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# Folding of aromatic oligoimides of *trans*-1,2-diaminocyclohexane†

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**Chiral oligomeric diimides prepared from pyromellitic dianhydride, (*R*,*R*)-1,2-diaminocyclohexane and phthalic anhydride fold into *M* or *P* helical conformers; trimer 1 folds into the *P* conformer in the crystal but the *M* conformer dominates in solution; longer chain oligomers 2 and 3 form preferentially *P* conformers in solution, as a result of intermolecular interactions.**

Chiral oligomeric structures of defined *M* or *P* (left or right handed) helicity exist either due to the presence of center(s) of chirality in the monomer or due to the commanding effect of a chiral auxiliary strategically placed in the oligomer chain. The latter case, referred to as ″majority rule″ situation (Green[1]), represents a macromolecular route to dynamic chiral amplification and has been thoroughly discussed in the current literature.[2] The former case recognised early by Farina in chiral isotactic polyolefins,[3] is the essential one for chirality of biopolymers, such as polynucleotides and polypeptides, where hydrogen bonding is crucial for stabilizing the helical structure. Significantly, helical structure is not restricted to α-peptides; β-peptides[4] are also capable of forming helical foldamers (Seebach,[5] Gellman[6]), as are other synthetic oligomeric carboxamides (Hamilton, Lehn[7]). Helical programming of molecular architecture is of current interest in supramolecular and materials science chemistry.[8–13]

Polyimides have been the subject of extensive studies, in part due to their industrial applications.[14] Polyimides made of achiral components, even if helical, do not show discrimination for either *P* or *M* helices.

We reasoned that the use of chiral $C_2$-symmetrical (*R*,*R*)-1,2-diaminocyclohexane and $D_{2h}$-symmetrical 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride) for oligomerisation would lead to two different chiral diastereomeric conformers taking either *C* shape (here *M* helicity) or *S* shape (here *P* helicity). At the imide triad level these conformers are visualised in Fig. 1 (see also ESI†).

Referring to imide triad **1**[15] we detect both conformers by $^1$H NMR spectra in CDCl$_3$ solution. At 293 K the pyromellitic diimide protons slowly exchange, whereas at 233 K separate signals are observed (Fig. 2), with the integrated ratio *C*:*S* = 3:2. It is evident from the NMR data that the more compact, better solvated structure *C* is the prevailing one in solution.

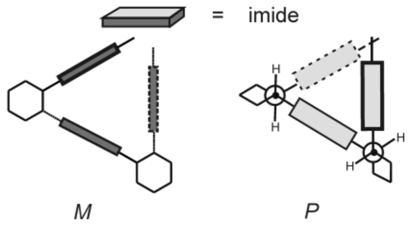


**Fig. 1** Conformers of the chiral imide triad.

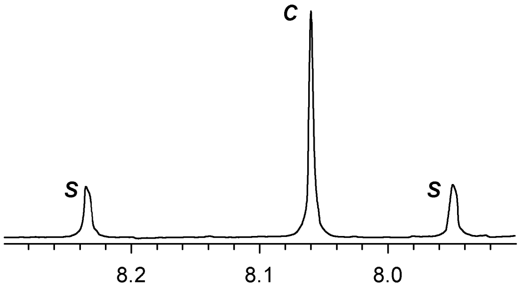
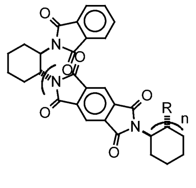
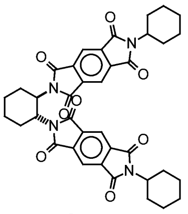


**Fig. 2** Pyromellitic diimide proton signals of **1** at 233 K



**1** n = 1, R = NPht
**2** n = 2, R = NPht
**3** n = 3, R = NPht
**4** n = 0, R = NH$_2$
**5** n = 0, R = NPht
**6** n = 1, R = H
**7** n = 2, R = H



**8**

Similar conclusion could be drawn from the analysis of the CD spectrum of **1** in dioxane (Fig. 3). The CD of **1** is a hybrid of exciton Cotton effects due to interactions of all pairs of the chromophores. After deduction of the contributions due to two negative vicinal imide–imide exciton Cotton effects, which are represented by the CD of **6**, we obtain the differential spectrum (**3**–2 × **6**) which reflects the exciton interaction of the two terminal phthalimide chromophores.[16] The negative exciton Cotton effect ($\Delta\varepsilon = -63$ at 222 nm and +22 at 211 nm) is evidently due to the dominant *C* shaped conformer, with the amplitude over half of that measured for **5**.[17]

By contrast, X-ray structure analysis of **1**[18] reveals the *S* shaped conformer (Fig. 4), readily forming inclusion complexes with various donor molecules, such as pyridine, benzene,

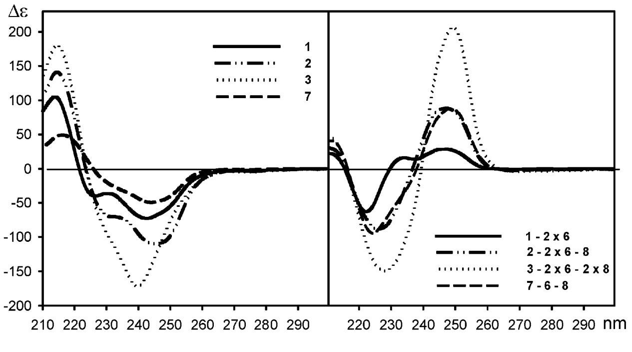


**Fig. 3** CD spectra of oligoimides in dioxane (left panel) and the corresponding differential CD spectra (right panel).

