

Nathaniel W. Alcock* and
Jonathan P RourkeDepartment of Chemistry, University of
Warwick, Coventry CV4 7AL, EnglandCorrespondence e-mail:
n.w.alcock@warwick.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 180\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in main residue
 R factor = 0.060
 wR factor = 0.168
Data-to-parameter ratio = 14.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

2,6-Bis[2,4-bis(heptyloxy)phenyl]pyridine

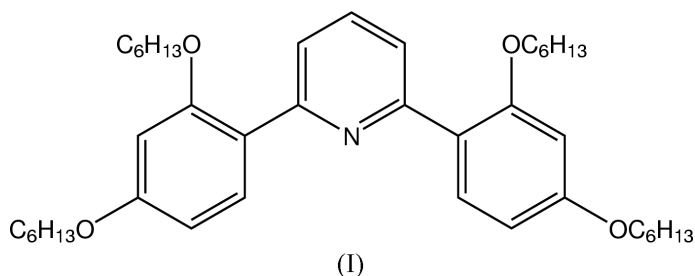
The title 2,6-disubstituted pyridine, $\text{C}_{41}\text{H}_{61}\text{NO}_4$, with a crystallographic twofold axis, has an arrangement of molecules well organized to undergo multiple cyclometallation reactions.

Received 16 December 2004

Accepted 13 January 2005

Online 22 January 2005

Comment

2,6-Disubstituted pyridines are ideally set up to undergo multiple cyclometallations, reactions of considerable interest to us (Cave *et al.*, 1999, 2000). In addition to their ability to undergo multiple cyclometallations, such compounds have also been shown to be activated by other reagents (Cave *et al.*, 1998).

The title molecule, (I) (Fig. 1), has crystallographic twofold symmetry and the aliphatic chains are each in an extended form. Within the unit cell, the molecules are aligned in an antiparallel fashion (Figs. 2 and 3).

Experimental

1-Chloro-2,4-bis(heptyloxy)benzene (15.0 g, 48.0 mmol) was added dropwise to a stirred solution of magnesium (1.22 g, 50.0 mmol) and methyl iodide (0.30 g, 2.11 mmol) in tetrahydrofuran (THF, 25 ml) under an inert atmosphere. The resulting Grignard reagent was transferred *via* a cannula to a stirred solution of 2,6-dichloropyridine (2.96 g, 20.0 mmol) and tetrakis(triphenylphosphine)palladium (0.45 g, 0.50 mmol) in THF (25 ml). The reaction mixture was then heated under reflux (24 h) under an inert atmosphere. Excess Grignard was destroyed with water (20 ml) and hydrochloric acid (5 ml, 2 M). The neutralized (aqueous NaOH) reaction mixture was extracted with diethyl ether (2 × 200 ml) and dried (saturated NaCl and magnesium sulfate). The solvent was removed under vacuum and the product crystallized out as white needle-like crystals (yield: 12.0 g, 19.0 mmol, 95%). $^1\text{H NMR}$ (CDCl_3 , 250.13 MHz): δ 7.96 (2H, *d*, $^3J = 8.5\text{ Hz}$), 7.75 (2H, *d*, $^3J = 7.3\text{ Hz}$), 7.60 (1H, *t*, $^3J = 7.3\text{ Hz}$), 6.59 (2H, *dd*, $^3J = 8.5$, $^4J = 2.1\text{ Hz}$), 6.53 (2H, *d*, $^4J = 2.1\text{ Hz}$), 3.99 (8H, *t*, $^3J = 6.7\text{ Hz}$), 1.79 (8H, *m*), 1.48 (24H, *m*), 0.89 (12H, *m*). $^{13}\text{C NMR}$ (CDCl_3 , 250.13 MHz): δ 160.5, 157.7, 154.7, 134.8, 132.1, 131.5, 121.9, 105.6, 100.0, 68.2, 31.4, 25.7, 22.5. Elemental analysis found (expected): C 77.8 (77.9), H 9.6 (9.7), N 2.4% (2.2%).

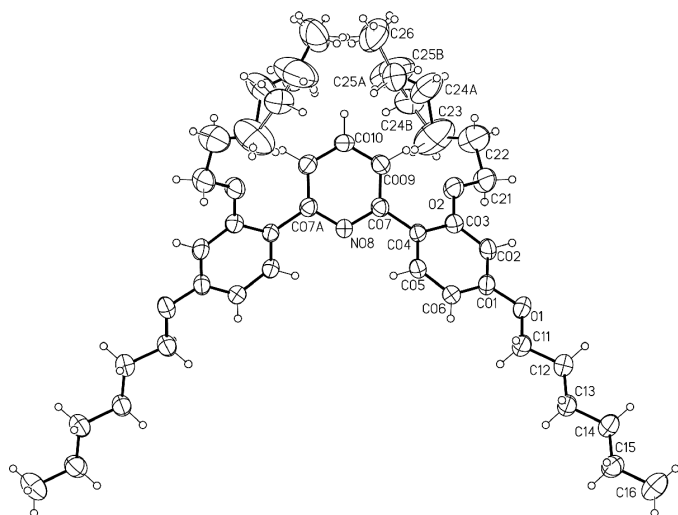


Figure 1
View of the title molecule, showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. Both disorder components are shown in all Figures.

