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Synthesis and characterization of a wholly aromatic rod-like macrocyclic tetraester mesogen from 4,4′-biphenyldicarboxylic acid and catechol

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The first example of a wholly aromatic rod-like macrocyclic mesogen has been synthesized by a two step polycondensation of catechol (**C**) with of 4,4′-biphenyldicarboxylic acid (**B**). Pure crystalline [2+2] *cyclo*-dimer was isolated from the polymerization mixture in 25% yield by a single silica gel column chromatogram and it was fully characterized by TLC, GPC, FAB$^+$ MS, FTIR, UV-Vis, ^{1}H NMR, differential scanning calorimetry and polarizing optical microscopy. Structural features and stereochemical aspects of this 28-membered cyclic tetraester were studied by semi-empirical AM1 calculations and Molecular Dynamics simulations. This calamitic macrocyclic mesogen has the two outer coplanar phenyl rings of the **C** entities linked by two stacked **B** units forming an extraordinarily rigid and strongly anisometric molecular structure with a long axis of *c*. 20 Å. Whereas its low molecular mass acyclic homologue is far from being mesomorphic, this macrocyclic compound exhibits an enantiotropic nematic mesophase with a clearing temperature higher than that of the high molar mass linear homologue [5.5×10^4 (1.9), M_n (M_w/M_n), GPC].

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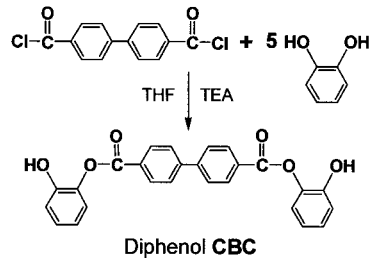
1. Introduction

Rod-like macrocyclic mesogens are a relatively recent development [1–5]. They can be classified into two types, those with the rod-like mesogenic units located outside the ring of the macrocycle [1] and those with the mesogenic units inserted within the ring of the macrocyclic structure [2–5]. In those of the latter type, the cyclic backbone efficiently restricts the conformational mobility of the rod-like units so that these macrocyclic mesogens are more rigid and thus exhibit higher isotropization temperatures than those of corresponding low and high molar mass linear homologues [2, 5]. In fact, according to experimental evidence from several laboratories, it can be affirmed that restricting conformational freedom in calamitic mesogens via macrocyclization (by terminally fixing them into a cyclic backbone) is the most powerful strategy for the stabilization of the LC phase known so far [2–5].

Modification of the conformational flexibility of rod-like macrocyclic mesogens by introducing different constraints into the framework is a very interesting possibility for use in the design of macrocyclic mesogens for studies of new strategies of mesophase stabilization. So far, all the rod-like main chain macrocyclic mesogens described are based on rod-like [2–4] or U-shaped [5] mesogens terminally linked by flexible spacers. We are interested in studying the effect of a further restriction of the conformational flexibility in these macrocyclic mesogens by incorporating rigid *ortho*-aromatic spacers instead of flexible aliphatic spacers into the cyclic backbone. We provide here the first illustration of this concept, a report on the synthesis of the first example of a wholly aromatic rod-like macrocyclic mesogen **1**, which is the [2+2] cyclic dimer of 4,4′-biphenyldicarboxylic acid (**B**) and catechol (**C**) (see schemes 1 and 2). Model compound **2**, an acyclic homologue of **1**, was also synthesized for comparative purposes (see scheme 3). Whereas compound **2** is not mesomorphic, macrocycle **1** exhibits an isotropization temperature higher than 400°C. However,



Scheme 1. Synthesis of complex diphenol **CBC**.

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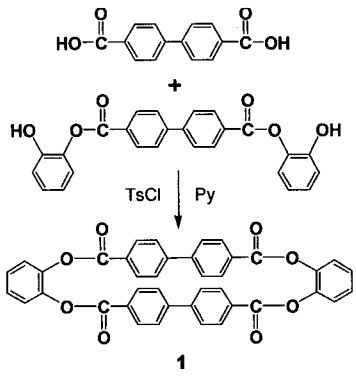
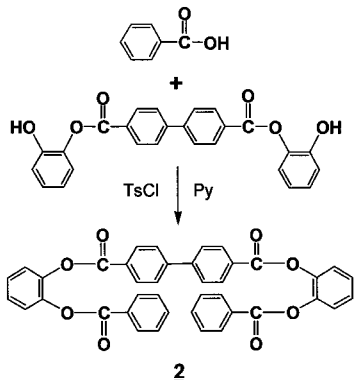


Scheme 2. Synthesis of [2+2] *cyclo*-dimer, compound **1**.



Scheme 3. Synthesis of model compound **2**.

