Triphenylamine-based rhombimine macrocycles with solution interconvertable conformation†

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Three imine macrocycles having rhomboidal shape were synthesized in good yields by [2+2] cyclocondensation reaction between equimolar quantities of (R,R)-1,2-diaminocyclohexane and 4,4′-*bis*formyl triphenylamine derivatives. The macrocycles structure was assigned by electrospray ionization mass spectrometry (ESI-MS), ^{1}H-NMR, and elemental analysis. UV, FTIR spectroscopy, and TG measurements were also used to characterize and prove the structure of these compounds. A conformational modification arising out of the rotation of triphenylamine group around the flexible cyclohexane-N bonds was observed in solution by ^{1}H-NMR and UV spectroscopy for all three macrocycles.

Introduction

The shape-persistent imine macrocycles[1] derived from aromatic dialdehydes condensed with aliphatic[2–6] or aromatic diamines[7] have attracted much attention in the past years due to their exotic shapes, academic interest, and potential applications in supramolecular chemistry. It has also gained interest in the materials science field as host–guest complexes, tubular channels, porous organic solids, nanocapsules, and nanoreactors, *etc.*[1b,8] They are built using condensation reaction between rigid diamines and π-conjugated dialdehydes and have specific two-dimensional (2D) shapes: rhombus, triangle, rectangle, *etc.* The most frequently encountered shapes of imine macrocycles are rhomb formed by [2+2] cyclocondensation or triangle obtained by [3+3] cyclocondensation. Unlike arylene-ethynylene macrocycles,[8] imine homologues can be obtained in a single step method with an almost quantitative yield. The common strategy used for the obtaining of imine macrocycles is based on one-pot synthesis, using Schiff base condensation reaction between aldehyde and amine compounds. The reaction is reversible, highly selective, and the intermediate reaction products are dynamically interchangeable. The composition of the library is determined by the thermodynamic stability of the library members.[9] Therefore, under thermodynamically controlled conditions and dynamic combinatorial chemistry, the imine condensation proceeds to completion, generating with almost quantitative yield, the most stable mixture of potential macrocycles.[10] The reversibility of the imine condensation allows it to self-correct the eventual errors in the bond-forming step and finally, to obtain with high efficiency, the most thermodynamically stable products. Formation of macrocyclics is favored over linear oligomerization if diamine, dialdehyde, or both reactants have structures favoring the formation of cyclic products.[2h] The size and shape of the macrocycle can be controlled by the selection of the diamine and dialdehyde geometry.[2c,2e] (1*R*,2*R*)-*trans*-1,2-Diaminocyclohexane is a rigid molecule with *ortho* NH_2 functions occupying equatorial positions and having in plane-projected angle between the two C–NH_2 close to 60°. With linear dialdehyde, *i.e.* terephthaldehyde or its derivatives, chiral trianglimines are obtained as main product by [3+3] cyclocondensation,.[2a,2d,2e3,4,5a,5c] When dialdehyde has a bent structure with an angle between aldehyde groups close to 120°, then rhombimines are obtained by [2+2] cyclocondensation,.[2c,4c,4f,5b6] Therefore, the shape of macrocycle can be anticipated from dialdehyde and diamine geometry. Imine macrocycles with more complex structures and aesthetically three-dimensional (3D) shapes have been also reported by Severin *et al.*[10] and Warmuth *et al.*[11] by thermodynamically controlled condensation reactions from multicomponent mixtures in a single step.

The purpose of this paper is to present our results about synthesis and the characterization of rhombimine macrocycles obtained by cyclocondensation of 4,4′-diformyl triphenylamine derivatives with (R,R)-1,2-diaminocyclohexane. In solution these macrocycles showed a conformational modification induced by rotation of triphenylamine group around two Cyclohexyl-N=C-Aryl bonds. The isomerization was evidenced by NMR and UV spectroscopy.

