

# A new liquid crystalline derivative of dibenzotetraaza[14]annulene: synthesis, characterization and the preliminary evaluation of mesomorphic properties

Jarosław Grolik,<sup>a</sup> Lesław Sieroń<sup>b</sup> and Julita Eilmes<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

<sup>b</sup>Institute of General and Ecological Chemistry, Technical University of Łódź, Żeromskiego 116, 90-924 Łódź, Poland

Received 2 August 2006; revised 11 September 2006; accepted 22 September 2006

**Abstract**—A new dibenzotetraaza[14]annulene ligand has been synthesized that contains two 2-hydroxybenzoyl and four 3,7-dimethyloctyloxy peripheral substituents. Its mesomorphic textures were observed by means of a polarizing optical microscopy.  
© 2006 Elsevier Ltd. All rights reserved.

It has been well established for over 28 years from Chandrasekhar's early work<sup>1</sup> that many compounds composed of disc-shaped molecules exhibit liquid crystalline properties. The conventional mesogenic molecule has a rigid core, usually flat and aromatic, and is equipped with several (4–8) flexible aliphatic side chains that surround the core. A remarkable number of known liquid crystalline materials are based on macrocyclic systems such as porphyrins, phthalocyanines, azacrowns and macrocyclic Schiff bases.<sup>2</sup> Among them, transition metal complexes of substituted dibenzotetraaza[14]annulenes<sup>3</sup> have been found to exhibit liquid crystalline properties. Hunziker<sup>4</sup> and Veber and co-workers<sup>5</sup> have studied their mesomorphic behaviour as a function of the structure, length and number of peripheral groups. An optical storage effect was later demonstrated in one of these mesomorphic nickel complexes.<sup>6</sup>

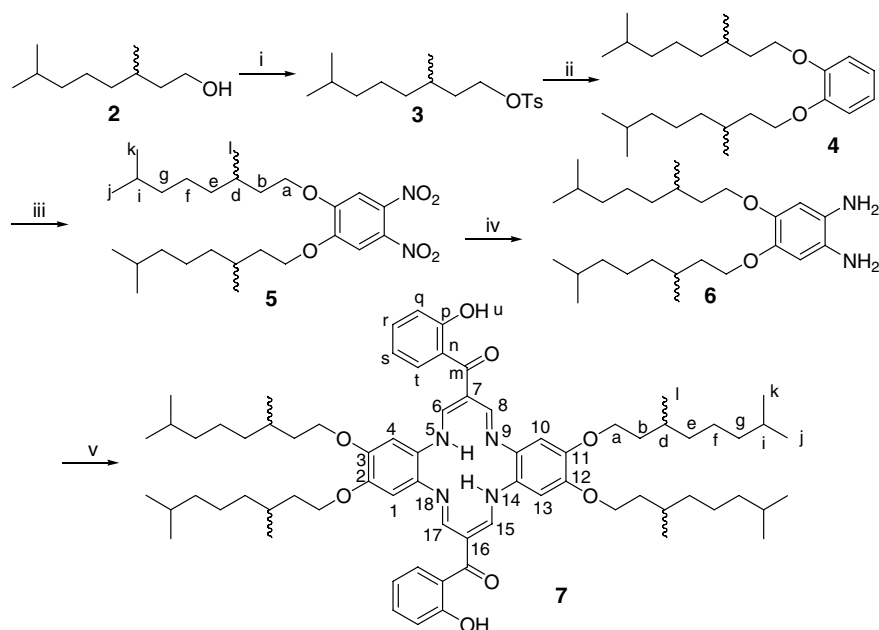
We have recently elaborated synthetic routes to various peripherally functionalized dibenzotetraaza[14]annulenes.<sup>7</sup> Herein, we describe a new liquid crystal based on a metal-free dibenzotetraaza[14]annulene macrocycle bearing two *meso* 2-hydroxybenzoyl substituents and four 3,7-dimethyloctyloxy groups attached to *o*-phenylene moieties (compound **7** in Scheme 1).

The properties-directed design of **7** was based on the known crystal structure<sup>8</sup> of *meso*-bis(2-hydroxybenzoyl)dibenzotetraaza[14]annulene precursor **1**.<sup>9</sup> As shown in Figures 1 and 2, **1** is nearly flat and is rich in  $\pi$  delocalized areas, and therefore seemed to be well suited to play the role of a disc-shaped building block. In addition, aromatic  $\pi \cdots \pi$  stacking interactions, involving planar central moieties and *meso* phenyl rings of neighbouring molecules, are clearly evidenced by the crystal structure (Fig. 3). Recent detailed studies on mesomorphic materials<sup>10</sup> have established that in the most often encountered *columnar* mesophases, the disc-like molecules self-assemble into columns by stacking one upon another and self-organize into various arrangements that differ in the degree of order and in the two-dimensional symmetry of the column packing. Accordingly, the *columnar* mesophases can be further sub-classified into those referred to as *hexagonal*, *rectangular* and *oblique*. Within discotic liquid crystals, there are also less common and less ordered *nematic* mesophases.

