

# Synthesis and crystal structure of a new noncyclic polyether†

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1,7-bis[2-(N-pyridinoylaniline)]-1,4,7-trioxaheptane has been prepared and its structure elucidated by X-ray analysis.

**Keywords:** noncyclic polyether

Noncyclic polyethers offer many advantages over the use of crown ethers in the extraction and analysis (ion-selective electrodes) of the rare earths.<sup>1–3</sup> This is because of their special structure characteristics, flexible chain and variable terminal groups.<sup>4,5</sup> Vögtle reported that some heptadentate species of open-chain neutral ligands have unusual complexing properties, and that one of them has a helical conformation in the crystallised RbI complex.<sup>6</sup> The helical twist may be favoured by the attachment of rigid and bulky terminal aromatic groups to oligo (ethylene glycol units).<sup>7</sup> So far, however, few free noncyclic polyethers have been structurally characterised. We report a new noncyclic polyether: 1,7-bis[2-(N-pyridinoylaniline)]-1,4,7-trioxaheptane (**4**) which was synthesised in three steps as shown in Scheme 1. In order to understand the structural character of **4**, and provide some information on its reactivities with different metal ions, we determined its crystal structure.

The crystal structure of **4** is illustrated Fig. 1a. In one molecule, the molecular chain adjusts its conformation creating a helical structure; the angle between two terminal rings is 76.8°. Along a diagonal of the yz plane, a helical supramolecular chain was formed (Fig. 1b) by intermolecular  $\pi$ - $\pi$  stacking of terminal rings whose intercentroid distances and dihedral angles are 3.41–3.48 Å and 0.0°, respectively. There is  $\pi$ - $\pi$  stacking of terminal rings from two adjacent helical chains, forming ladder-like arrays oriented along the x axis (Fig. 2). The corresponding intercentroid distance and dihedral angle are 3.478 Å and 1.0°. In the crystal, the helical supramolecular chains were arranged in order, forming a layered supramolecular structure (Fig. 2).

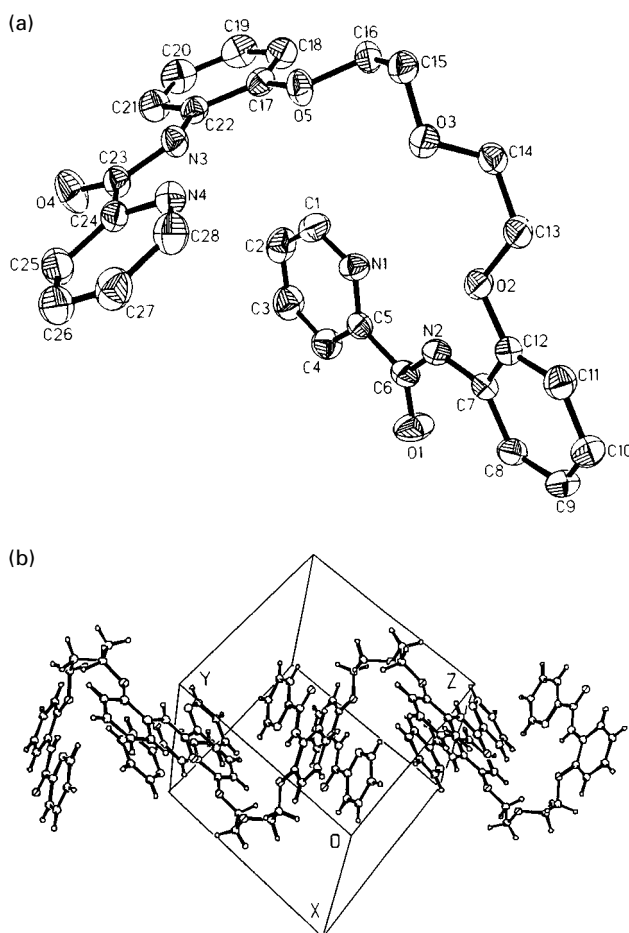
## Experimental

IR spectra were obtained with a Nicolet 170 SXFT-IR spectrometer (KBr pellets). <sup>1</sup>H spectra were recorded on DRX 200 MHz spectrometer. Column chromatography was performed using C300 silica gel. All commercially available reagents (A.R) were used without further purification.

General methods: Compounds **1**, **2** (see Scheme 1) were prepared according to the literature.<sup>8,9</sup>

**Preparation of 3:** A solution of 2 g (5.75 mmol) of **2** in 20 ml ethanol is added to a suspension of 0.8 g of Raney-Ni in 10 ml of ethanol. After the mixture had been stirred for 20 min, 15 ml of hydrazine hydrate (excess amount) was added dropwise. The reaction mixture was refluxed for 8 h, filtered and evaporated to dryness to provide a brown oil in 85 % yield.