Results and discussion

By reacting 4,4′-*bis*formyl triphenylamine (**1a**), 4,4′-*bis*formyl 4″-bromo triphenylamine (**1b**) or 4,4′,4″-*tris*formyl triphenylamine derivatives (**1c**) with (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane (**2**), we prepared three triphenylamine-based imine macrocycles (**3a–c**) having rhomb shape (Scheme 1). The reaction is a [2+2] cyclocondensation.

Rhombimine **3a** was previously synthesized by Gawronski *et al.*[2g] and reported without a detailed research of its spectral data.

Condensation of **1a–c** with **2** was carried out in CH_2Cl_2 at room temperature or under reflux, yielding the three rhombimines in nearly quantitative yield without the use of dehydrating conditions and without any external template. It is noteworthy that the [2+2]

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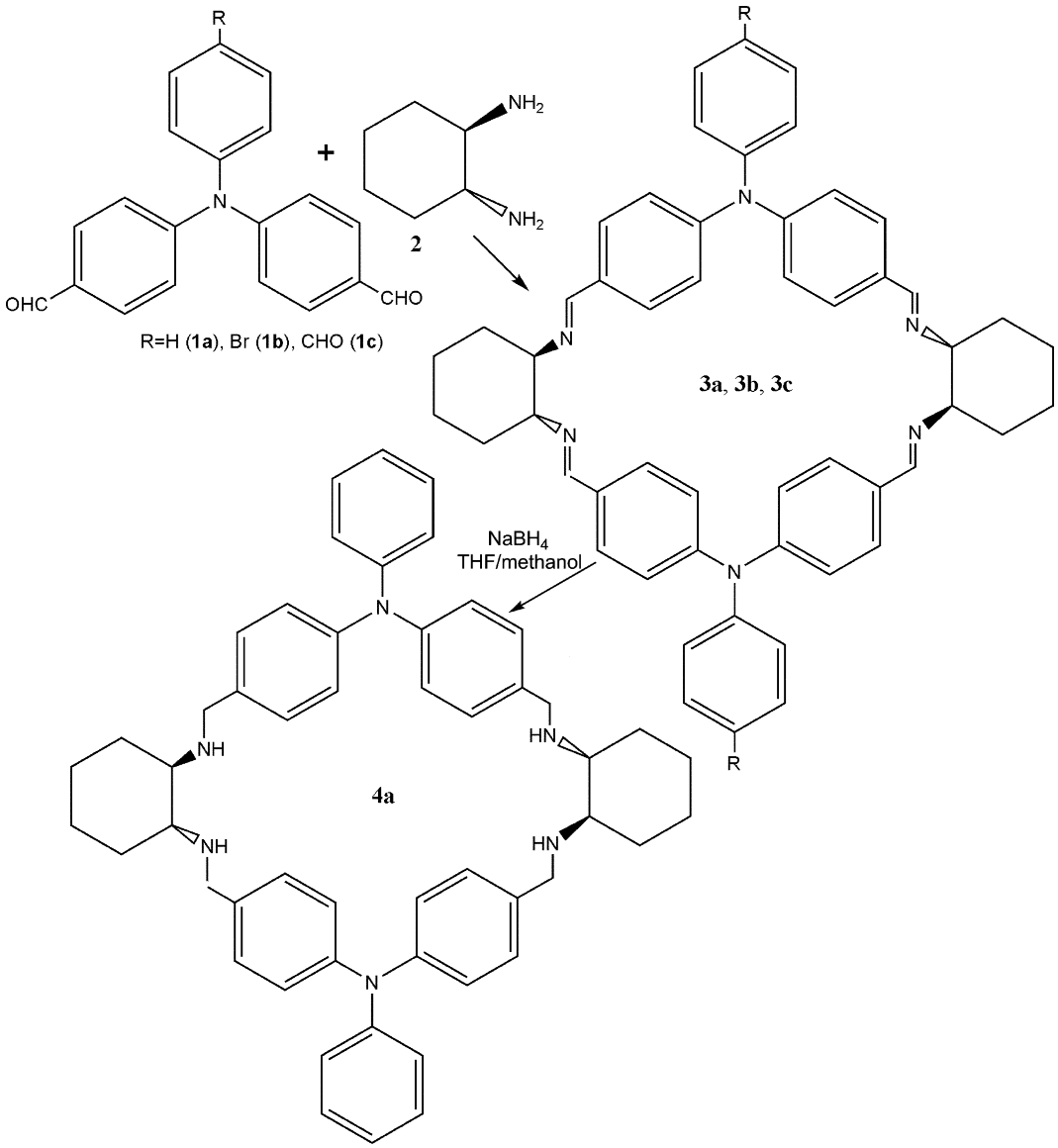
† Electronic supplementary information (ESI) available: Experimental section, ESI-MS spectra, TG measurements, FTIR spectra, in time-variable NMR spectra, syn and anti isomers. See DOI: 10.1039/c004999a



