Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Crystal Structure of 4-Cyano-4′-n-Undecylbiphenyl

T. Manisekaran [a], R. K. Bamezai [b], N. K. Sharma [b] & J. Shashidhara Prasad [c]

[a] Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, 600036, India

[b] Department of Chemistry, University of Jammu, Jammu, 570006, India

[c] Department of Studies in Physics, University of Mysore, Mysore, 570006, India

Version of record first published: 24 Sep 2006.

To cite this article: T. Manisekaran , R. K. Bamezai , N. K. Sharma & J. Shashidhara Prasad (1995): Crystal Structure of 4-Cyano-4′-n-Undecylbiphenyl, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 268:1, 45-50

To link to this article: http://dx.doi.org/10.1080/10587259508030991

Mol. Cryst. Liq. Cryst., 1995, Vol. 268, pp. 45–50
Reprints available directly from the publisher
Photocopying permitted by license only

Crystal Structure of 4-Cyano-4′-*n*-Undecylbiphenyl

T. MANISEKARAN[1], R. K. BAMEZAI[2], N. K. SHARMA[2] and J. SHASHIDHARA PRASAD[3,*]

[1] *Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras-600 036, India*
[2] *Department of Chemistry, University of Jammu, Jammu-570 006, India*
[3] *Department of Studies in Physics, University of Mysore, Mysore-570006, India*

(Received May 23, 1994; in final form September 23, 1994)

4-Cyano-4′-*n*-undecylbiphenyl, $C_{24}N_1H_{31}$, $M_r = 333.52$, triclinic, P1, $a = 9.755(2)$, $b = 11.322(1)$, $c = 19.911(2)$Å, $\alpha = 96.86(1)$, $\beta = 94.41(2)$, $\gamma = 109.16(1)°$, $V = 2046.46$Å, $Z = 4$, $D_x = 1.082$ g/cc, $\mu = 0.574$ cm^{-1}, $F(000) = 728.0$, $\lambda(MoK_\alpha) = 0.71073$ Å, $T = 326$ K, final R and wR are 0.0476 and 0.0625 respectively for 7225 reflections included in least squares calculations.

Keywords: Crystal structure, 4-cyano-4′-n-undecylbiphenyl, smectic A

INTRODUCTION

The structure 4-cyano-4′-decylbiphenyl is reported in our paper on page 83 of this volume.[1] To achieve greater insight into molecular packing in homologous series of 4-cyano-4-*n*-alkylbiphenyl[2-3] the structure of the higher homolog 4-cyano-4′-*n*-undecylbiphenyl was determined. The title compound (Figure 1) was recrystallised before mounting it on a diffractometer. The needle like crystals undergo transformation to a smectic A phase at 326 K which finally becomes an isotropic liquid at 330.5 K.

EXPERIMENTAL

White crystals suitable for X-ray data collection were grown by slow evaporation of the solution of the compound in acetone. X-ray diffraction intensity data were collected from a single crystal of approximate dimensions 0.1 × 0.3 × 0.5 mm on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated MoKα radiation. The accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflections. Intensities were collected by $\omega - 2\theta$ scan. 6544 unique reflections were measured in the range $2 < \theta < 25°$; $0 < h < 11$, $-13 < k < 13$, $-23 < 1 < 23$. Two strong reflections monitored every hour of X-ray exposure did not show significant decay of their intensities. The intensities were corrected for Lorentz

* Author to whom correspondence should be addressed.

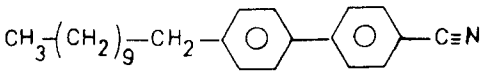

FIGURE 1 General view of the molecule.

and polarization factors. The crystal structure was solved by SHELXS 86[4] and was refined by full matrix least squares using the Enraf-Nonius structure determination package.[5] Hydrogen atoms were placed at calculated positions[5] (C–H 0.95Å) and assigned isotropic thermal parameters equivalent to those of the atoms to which they are bonded. In final refinement, 451 parameters were refined using 6544 unique reflections with $R = 0.0476$, $wR = 0.0625$, {where $w = k/[\sigma(F)^2 + P^*F^2]$ with $k = 1.000$, $P = 0.04$}. The maximum and minimum electron densities in final electron density map were $(\Delta\rho)_{max} = 0.199$, $(\Delta\rho)_{min} = -0.249$ eÅ^{-3} respectively, $(\Delta/\sigma)_{max} = 0.022$. All calculations were performed on Micro Vax 3100 computer.