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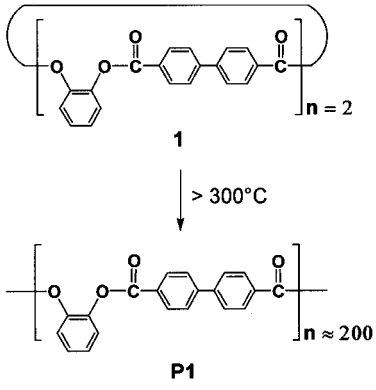
1 undergoes a ring-opening polymerization (ROP) process in the nematic melt, at temperatures above 300°C, to produce a high molecular mass thermotropic polyester **P1** which exhibits a lower isotropization temperature (*c.* 330°C) than that of the cyclic compound **1** (see scheme 4).

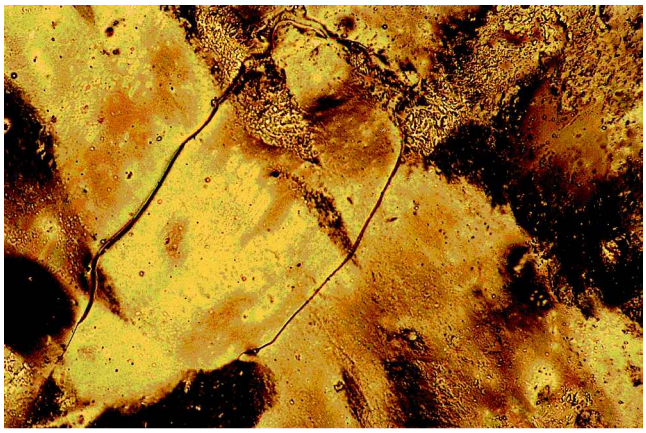
2. Synthesis, characterization and ring-opening polymerization of [2+2] *cyclo*-dimer 1

Since Pedersen synthesized the first examples of crown ethers, catechol has been widely used for crafting macrocyclic systems [6]. Catechol has the torsionally rigid group O–C–C–O (the four atoms are coplanar) and hence provides conformational constraints for efficient macrocyclization. In fact, polyesterifications of catechols with dicarboxylic acids are selective towards cyclic, rather than linear product formation, and thus the use of high dilution techniques can be avoided [5, 7]. However, these polycondensations produce many different rings necessitating extensive purification. In order to reduce the variety of cyclic products, [2+2] *cyclo*-dimer **1** was obtained by a two-step synthetic approach which involved first the condensation of the acid chloride of **B** with an excess of **C** to give diphenol **CBC** (see scheme 1) which in the second step was condensed with another molecule of **B** to give **1** in 30% yield (GPC peak area ratio) (see scheme 2). TLC analysis of the mixtures of polycondensation of **CBC** with **B** indicated that the predominant species was **1**, the least polar compound which migrated on TLC plates much further than the rest of the sample. Thus, the separation of macrocycle **1**, from the reaction mixture was not troublesome. It was isolated in good yield, as a pure compound, by only a single column chromatogram using methylene chloride as eluent (the unoptimized yield was 25%). Pure crystalline compound **1** was soluble in chloroform and methylene chloride at very low concentrations, but in the presence of trifluoroacetic acid it was moderately soluble in these solvents so that it could be fully characterized by TLC, GPC, FAB$^+$ MS, FTIR, UV-Vis, ^{1}H NMR, differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

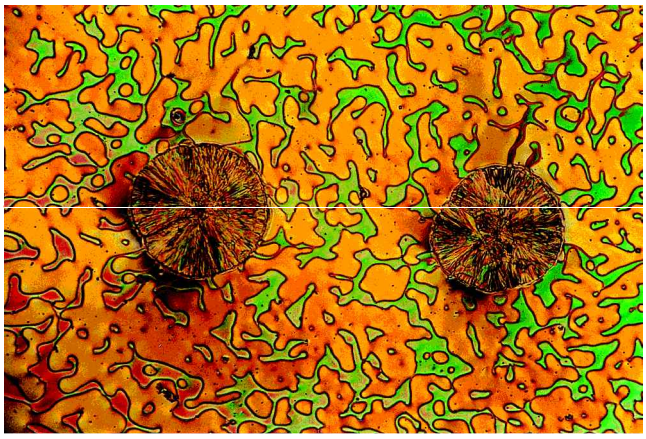


Scheme 4. Ring-opening polymerization of macrocyle **1**.

Samples of **1** in the hot stage of the polarizing microscope melted at *c.* 325°C to form an enantiotropic nematic mesophase which isotropized at temperatures well above 400°C, see figure 1 (*a*). The first DSC heating scan (20° min^{-1}, heating and cooling rate) of a sample of **1** shows a melting endotherm at 324°C on heating to 400°C and a crystallization peak at 276°C on cooling from this temperature. The peak corresponding to the isotropization transition of the nematic phase was not observed in the DSC curves because **1** undergoes a very rapid ring-opening polymerization (ROP) process at temperatures above 400°C. However, samples of **1** placed on the hot stage preheated to 400°C, developed nematic mesophases that crystallized on cooling at *c.* 270°C, proving that its isotropization temperature was higher than 400°C. Furthermore, DSC traces of subsequent scans were very different from that of the first one, due to the ROP of **1** at temperatures above 300°C (during the course of the DSC scans) to produce a high molecular mass thermotropic polyester. Accordingly, during the subsequent DSC scans only the $T_g = 150$°C and $T_i = 315$°C of the high polymer were observed. In fact, the ROP process of **1** can be easily followed by DSC, GPC and POM.