Scheme 1 Synthesis of functionalized triphenylamine-based rhombimine macrocycles by [2+2] cyclocondensation of 4,4′-*bis*formyl triphenylamine derivatives (**1a–c**) and (*R*,*R*)-1,2-diaminocyclohexane (**2**).

macrocycle is the main product (observed by ESI-MS) of the crude product of all condensation reactions between **1** and **2** at equimolar feed ratio (see ESI†). The rhombimine shape of macrocycles **3** was anticipated because (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane (**2**) is a rigid molecule with equatorial positioned *ortho* NH_2 functions and the angle between the two cyclohexyl-N bonds is close of 60°. Dialdehydes **1a**, **1b** and **1c** have the dihedral angle between OHC–C_6H_4–N–C_6H_4-CHO bonds close to 120°. Therefore, free-strain macrocycles (**3a–c**) of rhomboidal shape should be obtained as the dominant product by [2+2] cyclocondensation and all analysis methods have confirmed this assumption.

Characterization of imine macrocycles

All three macrocycles were highly soluble in halogenated solvents; CH_2Cl_2, $CHCl_3$ or CCl_4 and less soluble in polar solvents (DMF, THF or DMAc), and insoluble in methanol and ethanol. Macrocycles retained solvent molecules and even after 24 h of vacuum drying at 50 °C, the presence of solvent and other low molecular compounds was observed by TGA or ^{1}H-NMR spectroscopy. The differences between calculated and founded values given by elemental analysis can be explained by retention of the solvent in macrocyclic cavity. The thermal stability of macrocycles was studied by TGA measurements in a nitrogen atmosphere. They showed a high thermal stability, up to 340 °C, with an onset degradation temperature at 348 °C (**3a**), 322 °C (**3b**), and 300 °C (**3c**), respectively, and a high melting temperature (325 °C for **3a**) (see the ESI†). The high thermal stability is due to the imine structure and the absence of end groups. The weight loss (1–10%) observed in the temperature range 80–200 °C is caused by the release of the solvent molecules that left their host. The loss of solvent was also observed from the first heating scan

of DSC studies by an endothermic effect. In the second DSC heating scan, this endothermic effect was absent. The DSC runs showed no glass transitions occurred in the temperature range –40/+300 °C. The structure of the compounds was assigned on the basis of ESI-MS, FTIR, ^{1}H-NMR and UV spectroscopy. X-ray data also showed that all the compounds are crystalline but single crystals suitable for exact structure determination could not be obtained.

The FTIR spectra of macrocycles **3a** and **3b** does not show any absorption for aldehyde C=O (1680 cm^{-1}) and amine N–H (3390 and 3315 cm^{-1}) stretches, while **3c** shows the presence of C=O absorption band (1695 cm^{-1}). The characteristic peaks corresponding to the stretching vibration of the *ν*CH=N bond (1634 cm^{-1}) and *ν*C=C bond (1597 and 1507 cm^{-1}) are observed for all compounds. The absorption bands localized between 697 and 837 cm^{-1} (*ν* C–H aromatic from benzene rings), 1268–1286 cm^{-1} (the stretching vibration of tertiary amine) and 2856–2930 cm^{-1} (C–H aliphatic from cyclohexane) are also evident in **3a**, **3b** and **3c**.