DISCUSSION

The fractional atomic coordinates with the equivalent isotropic temperature factors of the non-hydrogen atoms, bond lengths and bond angles are given in Tables 1–3, respectively. Figure 2 shows an ORTEP[6] plot of the molecule with atom numbering scheme. Selected torsion angles are presented in Table 4. The packing of the molecules in the unit cell is shown in Figure 3. The best planes for the two benzene rings of molecule 1 and 2 in the asymmetric unit are given by $0.2320x + 0.6337y - 0.7380z + 1.5443 = 0$, $0.6893x + 0.4561y - 0.5682z + 2.6615 = 0$; $-0.1471x + 0.7379y - 0.6587z + 3.3564 = 0$, $-0.6559x + 0.6850y - 0.3170z + 0.4476 = 0$. The dihedral angle between the phenyl rings in molecule 1 is 30.19(11), while the dihedral angle between the corresponding rings in molecule 2 of the asymmetric unit is 35.83(9). This shows that the two molecules in the asymmetric unit have slightly different conformations. As shown in Figure 2, the projection of the thermal ellipsoids on the best plane of the molecules 1 and 2 are $(0.2506x + 0.7071y - 0.6612z + 0.6030 = 0$; $-0.1188x + 0.7284y - 0.6748z + 3.7088 = 0)$. The molecular packing down a axis is shown in Figure 3. As can be seen from the packing diagram, pairs of molecules form an anti parallel arrangement with their N-C dipoles opposed attractively with each other. The diphenyl parts of neighbouring molecules overlap. There are slight conformational differences betweeen the two molecules in the asymmetric unit. (N1–C1 = 23.26 Å; N2–C25 = 23.1Å). The molecule in one sheet is related to its neighbour in the next by inversion through a centre. It is clear from the packing diagram (Fig. 3) that the two molecules of the asymmetric unit are bent at C11 and C35. Atoms C1 to C12 and C25 to C36 form chains with extended configuration. The cohesion between the molecules is predominant through dipolar interactions of N≡C. The molecular pairs of the asymmetric unit are packed in layers which is a requirement for the material to be a smectogen. The thermal stability is not high due to the non-planarity of phenyl groups (dihedral angle of $\approx 30°$) and smaller overlap of the molecules of asymmetric group.

TABLE I

Thermal and postional parameters and their estimated standard deviations for the non- hydrogen atoms