(*a*)



(*b*)

Figure 1. Representative optical polarized photomicrographs showing the nematic melt of macrocyle **1** before (*a*) and after (*b*) its melt ROP process (samples viewed between crossed polarizers, magnification 200×). (*a*) nematic mesophase of **1** at 400°C, showing a characteristic marbled polished texture. The photomicrograph was taken immediately after melting the sample on the hot stage of the polarizing microscope preheated to 400°C. (*b*) The same preparation after 10 min at 330°C, quenching to room temperature, reheating to 235°C and maintaining at this temperature for 2 h. This photograph shows (i) the size of the nematic domains of the polymer derived from ROP of **1**, just below the isotropization temperature (*c*. 330°C), and (ii) spherulites of this polymer obtained by crystallization of its nematic melt at 235°C.

For instance, by holding a sample of **1** for about 10 min at 350°C on the hot stage of the polarizing microscope, drops of isotropic liquid evolve from the nematic melt until all the preparation becomes isotropic. Simultaneously, the viscosity of the preparation increases, resulting in a very viscous isotropic melt. On cooling, this melt forms at 330°C a nematic mesophase which can be supercooled to room temperature, see figure 1 (*b*). TLC and GPC analysis of the preparation showed that it was a high polymer [5×10^4 (2.3), M_n (M_w/M_n), GPC] contaminated with *c*. 20% of residual cyclic oligomers.

The ring-opening polymerization of **1** was performed on a 1 g scale without a catalyst, in a polymerization tube under nitrogen. Purification of the polymer derived from ROP of **1** was carried out by dissolution in a mixture of chloroform and trifluoroacetic acid (5/1, v/v) and reprecipitation in toluene to yield high molar mass nematic polymer **P1** [5.5×10^4 (1.9), GPC] with a contamination of residual cyclic oligomers lower than 5%, see figure 2. DSC analysis of **P1** gave the following transitions: $T_g = 150$°C, $T_m = 290$°C and $T_i = 310$°C. According to POM observations, samples of **P1** melted at *c*. 295°C to form a nematic melt exhibiting a clearing temperature of *c*. 325°C. The nematic melts of **1** and **P1** exhibited not only very different viscosities and clearing temperatures, but also very different nematic textures. Polyester **P1** forms a very viscous nematic melt which displays characteristic multidomain textures with small nematic domains, whereas macrocycle **1** develops a very fluid nematic melt which exhibits a distinctive marbled polished texture with large nematic domains, see figure 1 (*a*). Furthermore, the melt of **P1** has a low tendency to crystallize, forming a glassy nematic mesophase on cooling to room temperature at 40° min^{-1}. Slow crystallization occurs after prolonged annealing of the nematic melt of **P1** at 235°C, see figure 1 (*b*).

IR and UV spectra of **1** and **P1** are similar. However, the UV spectrum of **1** shows a characteristic slight red shift of 5 nm in the wavelength absorption maxima which can be ascribed to a transannular interaction between the benzene rings of the **B** units and to some ring strain. However, the carbonyl stretching frequencies in **1** and **P1** are very similar, typical for aromatic phenolic esters,

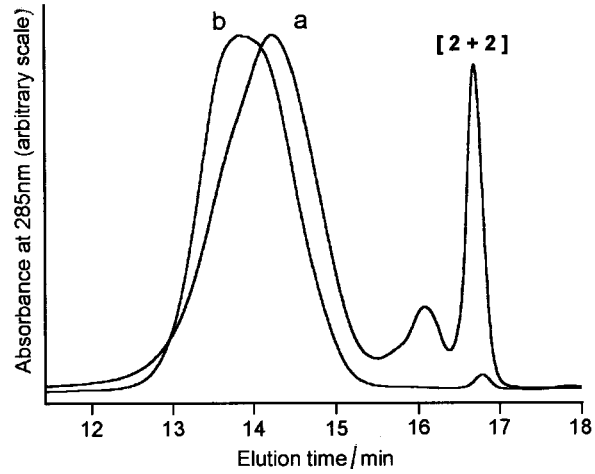


Figure 2. (*a*) Representative GPC elution traces of the products derived from the melt ROP of macrocyclic compound **1** after 30 min at 330°C; (*b*) GPC curve of the purified polymer **P1**.