The ESI-MS spectrum of **3a** (macrocycle solution in chloroform–methanol = 3/1) presented in Fig. 1 shows signals with the molecular ion peak (M+H$^+$) at 759.28 Da (**3a**$^+$+1) and a fragmentation ion peak at 380.13 Da. That is consistent with the chemical structure proposed in Scheme 1. For **3b**, molecular ion peak is at 917.09 Da (**3b**$^+$+1), 839.2 Da (**3a**$^+$ +1-Br) and fragmentation peak at 458.06 Da. The peak at 478.06 Da could be assigned to the linear [1+1] compound or to ions (**3b**+2Na$^+$)/2.

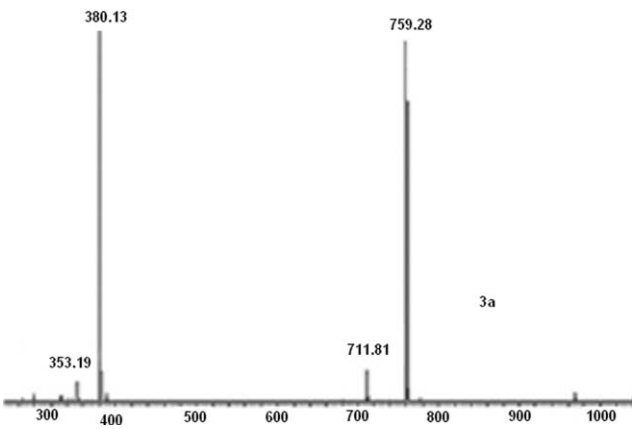


Fig. 1 ESI-MS for **3a**.

The ESI-MS spectrum of the crude product **3c** displayed a major signal with the molecular ion peak at 815.36 Da (**3c**$^+$ +1).

Macrocycle **3a** was purified by dissolving in DMF at high temperature, but the solution immediately became gel-like by cooling. The macrocycle was then separated by filtration and drying. The gel structure results due to inclusion of solvent as guest in macrocyle's cavity. Tanaka *et al.*[12] have recently reported obtaining a gel when the macrocyle synthesized by [3+3] cyclocondensation of *trans*-1,2-diaminocyclohexane with azobenzene-4,4′-dicarbaldehyde was dissolved in benzene.

The ^{1}H-NMR spectrum of **3a** fresh solution in $CDCl_3$ is well resolved (Fig. 2). It illustrated signals assigned to the proposed structure in Scheme 1, with only a singlet signal at 7.91 ppm for the four imine protons suggesting a highly symmetric macrocycle. Some signals positioned at 7.26 ($CHCl_3$), 2.96, and 2.88 ppm (DMF) and 1.69 ppm came to solvents used in different steps. By maintaining **3a** in solution, its proton NMR spectrum evidenced significant modifications, mostly observed for the imine, aromatic, and –CH–N= protons region (Fig. 3).

Thus, new signals appeared for imine (8.11–8.13 ppm), aromatic (7.42–7.44 ppm), and –CH–N= diamine (3.35 ppm) protons, suggesting the presence of two non-equivalent triphenylamine groups. The intensities of the new signals integrals are correlated between them. This behavior was observed for all three rhombimines.

Having in mind the reversibility of imine condensation reaction, the first thing done was to check if an expansion or hydrolysis of macrocycle is responsible for NMR spectrum changes. The ESI-MS spectrum of **3a** was unchanged after evaporation of NMR chloroform solution, showing the same molecular ion peak at 759.28 Da and fragmentation peak at 380.13 Da. Therefore, the modifications observed by NMR spectroscopy could only be assigned to an isomerization or hydrolysis process.

