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

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4-Cyano-4′-*n*-decylbiphenyl, $C_{23}NH_{29}$, M_r = 319.49, monoclinic, $P2_1/n$, a = 15.813(1)Å, b = 5.479(1)Å, c = 23.179(2)Å, β = 102.2(1)°, V = 1963.26Å^3, Z = 4. D_X = 1.067 gm/cc, μ = 0.569 cm^{-1}, F(000) = 680, (MoK_α) = 0.71073Å, final R and wR are 0.054 and 0.062 respectively using 1281 reflections taken in least squares calculations.

Keywords: Crystal structure, 4-Cyano-4′-n-decylbiphenyl, nematic

INTRODUCTION

The discovery of room temperature nematic liquid crystals in cyano alkylbiphenyl homologous series by Gray *et al.*[1] and their subsequent electrical and electro-optic measurements by Ashford *et al.*[2] showed that these compounds are extremely useful for display device applications. Important experimental differences between solid crystals and liquid crystals with three dimensional order were suggested to be that liquid crystals with optically active molecules form twisted structures whereas solid crystals do not and that similar mesomorphic phases of different compounds mix in all proportions while crystalline solid phases do not.[3–5]

Later a new model proposed by de Vries[6] suggested that the main difference between solid crystals and liquid crystals is that in the solid crystals the alkyl chains at the ends of the molecule have very little disorder or no disorder at all whereas in the liquid crystals the alkyl chains are slightly disordered.

The structure of liquid crystalline phases have been very well established and reported by many authors.[7–10] In the present work, the aim was to study the molecular

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packing in a homologous series. For this purpose, we have chosen 4-cyano-4'-*n*-decylbiphenyl. The subsequent papers will deal with some of its higher as well as lower homologs. The title compound was obtained from BDH (England) and was recrystallised before mounting it on a diffractometer. The compound forms a nematic phase at 44.0°C, and finally goes into the isotropic liquid phase at 50.5°C. The structural formula is given in Figure 1.

EXPERIMENTAL

White needles of dimensions 0.18 × 0.33 × 0.5 mm were obtained from a solution in acetone. The accurate cell dimensions and orientation matrix were obtained by

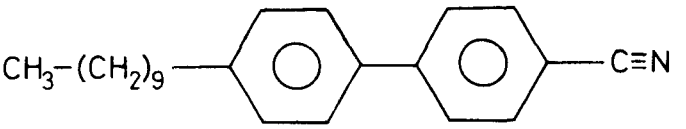

FIGURE 1 Structural formula of the molecule.

TABLE I

Positional and thermal parameters and their estimated standard deviations for the non-hydrogen atoms

ATOM	X	Y	Z	B_{eq} Å^2
N	0.3202(2)	0.1753(5)	0.75823(9)	8.86(7)
Cl	−0.2011(2)	0.4632(6)	−0.1925(1)	10.0(1)
C2	−0.2033(2)	0.2850(5)	−0.1432(1)	7.63(8)
C3	−0.1413(2)	0.3483(5)	0.08619(9)	6.17(6)
C4	−0.1438(2)	0.1791(4)	−0.03544(9)	5.84(6)
C5	−0.0828(2)	0.2447(5)	0.02109(9)	5.96(6)
C6	−0.0863(2)	0.0743(6)	0.07187(9)	5.74(6)
C7	−0.279(2)	0.1405(5)	0.13056(9)	6.19(6)
C8	−0.376(2)	0.0303(5)	0.1797(1)	6.15(6)
C9	0.0138(2)	0.0334(4)	0.2406(1)	6.13(6)
C10	−0.0079(2)	−0.1367(5)	0.2870(1)	7.12(7)
C11	0.0379(2)	0.0823(5)	0.34923(9)	5.78(6)
C12	0.1017(2)	0.2259(5)	0.3791(1)	8.03(8)
C13	0.1409(2)	0.1818(5)	0.4367(1)	8.14(8)
C14	0.1192(1)	0.0129(4)	0.46801(9)	4.89(5)
C15	0.0551(2)	0.1581(5)	0.4374(1)	7.10(7)
C16	0.0155(2)	0.1125(6)	0.3796(1)	7.87(8)
C17	0.1608(1)	0.0568(4)	0.53038(9)	4.94(5)
C18	0.2234(2)	−0.0965(6)	0.5599(1)	8.75(8)
C19	0.2619(2)	−0.0631(6)	0.6177(1)	9.76(9)
C20	0.2406(1)	0.1265(5)	0.64908(9)	5.80(6)
C21	0.1786(2)	0.2846(6)	0.6210(1)	7.53(7)
C22	0.1408(2)	0.2495(5)	0.5628(1)	7.59(7)
C23	0.2837(2)	0.1570(5)	0.7104(1)	7.01(7)