**Preparation of 4:** The benzene solution containing compound **3** (1 g, 3.47 mmol) was added dropwise to another benzene solution of pyridinoyl chloride (1.48 g, 10.41 mmol), and 2 ml anhydrous pyridine. The mixture was stirred at 50 °C for 6 h, then the crude product was chromatographed on silica gel. (CHCl<sub>3</sub>/CH<sub>3</sub>COOEt 5:1) to afford



**Fig. 1** The crystal structure (a) and the helical supramolecular chain in the unit of **4** (b).

the compound **4** in 50 % yield as a pale white solid, m.p. = 159–160 °C. IR:  $\nu_{\max}$ /cm<sup>-1</sup> 3342.1, 3319.7 (N–H, m), 2982.9 (CH–H, m), 1718.6 (C=O, s), 1599.5, 1532.6 (Ar-ring, s), 1129.7 (C–O–C, s), <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$ : 10.68 (s, 2H, NH), 8.62–7.79 (m, 8H, Py–H), 7.36–6.89 (m, 8H, Ph–H), 4.31–4.17 (q, 8H, CH<sub>2</sub>–O–CH<sub>2</sub>). **Crystal data:** C<sub>28</sub>H<sub>26</sub>N<sub>4</sub>O<sub>5</sub>, *Mr* = 498.53, triclinic, space group *P*-1, *a* = 9.089 (2), *b* = 11.402 (2), *c* = 12.5090(10) Å,  $\alpha$  = 75.890 (10),  $\beta$  = 82.510 (10),  $\gamma$  = 87.36(2)°, *V* = 1246.4 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.328 g/cm<sup>3</sup>, *T* = 291K.  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å, *F* (000) = 524,  $\mu$ (Mo *K* $\alpha$ ) = 0.093 mm<sup>-1</sup>. Intensity data for a crystal 0.50 × 0.44 × 0.36 mm were measured on a P<sub>4</sub> four-circle diffractometer with graphite monochromatized Mo *K* $\alpha$  radiation, using a  $\omega/2\theta$  scan. Lorentz and polarisation corrections were applied, but no absorption correction was made. The structure was solved by the Patterson method and subsequent difference Fourier techniques, and refined by block-matrix least-squares procedures based on *F*<sup>2</sup>. Non-hydrogen atoms were refined anisotropically. A total of 4750 reflection was

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

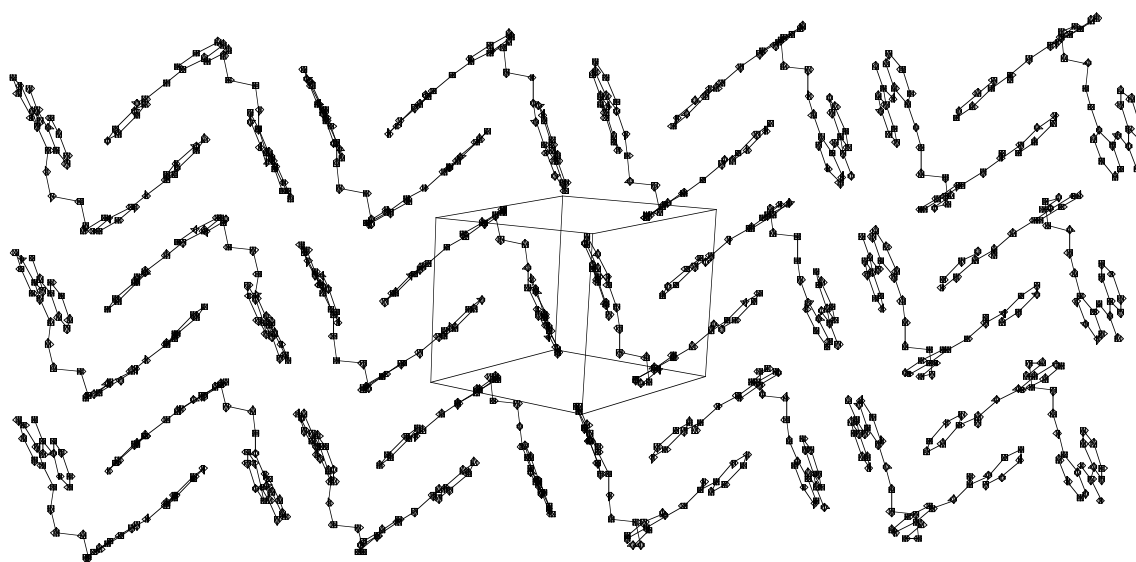
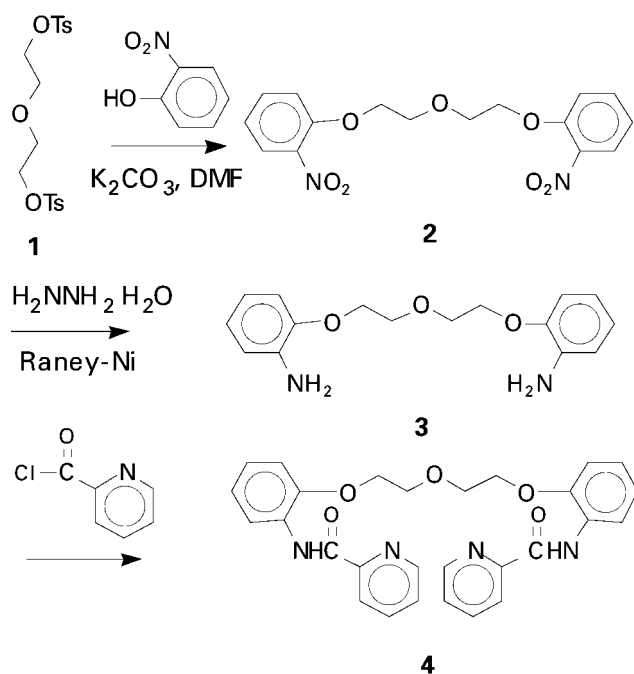


Fig. 2 Layered supramolecular structure of **4** in the crystal.



Scheme 1

collected and 4292 observed reflections with  $[I > 2\sigma(I)]$  were used for further calculations. Find  $R = 0.036$ ,  $R_w = 0.087$ . Full crystallographic details have been deposited at the Cambridge Crystallographic Data Center and allocated deposition number CCDC 158987.

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