It was concluded that the MS and NMR data support structures of [2+2] macrocycles for the reaction products. On the other hand, the NMR spectrum of macrocycle is, as a rule, an overlap of spectra arising from several conformers. The structure of these isomers can be intuited by considering that:

(i) the cyclohexyl rings are in the chair conformation, which is the most stable one, and

(ii) the fact that a conformation of a macrocycle can be changed to the other *via* the concerted rotation of triphenylamine group around flexible cyclohexane-N bonds.

The imine linkage in Schiff base compounds could adopt *E* or *Z* configuration, therefore the four imine linkages in macrocycles **3a–c** would exist as all-*E*, all-*Z*, or mixture of *E*-*Z* configuration. However, the *E* isomer has lower energy when compared to the *Z* isomer and it is accepted that all-*E* isomer is the product obtained due to its higher thermodynamic stability. In addition, all-*E* isomer can exist in many conformations, according to the orientation of the lone electrons pair located at imine nitrogens as *syn* or *anti* rotamers. The lowest energy was observed for the structures where the lone electrons pair is oriented outside (*exo*) of the macrocycle, as *syn* conformer where imine and =N–CH– (from cyclohexane) hydrogens are in *syn* position.[2a]

As normally expected all imine bonds have *E* configuration. One can conclude that the connection bridges between the two cyclohexyl rings of a macrocycle may be in one of three forms due to relative orientation of imine bond: A (*syn-syn*), B (*anti-anti*) and C (*anti-syn*), as well as in the forms A′, B′ or C′, as mirror images of A, B and C, respectively. MM2+ molecular modeling of fragments and macrocycles indicated a preference for the fragments in order: A > C>B, and also for [2+2] macrocycles in order: A–A′ > C–C′ > B–B′ (see ESI†). Therefore, twelve macrocycle conformations would result by combination of fragments A (A′), B (B′) and C (C′) but only A–A′ and B–B′ forms have centers of symmetry. Their imine protons (–N=CH–) are magnetically equivalent and, consequently, they give singlet NMR signals. On the other hand, the other isomers have plane symmetry and the imine protons will give two singlet NMR signals because they are two by two magnetically equivalent. Since there being a singlet signal for the all imine protons, the spectrum in Fig. 2 must belong to one of the isomers A–A′ or B–B′. Being placed at the lowest field in comparison with other imine signals, this signal (7.91 ppm) may be assigned to the isomer A–A′ where the imine protons are placed

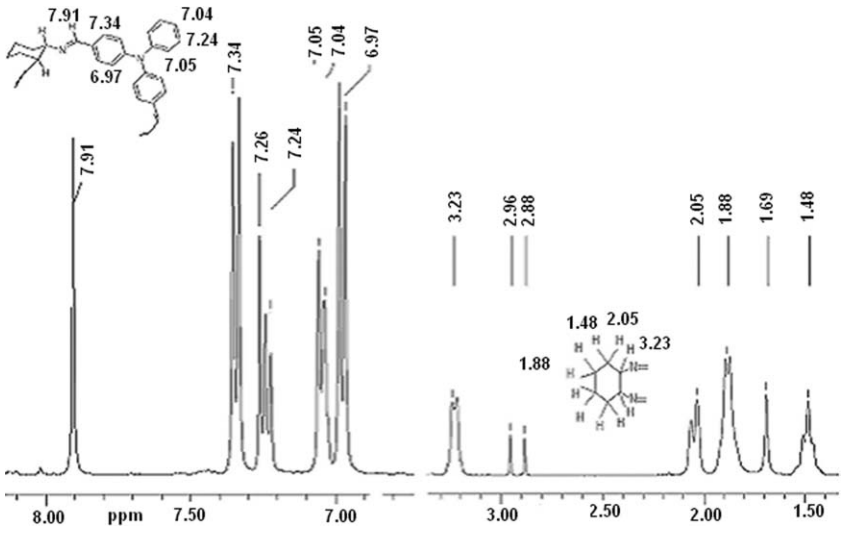


Fig. 2 ^{1}H-NMR spectrum ($CDCl_3$) of **3a** after purification from DMF.

