achieved by functionalization of the substrate, change of solvent and susceptibility to tautomerism. Highly solvated crystals show 3D system of interconnecting channels containing loosely bound guest molecules.



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One-step Access to Resorcinsalens – Solvent Dependent Synthesis, Tautomerism, Self-sorting and Supramolecular Architectures of Chiral Polyimine Analogues of Resorcinarene