Atom	x	y	z	B_{eq}(Å^2)
		Molecule 1		
C(1)	−0.4036(2)	−0.4914(12)	−0.2321(1)	6.78(6)
C(2)	−0.2908(2)	−0.3811(2)	−0.1857(1)	5.79(5)
C(3)	−0.3580(2)	−0.2973(2)	−0.1456(5)	5.59(5)
C(4)	−0.2486(2)	−0.1848(2)	−0.0986(1)	5.44(5)
C(5)	−0.3174(2)	−0.1074(2)	−0.0545(1)	5.21(5)
C(6)	−0.2083(2)	0.0034(2)	−0.0071(1)	5.33(5)
C(7)	−0.2781(2)	0.0778(2)	0.0391(1)	5.20(5)
C(8)	−0.1689(2)	0.1877(2)	0.0877(1)	5.35(5)
C(9)	−0.2384(2)	0.2618(2)	0.1339(1)	5.32(5)
C(10)	−0.1300(2)	0.3701(22)	0.1826(1)	5.41(Y)
C(11)	−0.2009(2)	0.4442(2)	0.2271(1)	5.72(5)
C(12)	−0.1012(12)	0.5577(2)	0.27558(9)	4.91(5)
C(13)	0.0412(2)	0.5716(2)	0.2991(1)	5.67(5)
C(14)	0.1276(2)	0.6735(2)	0.3466(1)	5.51(5)
C(15)	0.0744(2)	0.7664(2)	0.37314(9)	4.50(4)
C(16)	−0.0675(2)	0.7530(22)	0.3482(1)	5.30(5)
C(17)	−0.1529(2)	0.6522(2)	0.3015(1)	5.30(5)
C(18)	0.1619(2)	0.8700(2)	0.42798(9)	4.60(4)
C(19)	0.2637(2)	0.8533(2)	0.4748(1)	5.00(5)
C(20)	0.3392(2)	0.9457(2)	0.5288(1)	5.19(5)
C(21)	0.3145(2)	1.0594(2)	0.53657(9)	4.96(5)
C(22)	0.2157(2)	1.0792(2)	0.4897(1)	6.53(6)
C(23)	0.1406(2)	0.9858(2)	0.4366(1)	6.10(5)
C(24)	0.3901(2)	1.1570(2)	0.5936(1)	5.85(6)
N1	0.4500(2)	1.2330(2)	0.6382(1)	7.82(6)
		Molecule 2		
C(25)	−0.3751(3)	−0.9696(2)	−0.2486(1)	9.07(8)
C(26)	−0.2707(2)	−0.8650(2)	−0.1968(1)	6.47(6)
C(27)	−0.3450(2)	−0.7962(2)	−0.1506(1)	5.88(5)
C(28)	−0.2414(2)	−0.6858(2)	−0.1004(1)	5.48(5)
C(29)	−0.3144(2)	−0.6163(2)	−0.0540(1)	5.30(5)
C(30)	−0.2092(2)	−0.5036(2)	−0.0059(1)	5.18(5)
C(31)	−0.2822(2)	−0.4301(2)	0.0382(1)	5.26(5)
C(32)	−0.1751(2)	−0.3154(2)	0.0855(1)	5.22(5)
C(33)	−0.2473(2)	−0.2397(2)	0.1284(1)	5.30(5)
C(34)	−0.1402(2)	−0.1258(2)	0.17509(9)	4.99(5)
C(35)	−0.2141(2)	−0.0539(2)	0.2193(1)	5.46(5)
C(36)	−0.1162(2)	0.0589(2)	0.26962(9)	4.59(4)
C(37)	−0.1786(2)	0.1260(2)	0.3125(1)	5.61(5)
C(38)	−0.0946(2)	0.2261(2)	0.3609(1)	5.46(5)
C(39)	0.0568(2)	0.2637(2)	0.36865(9)	4.54(4)
C(40)	0.1205(2)	0.1981(2)	0.32448(9)	4.77(5)
C(41)	0.0343(2)	0.0981(2)	0.27624(9)	5.05(5)
C(42)	0.1473(2)	0.3673(2)	0.42330(9)	4.28(4)
C(43)	0.0988(2)	0.3829(2)	0.4865(1)	5.28(5)
C(44)	0.1809(2)	0.4754(2)	0.5383(1)	5.42(5)
C(45)	0.3156(2)	0.5566(2)	0.5290(1)	5.19(5)
C(46)	0.3669(2)	0.5433(2)	0.4659(1)	5.51(5)
C(47)	0.2821(2)	0.4490(2)	0.4144(1)	5.02(5)
C(48)	0.4033(2)	0.6532(2)	0.5832(1)	6.23(6)
N(2)	0.4720(2)	0.7299(2)	0.6260(1)	9.04(6)

Anisotropically refined parameters are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3)*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(cos gamma)*B(1,2)+ac(cos beta)*B(1,3)+bc(cos alpha)*(2,3)]

TABLE II

Bond Distances (Å) with e.s.d's in parentheses

Molecule 1		Molecule 2	
C(1) – C(2)	1.514(2)	C(25) – C(26)	1.503(3)
C(2) – C(3)	1.508(3)	C(26) – C(27)	1.511(3)
C(3) – C(4)	1.518(2)	C(27) – C(28)	1.515(2)
C(4) – C(5)	1.511(3)	C(28) – C(29)	1.509(3)
C(5) – C(6)	1.511(2)	C(29) – C(30)	1.515(2)
C(6) – C(7)	1.518(3)	C(30) – C(31)	1.510(3)
C(7) – C(8)	1.518(2)	C(31) – C(32)	1.527(2)
C(8) – C(9)	1.515(3)	C(32) – C(33)	1.508(3)
C(9) – C(10)	1.507(3)	C(33) – C(34)	1.516(3)
C(10) – C(11)	1.505(3)	C(34) – C(35)	1.506(3)
C(11) – C(12)	1.505(2)	C(35) – C(36)	1.514(2)
C(12) – C(13)	1.383(3)	C(36) – C(37)	1.380(3)
C(12) – C(17)	1.389(3)	C(36) – C(41)	1.378(2)
C(13) – C(14)	1.383(2)	C(37) – C(38)	1.375(2)
C(14) – C(15)	1.387(3)	C(38) – C(39)	1.387(2)
C(15) – C(16)	1.387(3)	C(39) – C(40)	1.393(3)
C(15) – C(18)	1.480(2)	C(39) – C(42)	1.485(2)
C(16) – C(17)	1.366(2)	C(40) – C(41)	1.379(2)
C(18) – C(19)	1.384(3)	C(42) – C(43)	1.389(3)
C(18) – C(23)	1.386(3)	C(42) – C(47)	1.376(2)
C(19) – C(20)	1.377(2)	C(43) – C(44)	1.367(2)
C(20) – C(21)	1.378(3)	C(44) – C(45)	1.375(2)
C(21) – C(22)	1.380(3)	C(45) – C(46)	1.398(3)
C(21) – C(24)	1.446(2)	C(45) – C(48)	1.433(2)
C(22) – C(23)	1.370(2)	C(46) – C(47)	1.380(2)
N(1) – C(24)	1.130(2)	N(2) – C(48)	1.133(3)