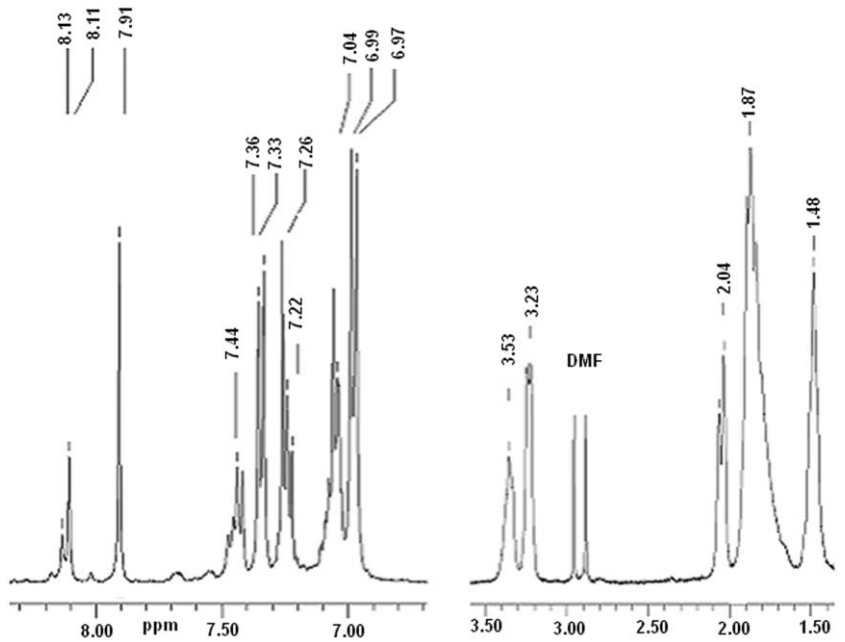


Fig. 3 ^{1}H-NMR spectrum ($CDCl_3$, 25 °C) of **3a**, (presented in Fig. 2) registered again after several days.

inside of the macrocycle, therefore feeling an aromatic ring current shielding which is stronger than in other isomers. An interesting observation is that the spectrum presented in Fig. 2 changes when the symmetrical macrocycle is maintained in solution; the signal at 7.91 ppm decreases while new imine proton signals appear between 8.1 and 8.25 ppm (Fig. 3). This fact might be explained by assuming that the macrocycle A-A′, changes to other isomer or to intermediate isomers by rotation of triphenylamine group around cyclohexyl–N single bonds.

Therefore, the changes observed in the NMR spectrum of **3a** can be assigned to an isomerization (interconversion) process that takes place in solution (Fig. 4). Interconversion takes place *via* the concerted rotation of triphenylamine group around flexible cyclohexane-N bonds. It was observed from NMR studies that the rotamer inversion is enhanced by increasing of the temperature

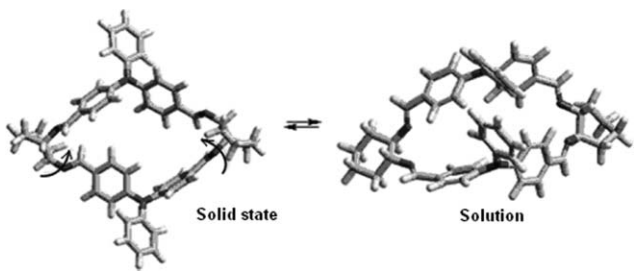


Fig. 4 Modification of the macrocycle conformation in solution.

and solvent polarity. Furthermore, using 2D NOE analysis, we investigated the 3D conformational structure of **3a**. The NOE correlations were observed between the imine proton (signal at 7.91 ppm), the –CH–N= (signal at 3.23 ppm), and imine *ortho*

