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Synthesis and characterization of new methyl-substituted azomethine-siloxane liquid crystal macrocycles

Influence of the methyl-substitution on the cycle formation

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Summary

This article is devoted to the synthesis of new methyl-substituted azomethine-siloxane macrocyclic dimers. They have been obtained by an intramolecular interiminination reaction of linear polydimethylsiloxane-*block*-polyazomethine main-chain liquid crystal polymers. The reaction has been studied on mono-, di- and tetramethyl-substituted azomethine moities to estimate the influence of methyl-substitution on the feasibility of the reaction. Specific conditions (diluted solution, strong acid catalysis, recrystallization) led to pure macrocyclic dimers, which have been characterized by SEC, ^{13}C NMR and X-ray crystallography. This reactional process is the first step for synthesis of substituted liquid crystal macrocyclic structures, which constitute a new family in the liquid crystal polymer field.

Introduction

In the study of linear polyazomethine-*block*-polysiloxane $(AB)_n$ copolymers appeared the existence of macrocyclic compounds $(AB)_2$ in addition to the expected linear polymers, when the syntheses are carried out in solution. Linear main-chain liquid crystal polymers have been obtained (see in this article scheme 3 with R: H) (1,2).

It has been shown that the linear copolymers can be rearranged into isomolecular macrocyclic dimers through an intramolecular transimination equilibrium which depends on the following parameters: concentration, temperature, nature of solvent, spacer length (see scheme 2 with R: H) (3-5). Thus new molecules offering both a macrocyclic host geometry with highly complexing functions (imine) and a very rich liquid-crystal character have been obtained.

Such a cyclic structure is in fact a basic one, whose main interest probably lies in the substitution either with non-reactive substituents, to acceed to new thermotropic properties, or with reactive ones leading to new highly organized macromolecular structures. These two aspects focus strongly our interest.

In this article in spite of methyl-substitution the transimination ability has been shown. It was naturally essential to prove this point, as it is the first step of a process allowing to obtain a new family of liquid-crystal macrocycles. Other successfull examples will be further described with various substituents, reactive or not (6).

The methyl-substitution has been studied from mono- to tetra-substitution on the central aromatic ring of the rod-like mesogen unit. Only syntheses and structural aspects are developped here. On one hand, a complete structural and conformational analysis (liquid and solid state NMR and X-ray crystallography) and, on the other, a deep study of liquid-crystal properties, will be further published.

Experimental

Materials - All solvents with a purity higher than 99.0% were used without further purification. 1,4-diamino-2-methyl-phenylene (MM), 1,4-diamino-2,5-dimethyl-phenylene (DM) and 1,4-diamino-2,3,5,6-tetramethyl-phenylene (TM) , allylbromide (from Aldrich; >99%); 4-hydroxybenzaldehyde (Aldrich; >96%) was used without further purification as 4-allyloxy benzaldehyde was recrystallized, and obtained with a purity higher than 99%. M'$_2$ and D$_4$ (for M'$_2$D synthesis) were supplied by Rhône-Poulenc, as well as the Karsted catalyst for hydrosilylation (in hexane solution; conc: 11%, g elementary platinum/solution volume (ml)). Trifluoroacetic acid (TFAA) (Aldrich; >99%).

Syntheses - All reactions were carried out in a glass reactor equipped with a condensor, a magnetic stirring and swept by dry nitrogen (free of oxygen traces). The temperature was controlled with a PID regulation device.

- *Models* - All syntheses were carried out in 250 ml flask; and after purification all models were characterized by ^{1}H and ^{13}C NMR, Size-exclusion chromatography (SEC), FT-IR and elementary analysis. Their purity is always higher than 99%.

