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Asymmetric dibenzophospholes: new phosphorus-based chiral liquid crystals

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Abstract— (S_P, S_C) -5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide, the first example in the literature of a new asymmetrically substituted dibenzophosphole-based group of systems with liquid-crystal properties is described. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Liquid-crystal synthesis has been investigated in recent years mainly because successful applications of liquid crystals have been developed, particularly in the area of electro-optical displays.¹ At present our research group is working on the synthesis of several chiral structures in order to generate chiral liquid-crystal monomeric and macromolecular systems. Here we report a chiral phosphorus-containing structure with liquid-crystal properties, specifically a molecule derived from the dibenzophosphole system, $(S_{\rm P},S_{\rm C})$ -5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxy-phenoxycarbonyl)-5*H*dibenzophosphole 5-oxide (1).



Scheme 1. Reagents and conditions: (i) Br₂, AcOH, MeOH, 45°C, 53%; (ii) HNO₃, H₂SO₄, 0°C, 100%; (iii) Fe, HCl/H₂O, EtOH, reflux, 82%; (iv) NaNO₂, H₂SO₄/H₂O, 0°C; (v) Cu(NO₃)₂·3H₂O, Cu₂O, rt, 87% (steps (iv) and (v)); (vi) *S*-2-methylbutyltosylate, K₂CO₃, DMF, reflux, 95%; (vii) KCN, Pd(OAc)₂, PPh₃, Ca(OH)₂, DMF, 100°C, 92%; (viii) HCl/H₂O, reflux, 80%; (ix) DCC, DMAP, CH₂Cl₂, rt; (x) 4-undec-10-enoxyphenol, rt, 80% (steps (ix) and (x)).

Keywords: liquid crystals; phosphorus heterocycles; resolution.

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2. Synthesis

The synthesis is summarised in Scheme 1. It should be emphasised that descriptions in the literature of methods of synthesis of asymmetrically substituted dibenzophospholes are very scarce and limited in scope.

3. Optical resolution and determination of the absolute configuration of the phosphorus atom

The synthesis procedure yields a 1:1 mixture of two diastereomers, with different configuration on the phosphorus atom. The diastereomers were too similar to be separated by physical methods, so we had to find a resolution method for this kind of compound. The literature only gave a resolution method of dibenzo-phospholes based on the recrystallization of chiral amides prepared from dibenzophospholes with a carboxylic acid function and a pure enantiomeric amine.² However, we needed a general method applicable not only to dibenzophospholes with a carboxylic acid function.

Dimeric cyclopalladated compounds react easily with a wide range of Lewis bases to give monomeric complexes of formulae [Pd(C-N)ClL] or $[Pd(C-N)ClL_2]$. This simple reaction, using optically pure cyclopalladated dimers, is used for the resolution^{3–8} and determi-

nation of the enantiomeric excess^{9,10} of Lewis bases such as phosphines and amines. In addition, phosphine oxides are easily reduced to phosphines by trichlorosilane.¹¹ Therefore, we used the following procedure to resolve our new dibenzophosphole 5-oxide (Scheme 2): the first step was to reduce the oxide **1** by use of trichlorosilane; then the reaction between the phosphine **2** obtained and the optically active dinuclear cyclopalladated compound **3** gave a mixture of diastereomers (**4**) that were separated by column chromatography, using a SiO₂ column with CHCl₃-acetone (100/3) as eluent. Up to 85% of each diastereomer was isolated, with d.e.>95%.

In the same way, we obtained (R)-[1-(1-aminoethyl)naphthyl- C^2 , N][3-cyano-5-methyl-5H-dibenzophosphole-P][chloro]palladium(II) **4a**, a related molecule simpler and easier to study than **4b**. After the diastereomers were separated, the crystal structure of (S)-**4a** was determined by X-ray diffraction[§] in order to establish the absolute configuration of the phosphorus atom, showing that the phosphorus atom in the dibenzophosphole ring is S.