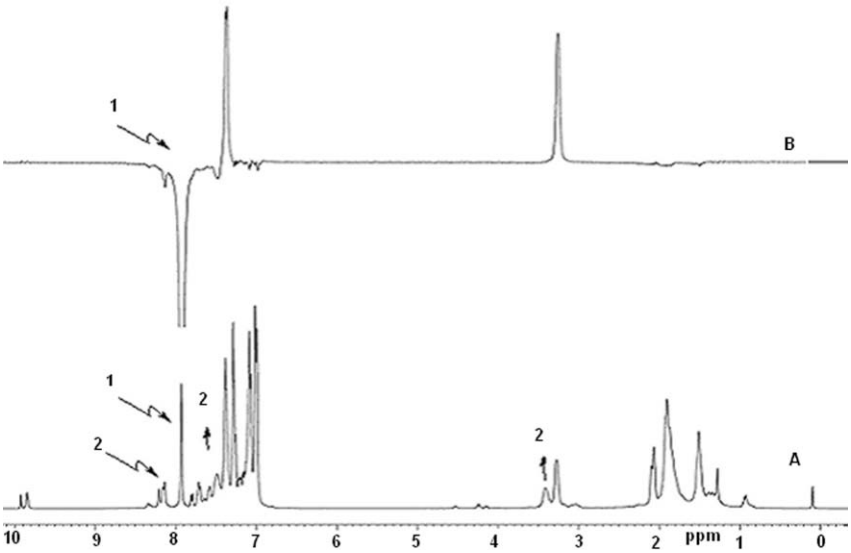


Fig. 5 Reference spectrum (A) and the ^{1}H-^{1}H NOE difference spectrum (B) for irradiation (1) on the imine proton resonance in the symmetrical isomer. There are also marked the NOE effects for the irradiation (2) on imine proton resonance in another isomer.

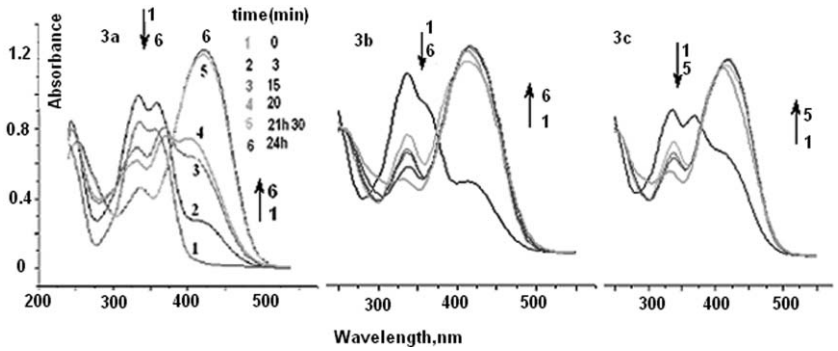


Fig. 6 In time-evolution of UV spectra ($CHCl_3$) of **3**.

phenyl (signal at 7.34 ppm) protons. The NOE difference spectra were recorded for irradiation on the imine proton resonances of the symmetrical isomer and of an unsymmetrical one (Fig. 5). As expected, one observes magnetic polarization transfer to the nearest protons, namely to the hexyl protons –CH–N= and to the aromatic protons in *ortho* position relative to the imine substitution. NOE effects between other protons were not clear due to the signal overlapping. In addition, due to the rather long acquisition times (3–5 h), the spectra became complicated due to the spontaneous isomerization. For instance, the starting spectrum for Fig. 5 was that of the symmetrical isomer, but significant signals from unsymmetrical isomers are already present at the end of the experiment.

Dibromine- and dialdehyde-functionalized rhombimines (**3b** and **3c**) were synthesized by a similar protocol as **3a**, reacting **2** with **1b** and **1c**, respectively, and recrystalized from tetrahydrofuran. The ^{1}H- NMR spectra are similar with that of **3a**, having all-*syn* structure. Therefore, a *syn* conformation can be assigned for **3b** and **3c**. The signal at 9.81 ppm is assigned to protons from CHO groups of **3c**. In solution, a rotamer inversion was also observed for both macrocycles.