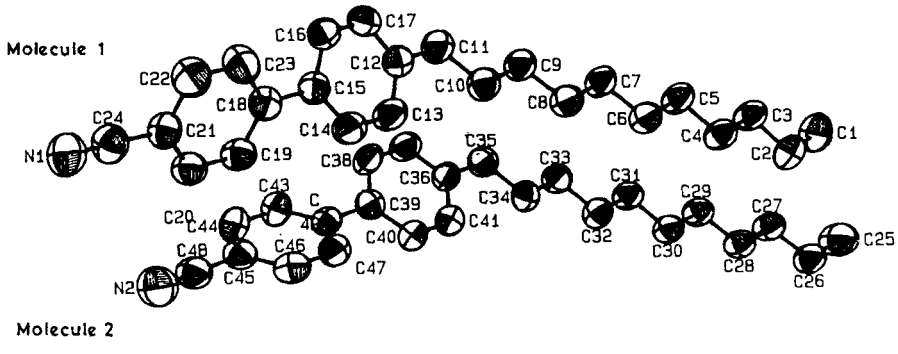

FIGURE 2 ORTEP plot of the molecule with thermal ellipsoids at 50% probability.

TABLE 3

Bond Angles (°) e.s.d' s in parentheses

Molecule 1		Molecule 2	
C(1) – C(2) – C(3)	112.7(2)	C(25) – C(26) – C(27)	113.8(2)
C(2) – C(3) – C(4)	114.5(2)	C(26) – C(27) – C(28)	114.6(2)
C(3) – C(4) – C(5)	114.2(2)	C(27) – C(28) – C(29)	115.1(2)
C(4) – C(5) – C(6)	114.0(2)	C(28) – C(29) – C(30)	114.3(2)
C(5) – C(6) – C(7)	113.8(2)	C(29) – C(30) – C(31)	114.3(1)
C(6) – C(7) – C(8)	114.0(2)	C(30) – C(31) – C(32)	113.8(1)
C(7) – C(8) – C(9)	114.1(2)	C(31) – C(32) – C(33)	114.1(2)
C(8) – C(9) – C(10)	114.0(2)	C(32) – C(33) – C(34)	113.8(2)
C(9) – C(10) – C(11)	113.3(2)	C(33) – C(34) – C(35)	113.1(2)
C(10) – C(11) – C(12)	117.2(2)	C(34) – C(35) – C(36)	117.1(2)
C(11) – C(12) – C(13)	123.2(2)	C(35) – C(36) – C(37)	119.4(2)
C(11) – C(12) – C(17)	120.1(2)	C(35) – C(36) – C(41)	123.4(2)
C(13) – C(12) – C(17)	116.6(1)	C(36) – C(37) – C(38)	121.6(2)
C(12) – C(13) – C(14)	121.9(2)	C(36) – C(41) – C(40)	122.1(2)
C(13) – C(14) – C(15)	121.2(2)	C(37) – C(36) – C(41)	117.2(1)
C(14) – C(15) – C(16)	116.4(1)	C(37) – C(38) – C(39)	121.2(2)
C(14) – C(15) – C(18)	121.4(2)	C(38) – C(39) – C(40)	117.4(1)
C(16) – C(15) – C(18)	122.0(2)	C(38) – C(39) – C(42)	121.2 (2)
C(15) – C(16) – C(17)	122.4(2)	C(39) – C(40) – C(41)	120.4(2)
C(12) – C(17) – C(16)	121.4(2)	C(39) – C(42) – C(43)	120.4(1)
C(15) – C(18) – C(19)	121.3(2)	C(39) – C(42) – C(47)	122.1(2)
C(15) – C(18) – C(23)	121.5(2)	C(40) – C(39) – C(42)	121.4(2)
C(19) – C(18) – C(23)	117.2(1)	C(42) – C(43) – C(44)	121.8(2)
C(18) – C(19) – C(20)	122.1(2)	C(42) – C(47) – C(46)	121.8(2)
C(19) – C(20) – C(21)	119.5(2)	C(43) – C(42) – C(47)	117.5(1)
C(20) – C(21) – C(22)	119.4(2)	C(43) – C(44) – C(45)	120.2(2)
C(20) – C(21) – C(24)	120.6(2)	C(44) – C(45) – C(46)	119.1(2)
C(22) – C(21) – C(24)	120.0(2)	C(44) – C(45) – C(48)	120.8(2)
C(21) – C(22) – C(23)	120.3(2)	C(45) – C(46) – C(47)	119.5(2)
C(18) – C(23) – C(22)	121.5(2)	C(46) – C(45) – C(48)	120.1(2)
N(1) – C(24) – C(21)	179.5(3)	N(2) – C(48) – C(45)	176.6(2)