The absolute configuration of the phosphorus atom and the NMR data were correlated, as has been done in other coordinated chiral phosphines,^{12,13} and the data obtained extrapolated to analogous compounds (4b). The ¹H NMR spectra of (S)-4a and (R)-4a showed



Scheme 2. Optical resolution of 1.

[§] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150264. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

clear differences in the aromatic protons H⁴ and H⁶, the nearest to the phosphorus atom in the dibenzophosphole ring (see Scheme 2). In (S)-4a, the δ values of these protons are respectively 8.62 and 7.58 ppm, and in (R)-4a are 7.89 and 8.22 ppm. That is, the proton H^4 appears in the diastereomer (S)-4a shifted to higher fields than in diastereomer (R)-4a ($\Delta\delta(H^4)=0.73$ ppm), and the opposite occurs in the case of the proton H^6 ($\Delta\delta(H^6)$ = -0.64 ppm). This difference can only be explained by the relative positions of the planes determined by the naphthyl group and by the phenyl groups of the dibenzophosphole ligand. Exactly the same phenomenon is observed in the ¹H NMR spectra of the diastereomers (S)-4b and (*R*)-4b: the δ values of H⁴ and H⁶ are 7.88 and 8.23 ppm in (S)-4b and 7.07 and 9.02 ppm in (R)-4b ($\Delta\delta$ (H⁴)=0.88 ppm and $\Delta\delta(H^6) = -0.79$ ppm), which shows that such criteria can be used for the determination of the absolute configuration of the phosphorus atom in our complexes. As such, (S)-4b is the S_P diastereomer.

The third step of the resolution process was to decoordinate dibenzophosphole through the reaction of the 1,2-bis(diphenylphospure diastereomer with phino)ethane; and the last step was to oxidate the optically pure ligand by hydrogen peroxide. The action of 1,2-bis(diphenylphosphino)ethane (dppe) on the optically pure cyclopalladated diastereomers (S)-4 led to the enantiopure free dibenzophospholes (R)-2. The displacement proceeds by retention of the configuration at the phosphorus atom, as verified by the quantitative regeneration of the starting material (S)-4 from the free ligand (R)-2 and the dinuclear cyclopalladated derivative 3. Change in nomenclature is due to priority changes of the phosphorus-attached groups.

The oxidation of free dibenzophospholes (R)-2 afforded the corresponding oxides (S)-1 with complete retention of configuration.¹⁴ Optical purity of (S)-1b was determined by ¹H NMR and by adding 0.6 equiv. of europium (III) tris{3-(heptafluoropropylhydroxy-methylene)-(+)camphorate} as resolution agent. Signals of the aromatic H^{23} and H^{24} (see Scheme 2) showed different δ values for each diastereomer and can be used to confirm that the (R)-1b diastereomer was not detected after the oxidation of (R)-2b with hydrogen peroxide. In addition, HPLC with a CSP-1,15 a non-commercial chiral stationary phase derived from N-[N-(3,5-dinitrobenzoyl)-(S)-phenylalanyl]-(3-triethoxysilyl)propylamide, was used to determine the optical purity of (S)-1b. Very good resolution was achieved ($R_{\rm s} = 1.41$) using 1 ml/min flow of heptaneisopropanol (9:1), and >99% optical purity was measured for (*S*)-1b.

4. Liquid-crystal properties

Just as practically no synthetic nor optical general resolution methods are described in the literature for the kind of molecules reported here, so this is the first example of liquid-crystal dibenzophospholes. The differential scanning calorimetry (DSC) study of (S)-**1b** showed two phase transitions, the first from the isotropic liquid at 25°C with an associated enthalpy of 0.6 J/g and a second one at -4°C with an enthalpy of 0.8 J/g. Observation of the compound in the polarised light optical microscope showed a clear Grandjean-type cholesteric texture below 25°C, and also a blue phase on the borders of the preparation after several days at 24°C. This cholesteric structure of (S)-**1b** was confirmed by X-ray diffraction; however, in both small-angle and wide-angle zones, reflections corresponding to smectic fluctuations or microstructures inside the cholecteric phase were also observed. The transition at -4°C could not be studied by X-ray diffraction for technical reasons.

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