MMM - A mixture of MM (6.6 g; 0.033 mol), 4-methoxy-benzaldehyde (9.0 g; 0.066 mol) and 10 ml acetic acid was heated at 80°C and stirred. After one hour 25 g sodium carbonate are added and MMM is precipitated in 1l water. After recrystallization in hexane, MMM is yellow flake-shaped. **BMM** - As MMM with MM (5.00 g; 0.025 mol) and 4-butoxy-benzaldehyde (9.0 g; 0.05 mol). **MDM** - As MMM with DM (4.49 g; 0.033 mol), 4-methoxy-benzaldehyde (9.0 g; 0.066 mol). Recrystallization in 700 ml acetone; MDM is yellow flake-shaped (yield: 63%). **BDM** - As MMM with DM (3.40g; 0.025 mol) and 4-butoxy-benzaldehyde (9.0 g; 0.05 mol). Recrystallization in 500 ml acetone; MDM is yellow flake-shaped (yield: 45%). **MTM** - A mixture of TM (5.42 g; 0.033 mol), 4-methoxy-benzaldehyde (9.0 g; 0.066 mol) and 150 ml methanol was refluxed and stirred during 2 hours. The solution is cooled to 0°C. A yellow powder precipitates and is filtrated. After recrystallization in 200 ml chlorobenzene and drying at 30°C under vacuum, MTM is a yellow powder (yield: 67%). **BTM** - As MTM with TM (4.15 g; 0.025 mol) and 4-butoxy benzaldehyde (9.0 g; 0.05 mol). Recrystallization is carried out in 200 ml cyclohexane. BTM is yellow flake-shaped (yield: 46%).

- *Reactants* - 4-allyloxy benzaldehyde (AB) is synthesized according to (7).

AMM - A mixture of MM (3.66 g; 0.03 mol), AB (9.72 g; 0.06 mol) and 20 ml acetic acid was heated at 80°C and stirred. After one hour 25 g sodium carbonate are added and AMM is precipitated in 2l water. After recrystallization in methanol, AMM is yellow flake-shaped (yield: 72%). **ADM** - As for AMM with DM (4.66 g; 0.034 mol) and AB (11.02 g; 0.068 mol) in 200 ml ethanol. Refluxing during 4 h. Filtration at 0°C. ADM is recrystallized in 1l acetone (yield: 65%). **ATM** - As for AMM with TM (4.57 g; 0.028 mol) and AB (9.02 g; 0.056 mol) in 100 ml ethanol. Refluxing during 2 h. Filtration at 0°C. ATM is recrystallized in 300 ml chlorobenzene. ATM is yellow crystal-shaped in the 1-4 mm length area (yield: 65%).

M'$_2$D - M'$_2$D is obtained according to (8); the reaction consists in an equilibration between M'$_2$ and D$_4$ in the presence of silicoaluminate at 50°C (aM'$_2$ + b D$_4$; a/b=4). M'$_2$D is distillated under vacuum in an adiabatic spinning band column (purity>99%).

- *Interimination on models* - All interimination reactions were carried out with 10^{-3} mol methoxy- and 10^{-3} mol butoxy compounds in 25 ml chlorobenzene at 120°C without added catalyst. For kinetic studies samples were immediately injected in a size-exclusion chromatograph.

- *Polymer syntheses* - All reactions were carried out in a 500 ml reactor equipped with a 50 ml dropping funnel.

PMM - A mixture of AMM (12.30 g; 0.03 mol) and 250 ml anhydrous toluene is heated under stirring to 60°C. 15 µl of the Karsted catalyst solution (8.5 x 10^{-6} eq Pt) are added. Then a 50 ml toluene solution of M'$_2$D (6.24 g; 0.03 mol) is slowly dropped (1 hour). Then the reaction mixture is heated to 100°C during 1 h more. After elimination of 1/3 solvent under vaccuum, polymer is precipitated in 1l methanol. PMM is obtained by filtration and drying at 30°C. **PDM** - As for PMM with ADM (12.74 g; 0.03 mol). **PTM** - As for PMM with ADM (13;58 g; 0.03 mol).

- *Macrocycle syntheses* - All reactions were carried out in a 500 ml flask.