UV absorption spectra of **3** showed important changes in the shape and positions of the absorption maxima of the $CHCl_3$ solution (Fig. 6). Thus, **3** in all-*syn* conformation presented three absorption maxima (in $CHCl_3$ solution), the first two being characteristic of the π–π* transitions in triphenylamine group (240–250 and 336 nm). The third absorption (356 nm) can be assigned to n-π* conjugation between the lone electron pair of the imine nitrogen conjugated with triphenylamine moiety. After a few minutes, the solutions of macrocycles showed a new and broader absorption band above 400 nm. In time this absorption band was bathocromically shifted and its intensity gradually increased in correlation with the disappearance of the absorption at 356 nm. A stationary state was reached after 24 h. We assume that, in $CHCl_3$ solution, the all-*syn* macrocycles **3** spontaneously isomerize to thermodynamically more stable rotamers, having better n-π* electronic conjugation between imine and triphenylamine bridge. This behavior could be explained considering the sterical structure of the Schiff base compounds. It is recognized that the imine group itself is nonplanar with adjacent groups of aldehyde and amine. The amine substituent at –N=C is out of the imine group plane with 40–55°, while the aromatic ring linked at –CH= is out of

plane with 10°, but in the opposite sense.[13] This arrangement allows lone electron pair of nitrogen to be in conjugation with the amine substituent (cyclohexyl) rather the π-conjugated imine functionality in symmetrical isomer. By rotation of triphenylamine groups around cyclohexane-N simple linkages, the conjugation of lone electron pair of imine nitrogen with triphenylamine group is possible having an effect on electronic absorption maximum (bathocromic shifting). Moreover, this rotation allows apparition of a transanular electronic interaction between the cofacial benzene rings of triphenylamine. The conjugation length increased also *via* the through space interactions, similar with [2,2] paracyclophane.

Gawronski *et al.*[2g] have stated that rhombimine **3a** is flattened around atom N that leads to puckering of the molecule about the imine fragments and is quite unstable in solution, making its crystallization and study difficult. In our opinion, macrocycles **3** are enough stable to be purified but in solution they changed their 3-D structure toward a more favorable conformation.

Reduction of **3a** with $NaBH_4$ in a methanol–THF mixture gave rhombamine **4a** in almost quantitative yield. The NMR spectrum showed the disappearance of the imine proton signals (7.9–8.2 ppm) and the appearance of new signals at 3.5–3.9 ppm (–CH_2–) and 2.3 ppm (–NH–). Rhombamine **4a** shows absorptions only at 250 and 310 nm, the absorption associated to imine group being absent. Furthermore, the UV and ^{1}H-NMR spectra were unchanged in time.

Conclusions

In this study, three imine macrocycles having rhomb shape were synthesized by [2+2] cyclocondensation of (*R*,*R*)-1,2-diaminocyclohexane with 4,4′ bis formyltripenylamine, 4,4′ bis-formyl 4″-bromo triphenylamine, and 4,4′,4″-trisformyl triphenylamine. They were characterized by a combination of ESI-MS, ^{1}H-NMR, FTIR, UV, and thermal methods. Imine linkages are in *E* configuration and all-*syn* conformation, concluding all macrocycles in this conformation have low energy and highly symmetrical structure. In solution, with rotation of a triphenylamine group around cyclohexane–nitrogen bonds, macrocycle may interconvert to a more stable conformational isomer with enhanced n-π* conjugation between triphenylamine and imine linkages and π stacking interactions between triphenylamine groups. In solution, the rotation is monitored by changes in the NMR and UV spectra. All three imine macrocycles are functional compounds and they could be used in chemical or electrochemical oxidative polymerization (**3a**), metal-catalyzed polycondensation of Suzuki, Heck or Stille type (**3b**) and Schiff base polycondensation with diamines (**3c**) to obtain polyrhombimines.

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