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

a least-squares fit to the setting angles of 25 reflections on Enraf-Nonius computer controlled four circle diffractometer employing MoK_α radiation. Intensities were collected by ω-2θ-scan. Two reflections measured every one hour showed no deterioration of the crystal. 3317 unique reflections were measured, of which 1281 had I greater than $2.5\sigma(I)$. Lorentz and polarization corrections were applied. The crystal structure was solved by SHELXS-86[11] and was refined by full matrix least-squares using the Enraf-Nonius Structure Determination Package.[12] Hydrogen atoms were included in calculated positions (C—H 0.95Å) in the structure and given isotropic thermal parameters equivalent to those of the atoms to which they are attached.[13] 333 parameters have been refined with $R = 0.054$, $wR = 0.062$, where $w = k/[\sigma(F)^2 + P^*F^2]$ with $k = 1.000$, $P = 0.04$. In the final difference map $(\Delta\rho)_{max} = 0.201$, $(\Delta\rho)_{min} = -0.189$ eÅ, $(\Delta/\sigma)_{max} = 0.013$. All calculations were performed on a MicroVax 3100 computer.

DISCUSSION

The final positional parameters of the non-hydrogen atoms with their estimated standard deviations are listed in Table I. Th^ bond distances and bond angles for the non-hydrogen atoms are presented in Table II. The projection of the thermal ellipsoids on the best plane of the molecule and packing down a axis are given in Figure 2 and Figure 3 respectively.

TABLE II

Bond distances (Å) and Bond angles (°) with e.s.d's in parentheses

N—C23	1.142(3)	C12—C13	1.369(3)
C1—C2	1.509(4)	C13—C14	1.374(3)
C2—C3	1.511(3)	C14—C15	1.364(3)
C3—C4	1.505(3)	C14—C17	1.477(3)
C4—C5	1.499(3)	C15—C16	1.377(3)
C5—C6	1.512(3)	C17—C18	1.366(3)
C6—C7	1.519(3)	C17—C22	1.371(3)
C7—C8	1.506(3)	C18—C19	1.362(4)
C8—C9	1.514(3)	C19—C20	1.351(4)
C9—C10	1.518(3)	C20—C21	1.366(3)
C10—C11	1.501(3)	C20—C23	1.451(3)
C11—C12	1.350(3)	C21—C22	1.370(3)
C11—C16	1.366(4)		
C1—C2—C3	113.6(2)	C13—C14—C17	122.3(2)
C2—C3—C4	115.0(2)	C15—C14—C17	122.9(2)
C3—C4—C5	114.7(2)	C14—C15—C16	122.4(2)
C4—C5—C6	114.2(2)	C11—C16—C15	121.9(2)
C5—C6—C7	115.8(2)	C14—C17—C18	121.1(2)
C6—C7—C8	112.9(2)	C14—C17—C22	123.7(2)
C7—C8—C9	116.2(2)	C18—C17—C22	115.2(2)
C8—C9—C10	111.3(2)	C17—C18—C19	122.4(3)
C9—C10—C11	115.1(2)	C18—C19—C20	121.5(3)
C10—C11—C12	122.3(2)	C19—C20—C21	117.8(2)
C10—C11—C16	121.7(2)	C19—C20—C23	119.8(2)
C12—C11—C16	116.0(2)	C21—C20—C23	122.4(2)
C11—C12—C13	122.2(3)	C20—C21—C22	120.1(3)
C12—C13—C14	122.7(2)	C17—C22—C21	122.9(2)
C13—C14—C15	114.8(2)	N—C23—C23	177.3(3)

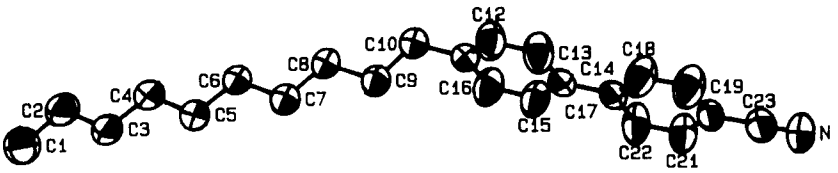

FIGURE 2 ORTEP plot of the molecule with thermal ellipsoids at 50% probability.