CMM - PMM (12.0 g) is dissolved in 250 ml toluene and heated to 100°C. Then 10 µl trifluoacetic acid are added and temperature is hold during 1h. Raw CMM is obtained by self precipitation at room temperature after 24 h. CMM (4 g) is recrystallized in 100 ml DMF. Precipitation is obtained at 70°C. CMM is yellow flake-shaped. **CDM** - PDM (3.33 g) is dissolved in 400 ml chlorobenzene and heated to 120°C. Then 10 µl trifluoacetic acid are added and temperature is hold during 1h. Raw CDM is obtained by precipitation in 1l methanol. CDM (2 g) is recrystallized in 100 ml chlorobenzene. Precipitation is obtained in methanol. CDM is yellow crystal-shaped (several mm length). **CTM** - PTM (4.3 g) is dissolved in 400 ml chlorobenzene and heated to 120°C. Then 40 µl trifluoroacetic acid are added and temperature is hold during 1h. Solvent is then distilled under vacuum; the viscous medium is washed with hexane. CTM precipitates and is recrystallized with DMF (2.25 g with 50 ml DMF; precipitation occurs at 75°C). CTM crystallize in large yellow crystals (length ≈ 5 mm).

One-step macrocycle syntheses

All syntheses may be carried out in a one-step process using either toluene or chlorobenzene both as polymerization and cyclization solvent (pure or as mixture). The cyclization is then done by dilution and acid addition as described above.

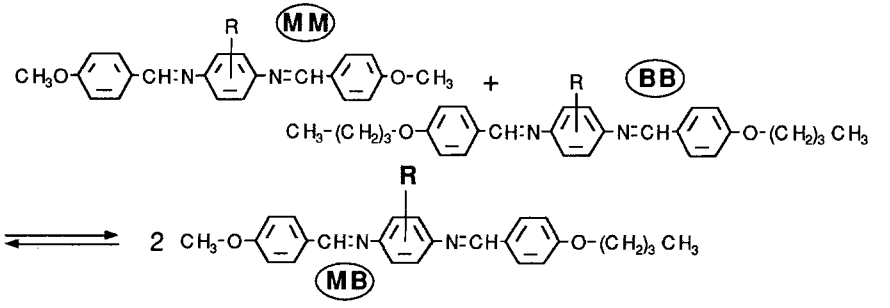
Analytical techniques

- *NMR spectroscopy* - ^{13}C NMR spectra were recorded on a Bruker AM300. The sample solutions in $CDCl_3$ or CD_2Cl_2 were prepared in 5 mm tubes. Experiment frequency:75.4 MHz; pulse angle: 90° (5.15 ms) ; spectral window: 16000 Hz; recycling delay: 5 s; acquisition number: 2048). Free induction decays were stored in 64K. Chemical shifts were calculated relatively to $CDCl_3$: 77.0 ppm or CD_2Cl_2: 53.1 ppm.
- *Size-exclusion chromatography* - Chromatograms were registered on a Waters chromatograph equipped with a Waters refractometric detection. Columns were of PL-gel (50 + 100 A: interimination on models) or µl-styragel (10^4 + 10^3 +500 A: polymers and macrocycles) types. The data treatment was carried out on a Shimazu data processor.
- *X-ray crystallography* - A selected crystal was set up on an automatic diffractometer. Computations were performed by using CRYSTALS program adapted on a MicroVax II. The view of the molecule is performed using CAMERON.

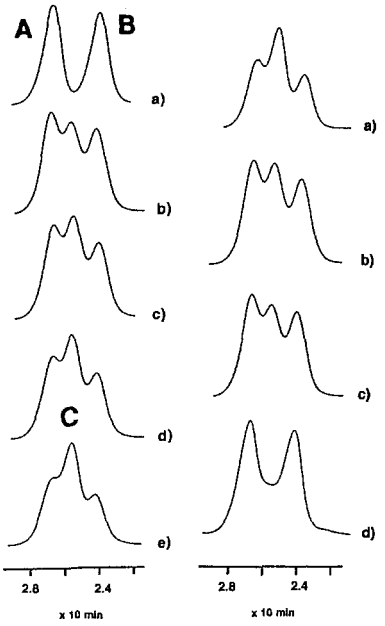
Results and discussion

a) Model study of the transimination reaction

Macrocycle synthesis depends on feasibility of the interimination reaction on one polymer chain (scheme 3). In order to verify the interimination ability on methyl-substituted structures, some model reactions have been carried out (see experimental part). Influence of the methyl-substitution has been studied. Evidence of interimination reaction has been shown by following a mixture of two azomethine compounds (α,ω-dimethoxy (MM) and α,ω-dibutoxy (BB)):