TABLE 4

Selected Torsion Angles (°) with e.s.d' s in parentheses

Molecule 1	
C(10) – C(11) – C(12) – C(13)	– 23.82(0.27)
C(10) – C(11) – C(121) – C(17)	159.21(0.18)
C(14) – C(15) – C(18) – C(19)	– 28.84(0.27)
C(14) – C(15) – C(18) – C(23)	154.30(0.19)
C(16) – C(15) – C(18) – C(19)	147.59(0.19)
C(16) – C(15) – C(18) – C(23)	– 29.27(0.27)
C(20) – C(21) – C(24) – N(1)	29.19(23.26)
C(22) – C(21) – C(24) – N(1)	– 151.44(23.12)
Molecule 2	
C(34) – C(35) – C(36) – C(41)	0.47(0.27)
C(34) – C(35) – C(36) – C(37)	– 178.30(0.17)
C(40) – C39) – C(42) – C(47)	35.72(0.26)
C(40) – C(39) – C(42) – C(43)	– 142.70(0.18)
C(38) – C(39) – C(42) – C(47)	– 146.10(0.19)
C(38) – C(39) – C(42) – C(43)	35.48(0.25)
C(46) – C(45) – C(48) – N(2)	127.63(32.62)
C(44) – C(45) – C(48) – N(2)	– 52.84(32.72)

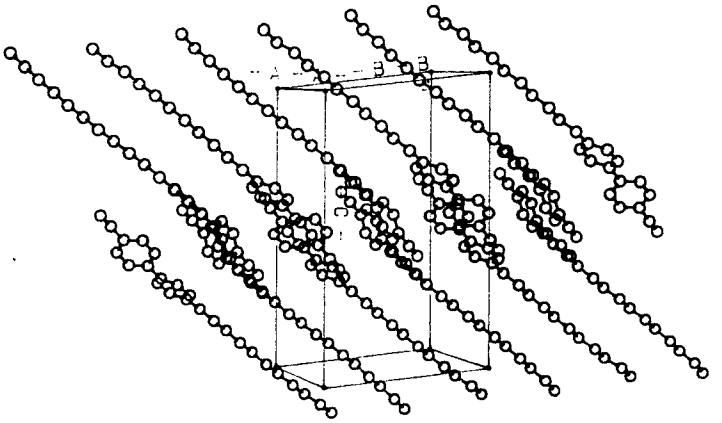

FIGURE 3 Packing of the molecules. Projection of the unit cell down a axis.

Acknowledgements

TMS, would like to express his thanks to the Head, RSIC, IIT, Madras for the facilities provided. JSP, would like to thank DST for the award of a project No. SP/S2/M-34-86. RKB, is thankful to CSIR, New Delhi for Pool Officership.

References

1. T. Manisekaran, R. K. Bamezai, N. K. Sharma and J. Shashidhara Prasad (communicated to Mol. Cryst. Liq. Cryst.).
2. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973).
3. A. Ashford, J. Constant, J. Kirton, and E. P. Raynes, *Electron. Lett.*, **9**, 118 (1973).
4. G. M. Sheldrick, SHELXS86. Program for crystal structure determination, p. 175, Crystallographic computing 3, edited by G. M. Sheldrick, C. Krüger and R. Goddard, Oxford Univ. Press, England (1985).
5. Mo1EN, An Interactive Structure Solution Procedure, Enraf Nonius, Delft, The Netherlands (1990).
6. ORTEP-II: A Fortran Thermal Ellipsoid plot program for Crystal Structure Illustrations. C. K. Johnson (1976) ORNL-5138.