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which suggests the absence of severe ring strain. Nevertheless, the IR spectrum of **1** was more complex than that of **P1** showing more absorption bands, especially, in the region of the C−O−C stretching frequencies. On the other hand, cyclo-dimer **1** has a distinctive and readily interpretable ^{1}H NMR spectrum, see figure 3. Comparison of the NMR spectrum of **1** with those of the acyclic homologues **2** and **P1** indicates a $\delta \sim 0.3$ ppm upfield shift of the resonances of the protons of the **B** units of **1**, a reflection of the close packing of **B** entities in the macrocycle.

3. AM1 structure of [2 + 2] *cyclo*-dimer 1

From AM1 conformational studies of **1** it emerges that the lowest energy structures (in the energy window of 4 kcal mol^{-1} from the most stable one) are enantiomeric and diastereoisomeric conformers that, consistent with the mesogenic properties of **1**, have a strongly anisometric shape with long axes of *c.* 20 Å, see figure 4. Their structures are highly symmetrical which is supported by the simplicity of the NMR spectrum of **1**. They present nearly self-filling conformations with the skeletons of the **B** units aligned approximately parallel along the long axis. The transannular phenyl rings of the **B** units are parallel and close enough for partial overlap, with

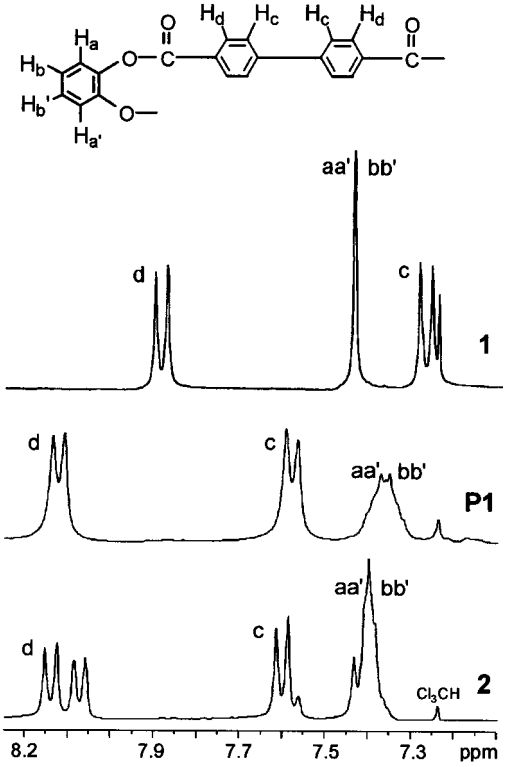

Figure 3. Structure (top) showing ^{1}H NMR peak assignments for the **B** and **C** moieties of homologues **1**, **2** and **P1**; (bottom) ^{1}H NMR spectra of **1**, **2** and **P1**, from 300 MHz, ^{1}H NMR spectra in $CDCl_3$ and TFA-d (3/1, v/v), TMS.

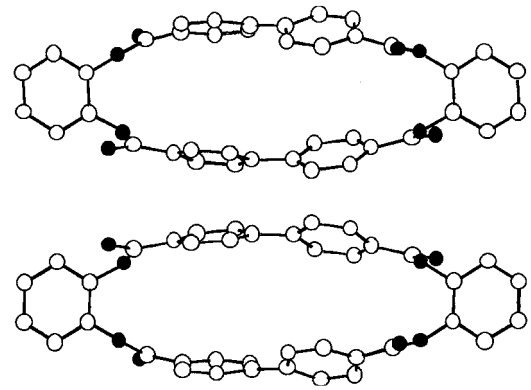

Figure 4. Ball-and-stick drawings of the AM1 minimized D_2 pair of enantiomeric conformations of macrocycle **1** (hydrogen atoms omitted for clarity, oxygen atoms are black).

mean interplanar separations from 4 to 5 Å, indicative of weak intramolecular, face-to-face, π-stacking (a feature also suggested in the NMR and UV spectra of **1** by the modest 0.3 ppm upfield shift of the **B** protons and the small 5 nm bathochromic shift in the wavelength absorption maxima, respectively, compared with those of **2** and **P1**).

We directed attention to seven extreme conformations in which all four ester linkages adopt *trans*-geometries with their carbonyl groups projecting upward or downward from the 28-membered mean ring plane of the macrocycle. Both carbonyl groups in each **B** unit can adopt either the *anti*- or the *syn*-conformations and both carbonyl groups can be situated on opposite sides of the aromatic ring in the **C** entities (antiparallel) or on the same side (parallel). We found seven minimum energy structures: two enantiomeric pairs of conformations of C_1 and D_2 symmetries and three diastereoisomeric conformations of C_i, C_2 and C_{2h} symmetries. The relative orientations of the carbonyl groups with respect to the 28-membered mean ring plane of the macrocycle in the seven conformations and the inversion and interconversion processes between them are schematically represented in figure 5. Each conformational change has to involve at least a 180° rotation of one ester carbonyl bond. However, the reorientations of the carbonyls in the macrocycles seem to be much more hindered than in simple acyclic analogues. Principally, this is due to (i) steric hindrance because of the close proximity of opposite ester groups, and (ii) restrictions imposed by the ring which cause the ester groups to assume a non-planar conformation [showing dihedral angles C−C(=O)−O−C of *c.* 160°–165° (see below)]. Therefore, apparently the rotations of the −COO− group about the Ar−C and the O−Ar single bonds are severely restrained. Nevertheless, Molecular Dynamics (MD) simulations carried out on any of these conformers clearly show that the carbonyls