Scheme1



(Fig. 1)

(Fig. 2)

Fig. 1 - SEC of the dimethyl model reaction (MDM/BDM) versus reaction time. **a**) t=0h; **b**) 6h; **c**) 10h; **d**) 16h; **e**) 24h.

Fig. 2 - SEC of the various model systems (reaction time: 6h). **a**) non-substituted; **b**)MMM/BMM; **c**) MDM/BDM; **d**) MTM/BTM.

b) Characterization of the methyl-substituted azomethine structures by ^{13}C NMR

In order to characterize on one hand the purity of models and, on the other, to assign the further macrocyclic dimers, all models have been studied by ^{13}C NMR (broad band and off resonance NMR experiments). All assignments agree with additivity rules of ^{13}C NMR for benzene substitution (11) (Tab.1).

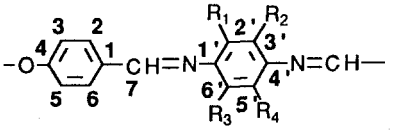
Tab. 1 - ^{13}C NMR assignments of azomethine models ($CDCl_3$). MMM: R1: CH_3; MDM: R1=R4: CH_3; MTM: R1=R2=R3=R4: CH_3; MNS: R1-R4: H. **a**) 2 peaks (161.01 and 161.02 ppm; **b**) idem (157.8 and 158.2 ppm)

The reaction was carried out in favourable conditions for an intramolecular reaction, i.e. in a diluted solution (**R**: Me (MMM, BMM); $(Me)_2$ (MDM, BDM); $(Me)_4$ (MTM, BTM)). In each case the reaction mixture is analyzed by size-exclusion chromatography (SEC). No catalyst (strong acid) (9,10) is added in order to follow the reaction on a time scale compatible with that of SEC. As an example chromatograms relative to the evolution of the MDM/BDM system versus reaction time is shown (Fig. 1). Starting reactants appear as two peaks (A, B) and the mixed compound (C) grows between them. After 24 h no evolution is observed and an equilibrium is reached as proved for the non-substituted system (5).

Reactivity of the different systems has been compared after 6 h reaction time (Fig.2).

It clearly appears that interimination is rather equivalent for methyl- or dimethyl-substitution (**b** and **c**), but less rapid that for the non-substituted system (**a**). Tetramethyl-substituted compounds react much more slowly; after 6h roughly 5% of the mixed compound are formed.

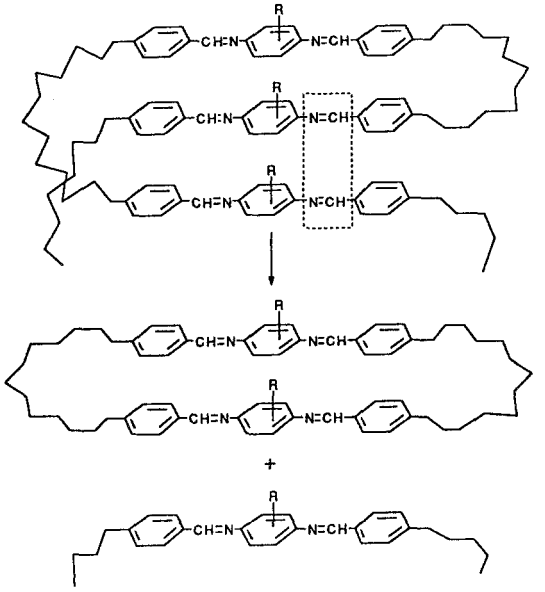
These results show that in all cases interimination reaction occurs, but less and less rapidly versus methyl-substitution. Proving the reaction (without catalyst), we did not carry out an extensive kinetic model study, as our main purpose was to apply the reaction to a polymer in order to obtain macrocyclic dimers.