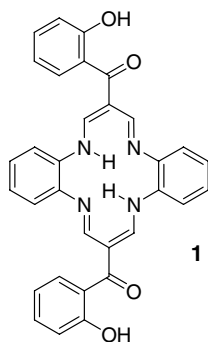
In designing mesogens it is of importance, that self-assembly and self-organisation, crucial for inducing mesomorphic behaviour to discotic materials, are mostly influenced by the structure and number of flexible pendant chains that surround the discotic units. Therefore, in order to generate such supramolecular processes in our product, we introduced four additional peripheral substituents to the macrocyclic core of the precursor **1**, by incorporating them onto the benzenoid rings. We chose 3,7-dimethyloctyloxy groups, since, as

**Keywords:** Dibenzotetraaza[14]annulene; Liquid crystal; Discotic; Textures; Polarizing optical microscopy;  $\pi \cdots \pi$  Stacking.

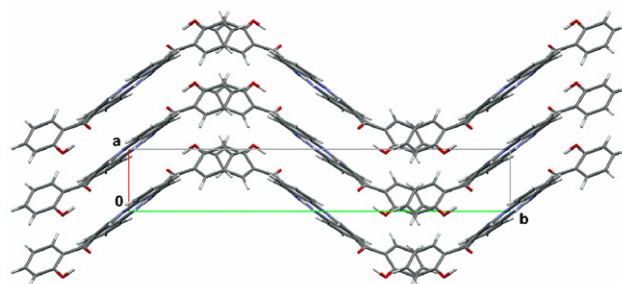
\* Corresponding author. Tel.: +48 12 6632294; fax: +48 12 6340515; e-mail: jeilmes@chemia.uj.edu.pl



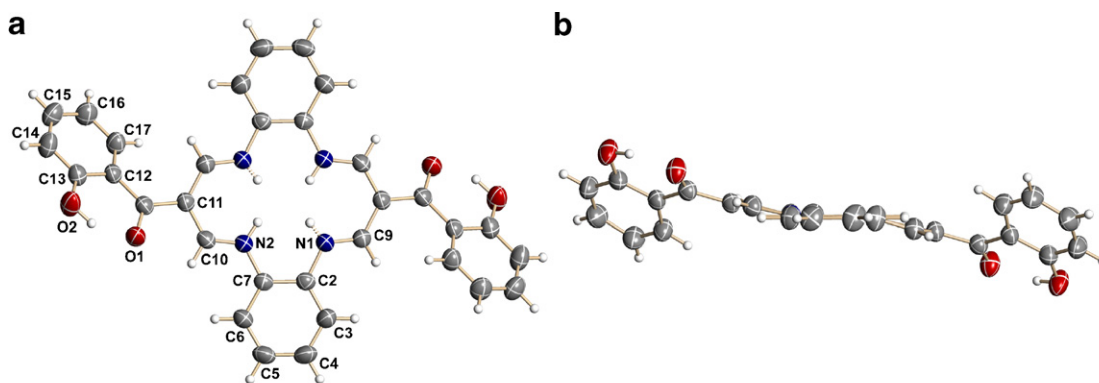
**Scheme 1.** Reagents and conditions: (i) py, TosCl, rt, (84%); (ii) catechol,  $K_2CO_3$ /DMF, 80 °C, (56%); (iii)  $CH_2Cl_2$ /HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, rt, (81%); (iv) 10% Pd/C, NaBH<sub>4</sub>, MeOH, Ar and (v) 3-formylchromone, MeOH, reflux, (41%).



**Figure 1.** 7,16-Bis(2-hydroxybenzoyl)-5,14-dihydrodibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecine **1**.<sup>9</sup>



**Figure 3.** Packing diagram viewed down the *c* axis, showing  $\pi \cdots \pi$  stacking interactions between adjacent molecules.



**Figure 2.** X-ray crystal structure of compound **1**: (a) top-view; (b) side-view. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

previously reported, this kind of flexible aliphatic chain appeared capable of inducing mesomorphic properties.<sup>11</sup>

To the best of our knowledge, **7** is the first mesomorphic metal-free dibenzotetraaza[14]annulene synthesized in a reasonable yield (41%). Previously, Veber and Forget

Download English Version:

<https://daneshyari.com/en/article/5288090>

Download Persian Version:

<https://daneshyari.com/article/5288090>

[Daneshyari.com](https://daneshyari.com)