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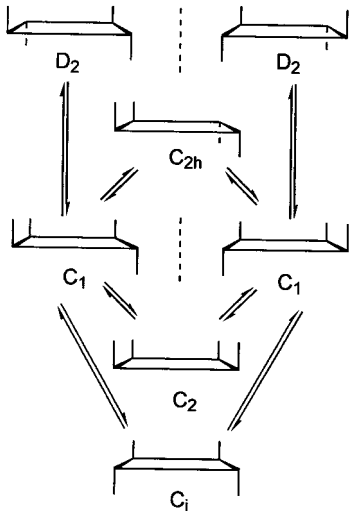

Figure 5. Relationship between possible enantiomeric and diastereoisomeric conformations of **1**. Diagrams represent the relative orientations of the ester carbonyl groups with respect to the 28-membered mean ring plane of the macrocycle.

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switch orientation even at moderate temperatures (above 300 K), producing stereoisomers in accordance with the conformational itinerary depicted in figure 5. The energy differences between them are very small, the pair of enantiomers with a D_2 symmetry being the lowest energy structures. Most probably, the seven conformers undergo rapid inversion and interconversion processes between them and are all present in significant proportions in solution at room temperature. Moreover, it is important to note that the overall rod-like geometry of these conformers was retained throughout all MD simulations.

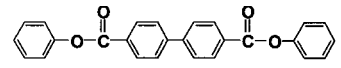
Bond lengths and valence angles for non-hydrogen atoms of these selected structures are quite normal and agree very well with appropriate standard values. Generally, some conformational characteristics of the **B** units and of the carboxylic parts of their structures compare well with those observed for a wide variety of similar derivatives [7*b*, 8, 9]. For instance, the **B** moieties are not planar, but show inter-ring dihedral angles lying between *c.* 30° and 40°, typical values for biphenyl systems with low conjugation between phenyl rings [8]. Besides, the phenyl rings of the terminal **C** units are close to coplanar forming dihedral angles with their adjacent **B** rings in the range between *c.* 60° and 80°, very close to the idealized value *c.* 70° [9].

On the other hand, keeping in mind that the two C–O bonds of catechol project at a 60° angle from the centre of the benzene ring, it is obvious that the formation of macrocycle **1**, connecting two **C** units by two parallel **B** units, involves some important distortions of the **B** units and/or of the ester groups. In fact, in the selected AM1 structures of **1**, the carbonyl groups do not approach coplanarity with their attached phenyl rings, but are rotated out of the plane of their attached phenyl rings by *c.* 5° to 25°. In addition, the ester groups are not planar, but show dihedral angles C–C(=O)–O–C of *c.* 160°–165°. Further evidence for ring strain is seen in the twisting of the rings of the **B** units (RMS from planarity *c.* 0.012–0.019 Å). Other distortions of the **B** units are also observed, the two bonds of the carbonyl carbons with the **B** units subtending an angle of *c.* 20°. The carbonyl carbons lie *c.* 0.5 Å out of the line of the long axis of the biaryl units. Furthermore, the phenolic oxygens are out of the plane of their attached phenyl rings (for example, dihedral angles O–C–C–O of *c.* 10°–14° for **C** units with antiparallel carbonyl groups).

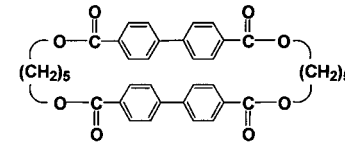
However, experimental observations indicate that **1** was not a severely strained macrocycle. For instance, figure 2 curve (*a*) shows that the mixture of the ROP of **1** contained *c.* 15% of this macrocycle after 30 min at 330°C, which indicates that **1** was fairly stable at very high temperatures. Large ring strain can be accommodated by bowing of the flexible **B** units, as seen in some aromatic macrocycles with the normally colinear bonds of the carbonyl carbons and the phenyl rings of the **B** units subtending angles of *c.* 65° [8*a*]. It seems that the bowing angles of the **B** units and thus the overall elliptical shape of **1** are the result of optimizing the ester dihedral angles C–C(=O)–O–C, more than a result of optimizing electronic interactions beween the confronting aromatic rings of the **B** units.