Crystal data

$C_{41}H_{61}NO_4$
 $M_r = 631.91$
 Monoclinic, $P2_1/n$
 $a = 11.2502$ (10) Å
 $b = 6.9682$ (6) Å
 $c = 24.014$ (2) Å
 $\beta = 93.963$ (2)°
 $V = 1878.0$ (3) Å³
 $Z = 2$

$D_x = 1.117$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2201 reflections
 $\theta = 3\text{--}15^\circ$
 $\mu = 0.07$ mm⁻¹
 $T = 180$ (2) K
 Block, colourless
 $0.45 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.896$, $T_{\max} = 0.989$
 8996 measured reflections
 3318 independent reflections

1753 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -8 \rightarrow 7$
 $l = -18 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.168$
 $S = 1.04$
 3318 reflections
 229 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.043$
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

H atoms were added at calculated positions ($C\text{--}H = 0.95\text{--}0.99$ Å) and refined using a riding model (including free rotation about $C\text{--}C$ bonds for methyl groups), with $U_{\text{iso}}(H) = 1.2$ (or 1.5 for methyl H atoms) times $U_{\text{eq}}(C)$. The terminal section of one of the heptane chains was found to be disordered between two positions [relative occupancies 0.43 (1):0.57 (1)]. This disorder is believed to be responsible for various anomalies in the displacement parameters of the atoms in this region of the molecule.

Data collection: SMART (Siemens, 1994); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

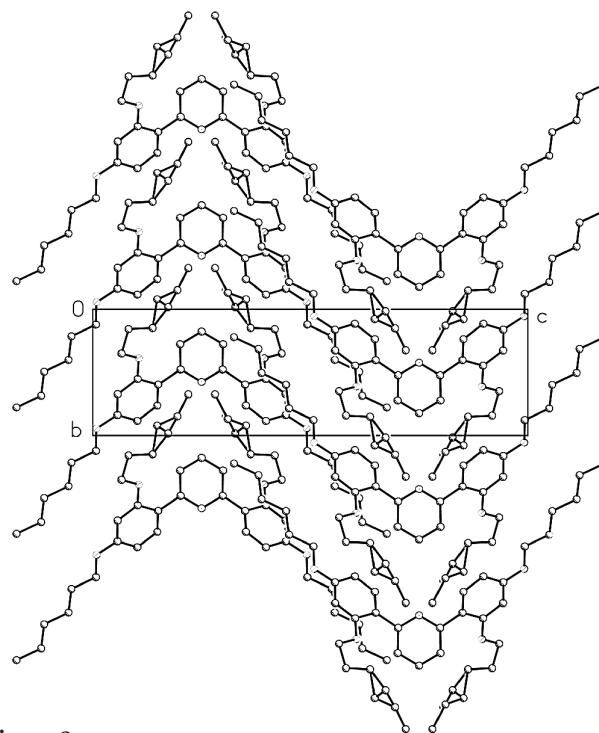


Figure 2
Packing diagram of (I), viewed down the a axis. H atoms have been omitted.

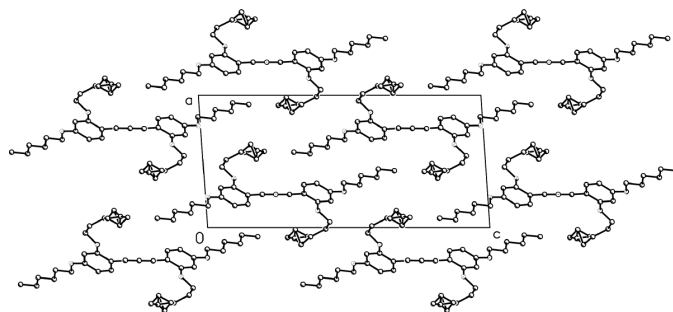


Figure 3
Packing diagram of (I), viewed down the b axis. H atoms have been omitted.

The EPSRC and Siemens generously supported the purchase of the SMART diffractometer.

References

- Cave, G. W. V., Alcock, N. W. & Rourke, J. P. (1999). *Organometallics*, **18**, 1801–1803.
 Cave, G. W. V., Fanizzi, F. P., Deeth, R. J., Errington, W. & Rourke, J. P. (2000). *Organometallics*, **19**, 1355–1364.
 Cave, G. W. V., Hallett, A. J., Errington, W. & Rourke, J. P. (1998). *Angew. Chem. Int. Ed.* **37**, 3270–3272.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997a). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Siemens (1994). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1995). *SAINTE*. Version 4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.