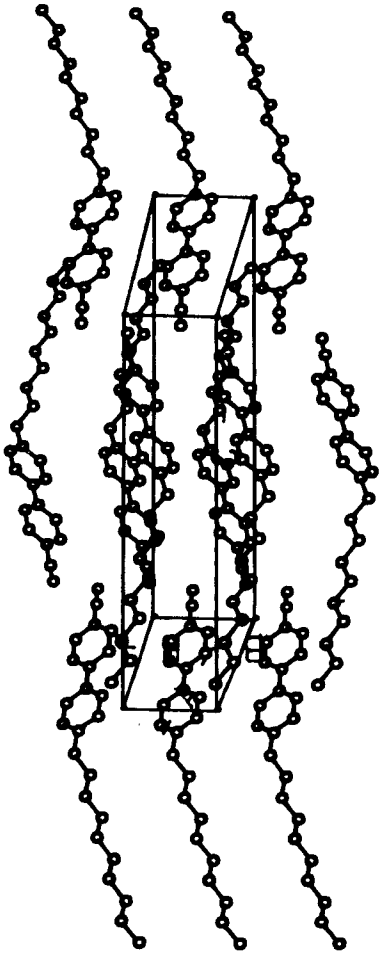

FIGURE 3 Packing of the molecules. Projection of the unit cell down a axis.

The phenyl rings are nearly co-planar, the angle between the normals to them being 2.2°. As can be seen from the packing diagram, pairs of molecules form an antiparallel head to tail configuration, the molecule in one sheet being related to its neighbour in the next by inversion through a centre. There is a pronounced imbricated packing but the

smaller angle between phenyl rings is the reason for the lower thermal stability. The results are consistent with the view that imbricated packing is a necessary requirement to form a nematic liquid crystalline phase. $C_{23} \equiv N$ group lies within the plane of the phenyl ring. The torsion angle between the linear chain and benzene ring is quite significant, angle C(9)—C(10)—C(11)—C(16) being of the order of 73.9(3)°.

It is clear from the packing diagram (Figure 3) that the molecule is bent at C10. Atoms C11 to C1 form a chain with an extended configuration. The cohesion between the molecules is through van der Waals interaction at the N—C terminal end of the molecule. The molecules stack along the b direction in such a way that normal to the plane of phenyl rings, makes an angle 55.89° with *b* axis.

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References

1. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973).
2. A. Ashford, J. Constant, J. Kirton and E. P. Raynes, *Electron. Lett.*, **9**, 118 (1973).
3. A. M. Levelut and M. Lambert, *C. R. Acad. Sci.* (Paris), **272B**, 1018 (1972).
4. Adrian de Vries and D. L. Fishel, *Mol. Cryst. Liq. Cryst.*, **16**, 311 (1972).
5. J. Doucet, M. Lambert and A. M. Levelut, *J. Physique, Colloque*, **32**, C5a, 247 (1971).
6. Adrian de Vries, *Mol. Cryst. Liq. Lett.*, **49**, 19 (1978).
7. S. Diele, D. Demus, A. Echtermeyer, U. Preukschas and H. Sackmann, *Acta Physica Polonica*, **A55**, 125 (1979).
8. S. Diele, D. Jaeckel, D. Demus and H. Sackmann, *Cryst. Res. and Technol.*, **17**, 1591 (1982).
9. D. Guillon, P. E. Cladis and J. Stamatoff, *Phys. Rev. Lett.*, **41**, 1598 (1978).
10. P. S. Pershan, Structure of Liquid Crystal Phases (World Scientific, Singapore, New Jersey, Hong Kong, 1988), 23.
11. G. M. Sheldrick, SHELXS86. Program for Crystal Structure Determination, p175, Crystallographic Computing 3, edited by G. M. Sheldrick, C. Kruger and R. Goddard, Oxford Univ. Press, England (1985).
12. MOLEN, An Interactive Structure Solution Procedure, Enraf Nonius, Delft, The Netherlands (1990).
13. ORTEP-II: A Fortran Thermal Ellipsiod Plot Program for Crystal Structure Illustrations. C. K. Johnson (1976) ORNL-5138.