4. Mesophase stabilization via macrocyclization

The series of ester analogues, compounds **1**, **2**, **3** and **P1** (see schemes 2–5), have the same aromatic core as diphenyl 4,4′-biphenyldicarboxylate **3**, but different molecular geometry and/or molar mass. Due to steric disturbance, attaching two bulky benzoyloxy side groups to the conventional mesogenic compound **3** [10], produces significant mesophase destabilization and compound **2** is far from mesomorphic. In fact, not even a monotropic mesophase was observed by supercooling the isotropic melt of **2** to room temperature. However,



3 (Cr 212 N 245 I) (°C)



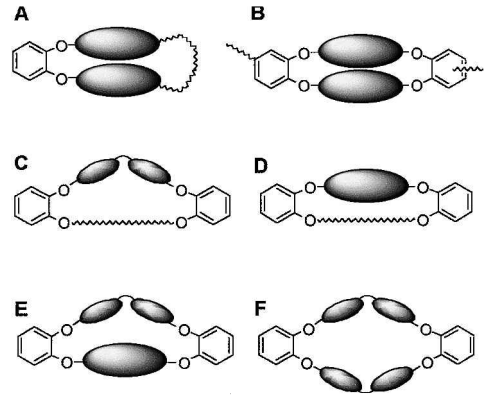
4 (Cr >300°C dec.)

Scheme 5. Comparison of the thermal properties of esters of different molecular geometry containing **B** units.

cyclization of **2** by terminally linking both benzoyloxy side groups with an Ar–Ar single bond, forces both side groups into perfect alignment with the mesogenic core, avoiding the undesired steric effect, so that the resulting macrocyclic molecules **1**, have both outer coplanar phenyl rings of the **C** units linked by two stacked **B** entities forming an extraordinarily rigid rod-like structure. This structure is more rigid and exhibits therefore a higher isotropization temperature than that of the traditional mesogen **3**, which has the two terminal phenyl rings connected by only one **B** unit. Furthermore, cyclic compound **1** exhibits a higher rigidity and thus a higher isotropization temperature than that of the high molar mass linear homologue **P1**. Probably, cyclic oligomer **1** exhibits both the highest rigidity and isotropization temperature of the entire copolyester system. Therefore, in this unconventional liquid crystalline copolyester system of catechol and 4,4′-biphenyldicarboxylic acid, macrocyclization leads to a higher mesophase stabilization than does linear polymerization.

Macrocyclic compound **4** was the only reported cyclic species [11] of the conventional liquid crystalline copolyester system, the poly(alkylidene 4,4′-biphenyldicarboxylates) [8*b*, 11, 12]. Unfortunately, **4** decomposes at temperatures above 300°C preventing the observation of any possible LC phase generated by this macrocycle. Consequently, rigidifying the ring of **4** by incorporating rigid *ortho*-aromatic spacers between the mesogenic **B** units, instead of the flexible aliphatic chains, causes an improvement in thermal stability and most probably, an increase in its isotropization temperature. Furthermore, all the main chain macrocyclic mesogens described until now incorporate flexible spacers in their cyclic backbones and they are therefore less rigid than **1**; they either exhibit clearing temperatures well below 300°C or decompose just above this temperature [2–5]. Totally aromatic macrocycle **1** is thermally stable even at 400°C, but at temperatures above 300°C undergoes a ring–chain equilibration process which at these high temperatures is displaced towards high polymer, so that after equilibration the polymerization mixture contains only approximately 15% of **1** (see figure 2).

Since **1** melts above 300°C and its ring-opening polymerization process can be an unwanted feature, we have adapted traditional methods in the design of calamitic mesogens to reduce the melting point below 300°C, without destabilizing the liquid crystalline properties. Essentially, the strategies consist of the incorporation of flexible units inside and/or outside the macrocyclic framework. Scheme 6 outlines some variants for fixing mesogenic groups into rod-like macrocyclic structures so that lower melting points, but higher isotropization temperatures, than those of the corresponding low and high molecular mass linear homologues become possible. The approaches involve one or more of the following modifications: (i) attaching one or more terminal chains to the rod-like macrocyclic structure (type B), (ii) crafting macrocyclic backbones based exclusively on one mesogenic unit (type C and D), (iii) copolymerizing with flexible rod-like and/or bent rod-like mesogenic units (type E and F).



Scheme 6. Variants for fixing rod-like units into macrocyclic mesogenic structures.

We have synthesized examples of each macrocyclic structure represented in scheme 6. Macrocyclic diesters of type A have been reported previously [5*b*] and the rest will be reported in due course. Those with terminal chains display conventional smectic and nematic mesophases, whereas the others exhibit only nematic mesophases. Particularly interesting are the bow-shaped macrocyclic mesogens of type C, based exclusively on a single, flexible, bent rod-like unit whose conformational rigidity, bowing angle and therefore mesogenic properties can be tailored by adjusting the strain in the bow (by modifying the length of the string by changing the length of the aliphatic spacer of the macrocycle).