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† Electronic supplementary information (ESI) available: CD spectra and experimental details. See http://www.rsc.org/suppdata/cc/b1/b110446b/

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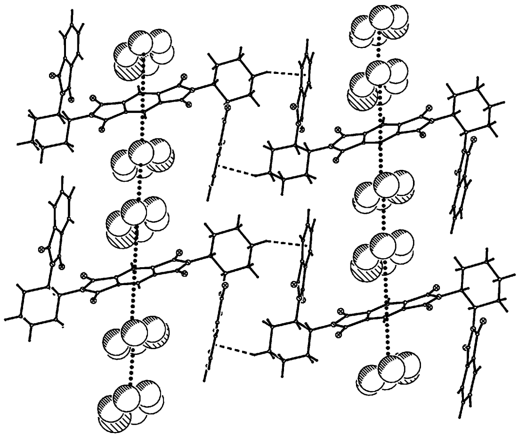

**Fig. 4** View of the (101) layer of the **1**–pyridine (1 : 2) complex.

dioxane, in a host to guest ratio of 1 : 2.[19] The stabilizing interactions involve face-to-face stacking between host and guest molecules in a sequence H : G : G : H : G : G… *etc.* and C–H/π interactions between the cyclohexane and phthalimide fragments (both operating within the *xz* layer, Fig. 4) as well as C–H (cyclohexane)…O=C (pyromellitic diimide) hydrogen bonds in between the layers.

Furthermore, the soluble homologues of **1**, *i.e.* **2** and **3** also show significant discrimination in favour of *S* shaped conformers. While the aromatic region of the $^1$H NMR spectra of **3** is too complex for analysis due to contributions from up to six conformers, in the case of **2** the signals of pyromellitic protons in conformers *CC*, *CS* and *SS* at 233 K are resolved, with those due to *S* of *ca.* 25% higher intensity. The CD spectra reveal strong contributions from chromophores in *P* (*S* shaped) conformers. These are obtained by the subtraction procedure (Fig. 3) which eliminates the contributions from vicinal (1,2) chromophoric couplings. *P* conformers are characterised by positive exciton Cotton effects, mainly due to interactions of the chromophores in 1,3 positions (Fig. 1), as is in fact observed in the differential CD spectra. This effect appears co-operative, judging from the increasing magnitudes of the differential Cotton effect of **1–3**. The unsymmetrical imide triad **7** also shows preference for the *P* conformer on the basis of a positive differential Cotton effect.

The presented data demonstrate for the first time that despite the fixed *R,R* configuration of the cyclohexane spacer oligoimides **2**, **3** and **7** fold in solution preferentially into *S* shaped conformers of *P* helicity, as does **1** in the solid state. On the other hand, **1** shows a preference for a *C* shaped conformation of *M* helicity in solution. We conclude that oligomers composed of monomers of appropriately high symmetry and stable chirality can still fold into dynamic structures of either *M* or *P* helicity. Folding preference is not due to intramolecular forces (such as hydrogen bonding) but rather due to intermolecular interactions.

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15 **1** is obtained by thermal condensation of pyromellitic anhydride with *N*-phthaloyl-(*R,R*)-1,2-diaminocyclohexane (**4**) in DMF at 130 °C. **4** is obtained in over 90% yield as the *p*-toluenesulfonate salt by thermal condensation of (*R,R*)-1,2-diaminocyclohexane with phthalic anhydride in xylene in the presence of *p*-toluenesulfonic acid.

16 The subtraction procedure is validated by obtaining a typical UV spectrum of pyromellitic diimide ($\varepsilon_{\max} = 53000$, $\lambda_{\max} = 240$ nm) by subtracting the UV of **1** from double UV of **6**.

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18 Compound $C_{38}H_{30}N_4O_8 \cdot 2C_5H_5N$. $M = 828.86$, monoclinic, $a = 18.283(4)$, $b = 11.023(2)$, $c = 11.901(2)$ Å, $\beta = 121.77(3)°$, $U = 2039.1(7)$ Å$^3$, $T = 150$ K, space group $C2$ (no. 5), $Z = 2$, $\mu$(Mo-K$_\alpha$) = 0.094, 5409 reflections measured, 1884 unique ($R_{\text{int}} = 0.052$) which were used in all calculations. The final $wR(F^2)$ was 0.097 (all data). CCDC 174750. See http://www.rsc.org/suppdata/cc/b1/b110446b/ for crystallographic files in .cif or other electronic format.

19 For clathrate formation by *S* shaped conformers see: K. Kishikawa, S. Tsubokura, S. Kohmoto and M. Yamamoto, *J. Org. Chem.*, 1999, **64**, 7568.