n° C	MMM δ (ppm)	MDM δ (ppm)	MTM δ (ppm)	MNS δ (ppm)
1'	149.0	148.6	147.6	149.8
2'	129.6	129.9	123.7	121.6
3'	119.1	119.5	123.7	121.6
4'	149.5	148.6	147.8	149.8
5'	117.9	129.9	123.7	121.6
6'	122.8	119.5	123.7	121.6
1	133.0	130.35	129.5	129.5
2	130.3	130.25	130.0	130.4
3	114.8	114.9	114.9	114.9
4	161.01[a]	161.0	162.0	161.2
5	114.8	114.9	114.9	114.9
6	114.8	114.9	114.9	114.9
7	157.8[b]	157.6	161.1	158.6

c) Methyl-substituted macrocycle syntheses

The reaction principle leading to macrocycles is based on an intramolecular interimination reaction of the linear polymer chain (scheme 2):



Scheme 2 - Intramolecular interimination

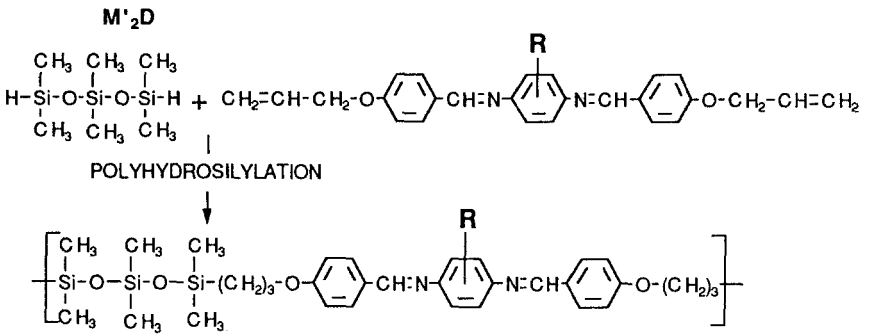
The acid-catalyzed reaction (ex. trifluoroacetic acid: TFAA) consists in an equilibrium between long polymer chains and a mixture of the macrocyclic dimer and shorter chains. The process lies on a preliminary linear polymer synthesis; after that favourable conditions lead to cyclization (diluted solution and strong acid as catalyst).

Therefore the whole process takes place in two steps:

1 - main chain polymer synthesis.
2 - cyclization.

The two steps can be separated or not, i.e. linear polymer can be isolated or not.

Main-chain liquid crystal polymers have been synthesized (PMM, PDM, PTM) according to an hydrosilylation reaction between α,ω-diallyloxy substituted reactants (AMM, ADM, ATM) and M'_2D (scheme 3):



Scheme 3: Main chain polymer synthesis

Evolution of the reaction medium to the polymeric system corresponds to (**a**) and (**b**) chromatograms (Fig.3 : 3A-3D). On each series aromatic reactants are presented in (**a**), linear polymer after hydrosilylation reaction in (**b**), reaction medium after cyclization reaction in (**c**) and the obtained macrocycles after a first precipitation (i.e. before recrystallization) in (**d**).

We observed that in the hydrosilylation conditions, i.e. in toluene solution, cyclization occurs on the three substituted systems, even without strong added acid (roughly 10% macrocycle in main-chain polymers after hydrosilylation). The formation of macrocycles is strongly enhanced by acid addition. Nevertheless, as observed on models, in the case of the tetramethyl substituted system [Fig.3-D, **b**) and **c**)], both a more

important dilution and an higher trifluoroacetic acid concentration is necessary to promote cyclization to an equivalent extent as for the two substituted other systems.