5. Conclusions

Restricting the conformational freedom of rod-like units by connecting them with rigid *ortho*-aromatic spacers via macrocyclization is a new approach to the design of macrocyclic mesogens which have a higher rigidity and therefore higher clearing temperatures than those of low and high molar mass linear homologues. Since wholly aromatic macrocyclic oligoesters usually melt at temperatures above 300°C and undergo melt ring–chain equilibration processes, some structural variations are suggested to reduce the rigidity of these macrocycles. In this connection, preformed linear oligoesters, such as complex diphenol **CBC** (see scheme 1), are particularly valuable since they efficiently favour macrocyclization in polycondensations with flexible dicarboxylic acids.

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6. Experimental

6.1. *General considerations*

Silica gel plates (Merck F_{254}) and silica gel 60 (Merck, 230–400 mesh) were used for TLC and flash chromatography, respectively. GPC analysis were carried out with a Waters 600 pump and controller and Millennium Analytical GPC software. The analysis were performed with a 996 photo diode array detector, THF or $CHCl_3$ (1 ml min^{-1} and 30°C), two sets of columns, and a calibration curve constructed with polystyrene standards. The two sets of columns were the following: for oligomers and polymers of molecular masses lower than 25 kg mol^{-1}, one set consisted of two PL gel columns of 10^3 and 10^5 Å and for higher polymers a set formed by a Waters Styragel HR JE column and a PL gel column 10^5 Å.

FTIR spectra were recorded using a Nicolet 205 spectrophotometer and mulls in KBr. Fast atom bombardment mass spectra (FAB^+-MS) were obtained with a Vacuum Generators (VG) Autospec instrument, by using a Cs gun as primary ion source. The matrix for the samples to be bombarded was a 3-nitrobenzyl alcohol/methylene chloride/trifluoroacetic acid (1/1/0.25 v/v/v) mixture. ^{1}H NMR (300 MHz) spectra were recorded with a Varian XL-300 spectrometer or a Bruker ARX-300. All spectra were recorded at room temperature using the solvent mixture $CDCl_3$ and CF_3CO_2D (3/1, v/v) and with TMS as internal standard.

Textures and the thermal behaviour of melts were examined using a Linkam THMSE 600 heating stage attached to an Olympus BX50 polarizing microscope. DSC was performed using a Perkin-Elmer DSC-7 calorimeter calibrated following standard procedure. The heating and cooling rate for thermal analysis was 20°C min^{-1}.

6.2. *Molecular modelling*

Molecular modelling was carried out with HyperChem professional release 6.03, using the MM+ force field for preoptimization of geometries and semi-empirical AM1 calculations for further optimizations. Minimized structures were used as starting geometries for subsequent Molecular Dynamics simulations. The molecules were heated from 100 K to the desired simulation temperature (300, 350, 400 and 500 K) and allowed to equilibrate for a period of 10 ps with a time step of 0.001 ps and a relaxation of 0.1 ps. No periodic boundaries or distance cut-offs were applied.

6.3. *Synthesis of diphenol* ***CBC***

This was prepared in a single step reaction by condensation of an excess of catechol with 4,4′-biphenyldicarbonyl dichloride (scheme 1), using the following synthetic procedure. 4,4′-Biphenyldicarbonyl dichloride (1 mol) was added slowly at 5°C to a solution of catechol (5 mol) in THF (500 ml) containing 2 mol % TEA. The reaction mixture was stirred for 12 h at 20°C and then poured into 4000 ml of ice–HCl (concentrated). The precipitate was filtered off, washed with boiling water and recrystallized from 1,4-dioxane yielding diphenol **CBC** containing about 10% of the higher diphenol **CBCBC**; yield 34%, purity *c.* 90% according to ^{1}H NMR (88%) and GPC (91%) analysis. ^{1}H NMR (DMSO-d_6) δ (ppm): 6.84–7.2 (m, 8H, **C** units), 8.02 (d, $J = 8.5$ Hz, 4H, *meta* to carbonyl of **B** unit), 8.25 (d, $J = 8.5$ Hz, 4H, *ortho* to carbonyl of **B** unit) and 9.77 (s, 2H, OH of **C** units).

