

## Synthesis of a Polar Discogen. A New Type of Discotic Mesophase<sup>1</sup>

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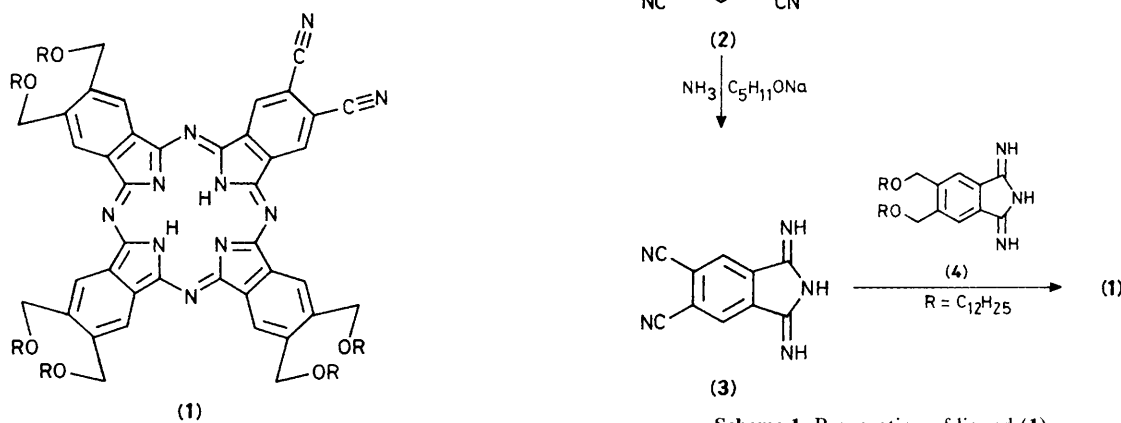
The synthesis of a discogen based on a phthalocyanine subunit is described; the discogen shows  $C_{2v}$  symmetry and possesses a high permanent electric dipole moment within the plane of the aromatic macrocycle, leading to a new type of discotic mesophase.

The elaboration of molecular materials is presently being actively investigated, and phthalocyanine-based liquid crystals have been described.<sup>2-4</sup> We now report a new ligand (**1**) allowing the formation of metallo-organic mesophases. Ligand (**1**) of  $C_{2v}$  symmetry contains six alkane chains and two cyano-groups; the cyano-groups lead to a permanent electric dipole moment which has been estimated to be 7 Debye by the vectorial additive method of calculation.<sup>5</sup> No other polar discogen has been described in the literature.<sup>6</sup>

There are few reports on the synthesis of unsymmetrically substituted phthalocyanines. The standard condensation of two different phthalonitrile derivatives gives hardly tractable mixtures of the various possible isomers.<sup>7</sup> A solid-phase approach has been reported but only analytically impure products in poor yields were obtained.<sup>8</sup> Ligand (**1**) was obtained in fair yields *via* the new route in Scheme 1. 1,2,4,5-Tetracyanobenzene<sup>9</sup> was treated with ammonia<sup>10</sup> in the presence of sodium pentoxide in pentanol to give the dicyano-di-imino derivative (**3**) (100% yield). The 'monoactivated' compound (**3**) was condensed with the dialkoxy-

substituted di-imino derivative<sup>2,4,11</sup> (**4**) (3 equiv.) in 2-*N,N*-dimethylethanol under reflux<sup>2,10,11</sup> to give ligand (**1**) in 20% yield<sup>†</sup> after separation by flash chromatography and recrystallization from ethyl acetate.

The <sup>1</sup>H n.m.r. spectra of ligand (**1**) were recorded in (CDCl<sub>2</sub>)<sub>2</sub> at various temperatures (20–90 °C) and in CCl<sub>4</sub>. The spectra are highly dependent upon the temperature and the solvent. Absorption spectrometry indicated the formation of dimers or higher molecular weight aggregates, as is well known for other types of phthalocyanines.<sup>12</sup> In very dilute solution, the monomeric form of (**1**) shows a single n.m.r. peak at  $\delta$  4.45 for the benzylic protons (CCl<sub>4</sub>) while the aggregated forms show three peaks centred at  $\delta$  4.67. The corresponding octadecyloxy substituted derivative does not show a splitting of the n.m.r. signals whatever the state of aggregation.<sup>4</sup> By comparison with n.m.r. results for silicon



Scheme 1. Preparation of ligand (**1**).

<sup>†</sup> Ligand (**1**) was characterized by <sup>1</sup>H and <sup>13</sup>C n.m.r., u.v.-visible, and i.r. spectroscopy, and elemental analyses.

phthalocyanine-siloxane dimers or oligomers,<sup>13</sup> these n.m.r. observations may be interpreted in terms of the formation in solution of dimers or higher aggregates in which rotation between adjacent macrocyclic rings is hindered and in which adjacent macrocyclic rings are staggered.

The liquid crystalline properties of ligand (1) were studied by differential scanning calorimetry and polarized light microscopy. A thermotropic mesophase stable between 80 and > 300 °C is observed. Preliminary X-ray determinations at small angles indicate a discotic-type structure; the aromatic cores stack in columns, the columns forming a two-dimensional hexagonal array.<sup>2,6</sup> The centre-to-centre distance between the columns is *ca.* 32.4 Å. We are currently attempting to determine the influence of the electric dipole moment on the structure and the degree of organisation within the columns.

As far as we know, a similar type of discotic mesophase has not been described previously. The possibility of orienting the liquid crystals is under study.

C.N.R.S., P.I.R.S.E.M., and E.E.C. are acknowledged for financial support. We thank M. J.-J. André and M. A. Skoulios for helpful and stimulating discussions, and M. R. Graf for the n.m.r. results.

Received, 9th November 1984; Com. 1586

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