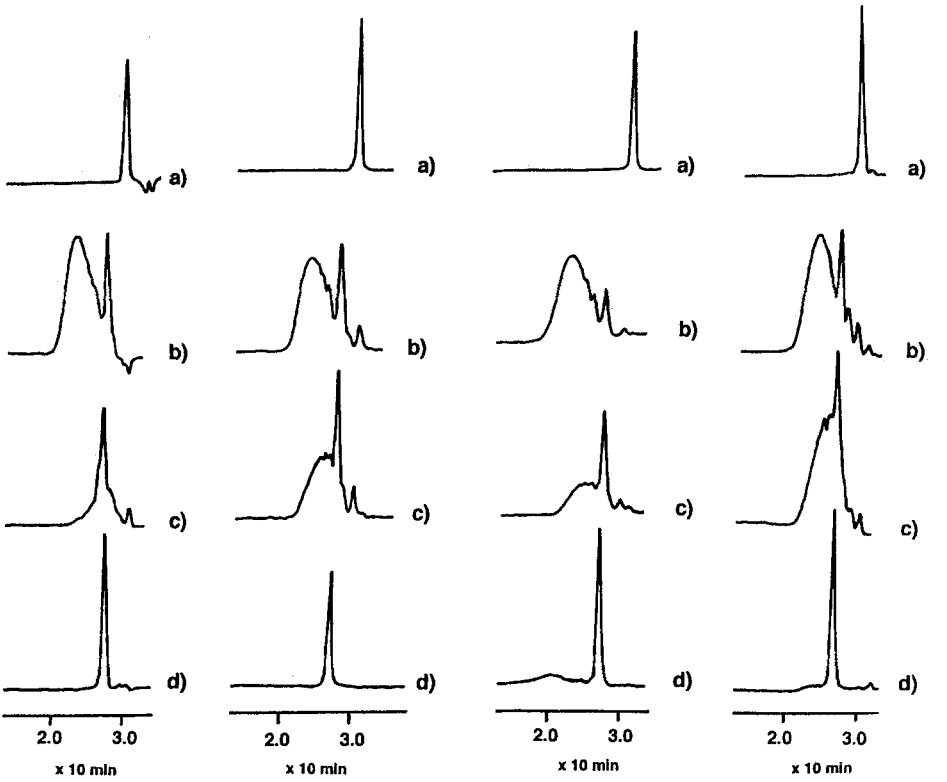


Fig.3-A Fig.3-B Fig.3-C Fig.3-D

Fig. 3 - SEC chromatograms of diallyloxy reactants [**a**] before reaction, block-polymers after synthesis [**b**], after enrichment in macrocycles by acidification [**c**], after a first precipitation of macrocycles [**d**]. 3-A: non-substituted system; 3-B: methyl-substituted system; 3-C: dimethyl-substituted system; 3-D: tetramethyl-substituted system. Operating conditions correspond to experimental part.

Effects of dilution and acid catalyst concentration have been studied on the tetramethyl substituted system (Fig. 4). The (**d**) conditions have been choosen for CTM synthesis, i.e. four time more TFAA than for CMM and CDM.

Polymer syntheses and cyclization have been studied mainly separately to characterize more precisely each step. Nevertheless some experiments showed that macrocycles may be obtained directely. When polymer growth is sufficient ($\overline{M_n} \approx$ 8-10000), it is possible to simply dilute and acidify the medium to generate mainly macrocycles. However in these conditions the solvent used for hydrosilylation is not necessarily optimal for the cyclization.

Substituted systems are now to be optimized to improve macrocycle yields which are up to now relatively low (30-40%), due to equilibria and probably to a partial precipitation as well.

d) Characterization of the macrocycles by ^{13}C NMR

^{13}C NMR of the methyl-substituted macrocycles have been recorded either in $CDCl_3$ or in CD_2Cl_2 depending on their solubility (Fig.5). Assignments totally match the model results (Tab.1). A complete study by ^{1}H and ^{13}C NMR (liquid and solid) will be the subject of a further article.