6.4. *Synthesis of [2+2] cyclo-dimer* (scheme 2)

A pyridine solution (10 ml) of tosyl chloride (0.033 mol) maintained at room temperature for 30 min was added quickly to a hot solution of diphenol **CBC** (0.015 mol) and 4,4′-biphenyldicarb oxylic acid (0.015 mol) in pyridine (70 ml) and DMF (70 ml) preheated to 110°C for 10 min; the whole mixture was maintained under nitrogen at 110°C for 0.5 h. The reaction mixture was poured into 1000 ml of ice–HCl (concentrated). The precipitate was collected, washed sequentially with water, 5% aqueous $NaHCO_3$ and water, and then vacuum dried to give a white powder (yield 98%) which was dissolved in methylene chloride (250 ml). The resulting solution was filtered and the components fractionated by preparative column chromatography: silica gel (250 g); eluent methylene chloride. Each fraction was checked by TLC (methylene chloride as the mobile phase). The first product eluted from the column was **1**. It alone was eluted as a pure compound over several fractions which were collected; the methylene chloride was evaporated producing a solid crystalline residue which was recrystallized from cyclohexanone (yield 25%). ^{1}H NMR, $CDCl_3$ and TFA-d (3:1, v/v), δ (ppm): 7.27 (d, $J = 8.3$ Hz, 8H, *meta* to carbonyl of **B** units), 7.43 (m, 8H, AA′BB′ system in **C** units), 7.87 (d, $J = 8.3$ Hz, 8H, *ortho* to carbonyl of **B** units). MS (FAB) *m/z*: 633 [$(M)^+$], 655 [$(M + Na)^+$]. FTIR, KBr (cm^{-1}): ν (C=O), 1739, 1729; ν (C–O), 1273, 1261, 1233, 1170, 1157. UV-Vis, $CDCl_3$, λ_{max} (nm), 287.5. DSC (20° min^{-1}): (first heating) crystal 324°C (81 J g^{-1}) nematic; (first cooling) nematic 276°C (53 J g^{-1}) crystal.

6.5. *Synthesis of model compound* ***2*** (scheme 3)

A pyridine solution (10 ml) of tosyl chloride (0.033 mol) maintained at room temperature for 30 min was added quickly to a hot solution of diphenol **CBC** (0.015 mol) and benzoic acid (0.03 mol) in pyridine (70 ml) and DMF (70 ml) preheated to 110°C for 10 min; the whole mixture was maintained under a nitrogen atmosphere at 110°C for 1 h. The mixture was then poured into 1000 ml of ice–HCl (concentrated). The precipitate was collected washed sequentially with water, 5% aqueous

$NaHCO_3$ and water, and vacuum dried to give a white powder (yield 91%) which was recrystallized from acetone to give pure **2** (yield 75%). ^{1}H NMR, $CDCl_3$ and TFA-d (3:1, v/v), δ (ppm): 7.40 (m, 8H, AA′BB′ system in **C** units), 7.43 (m, 4H, *meta* to carbonyl of terminal benzoyloxy units), 7.57 (m, 2H, *para* to carbonyl of terminal benzoyloxy units), 7.60 (d, $J = 8.3$ Hz, 4H, *meta* to carbonyl of **B** unit), 8.07 (dd, 4H, $J_{ortho} = 7.7$ Hz, *ortho* to carbonyl of terminal benzoyloxy units), 8.14 (d, $J = 8.3$ Hz, 4H, *ortho* to carbonyl of **B** unit). FTIR, KBr (cm^{-1}): ν (C=O), 1745; ν (C−O), 1264, 1241, 1169. Melting point, DSC (20° min^{-1}) = 138°C (64 J g^{-1}). MS (FAB^+) *m/z*: 634 [$(M)^+$], 657 [$(M + Na)^+$].

6.6. *Synthesis of linear polymer **P1** by ROP of [2 + 2] cyclo-dimer* (scheme 4)

Compound **1** (1 g) was introduced into a dry test tube fitted with a magnetic stirrer and sealed with a septum. Dry nitrogen was passed in at room temperature and the tube was placed in a salt bath preheated to 340°C until all the sample was melted; then the melt was held at 320°C for 15 min. After cooling, the polymer was dissolved in a mixture of chloroform and trifluoroacetic acid (5/1, v/v) and precipitated in toluene. The precipitated polymer was filtered off, washed with acetone and vacuum dried to give the linear polymer **P1** (65% yield). ^{1}H NMR, $CDCl_3$ and TFA-d (3:1, v/v), δ (ppm): 7.35 (m, 2H, BB′ portion of the AA′BB′ system in **C** units), 7.37 (m, 2H, AA′ portion of the AA′BB′ system in **C** units), 7.58 (d, $J = 8.5$ Hz, 4H, *meta* to carbonyl of **B** units), 8.124 (d, $J = 8.5$ Hz, 4H, *ortho* to carbonyl of **B** units). FTIR, KBr (cm^{-1}): ν (C=O), 1741; ν (C−O), 1262, 1239, 1168. UV-Vis, $CDCl_3$, λ_{max} (nm), 282.7. DSC, (20° min^{-1}): (second heating) nematic glass 150°C crystal 290°C (18 J g^{-1}) nematic liquid 310°C (0.8 J g^{-1}) isotropic liquid; (second cooling) isotropic liquid 306°C (0.8 J g^{-1}) nematic liquid 146°C nematic glass.

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