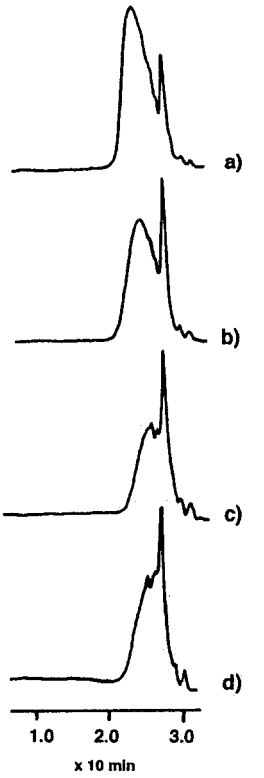


Fig. 4 - SEC chromatograms of CTM syntheses; operating cond. (see exp. part). Influence of dilution and of TFAA concentration. (chlorobenzene vol. (ml)/ µl TFAA: a)150/4; b) 200/8; c) 300/30; d) 400/40).

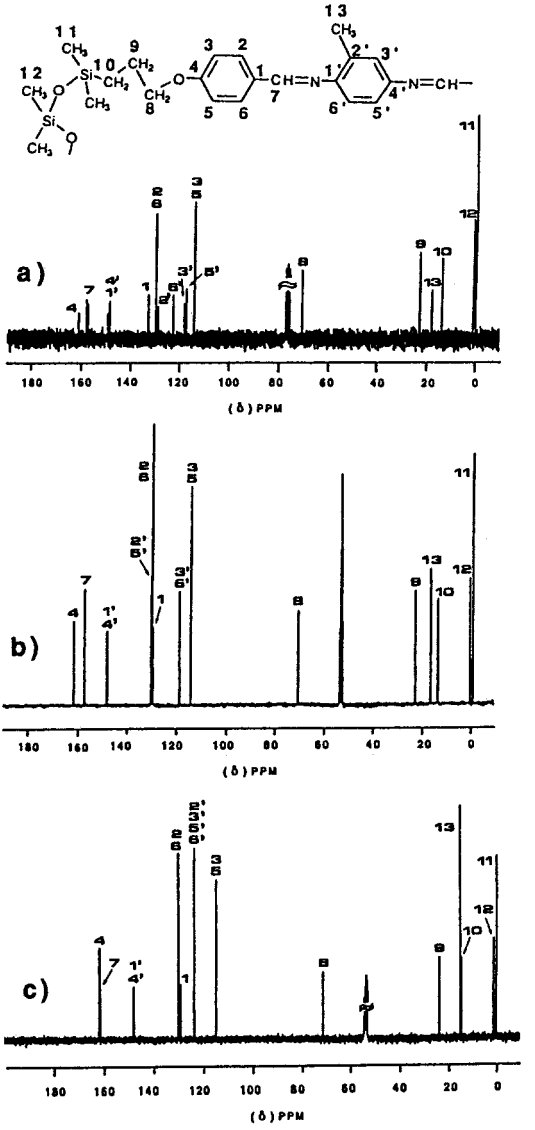


Fig. 5 - ^{13}C NMR spectra of CMM (a), CDM (b) and CTM (c). Numbering of CDM and CTM as azomethine model structures (Tab.1).

The best proof of the existence of a cyclic structure was given by X-ray crystallography since we succeeded in obtaining the tetramethyl-substituted macrocycle as a large crystal allowing its characterization (Fig. 6). The crystal sizes were also sufficient for observation of the dimethyl-substituted macrocycle as well as for the three dialloxy precursors. All crystallographic data, of the greatest importance to understand the very rich liquid-crystal behaviour of such macrocycles, will be published separately.

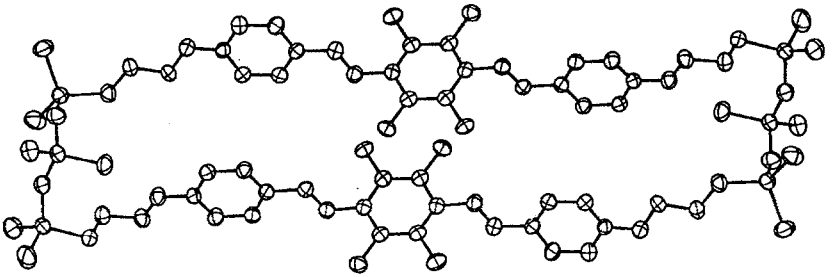


Fig. 6 - View of CTM by X-ray crystallography.

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