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Crystal structure of 4-*n*-nonyl-4′-cyanobiphenyl

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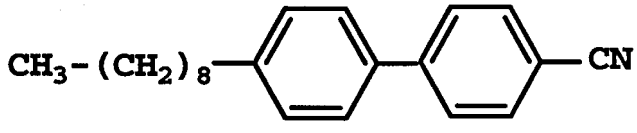
4-*n*-Nonyl-4′-cyanobiphenyl, $C_{22}H_{27}N$, $M_r=305{\cdot}45$, triclinic, $P\bar{1}$, $a=9{\cdot}765(1)$ Å, $b=11{\cdot}460(2)$ Å, $c=17{\cdot}860(2)$ Å, $\alpha=85{\cdot}460(2)$, $\beta=80{\cdot}870(1)$, $\gamma=71{\cdot}630(1)^\circ$, $V=1871{\cdot}9(3)$ Å^3, $Z=4$, $D_m=1{\cdot}079$ M g^{-3}, $D_c=1{\cdot}084$ M g^{-3}, $\mu=0{\cdot}463$ mm^{-1}, $F(000)=664$, λ (CuK$_\alpha$)$=1{\cdot}5418$ Å, final R and $wR2$ are 0·0523 and 0·1559, respectively.

1. Introduction

The two series of alkylcyanobiphenyl compounds with alkyl or alkyloxy substitutents [methyl (oxy) to dodecyl (oxy)] were discovered about two decades ago [1]. These compounds since then, have made possible dramatic advances in liquid crystal display technology due to their readily accessible nematic ranges around room temperature, particularly in the form of eutectic mixtures. The crystal structures of two such compounds were reported by us earlier [2, 3]. The aim of this paper is to elucidate the structure of 4-*n*-nonyl-4′-cyano biphenyl (9CB)



Thermal microscopy shows the formation of smectic A and nematic phases at 315 K and 312 K, respectively. The nematic–isotropic transition temperature is 322·5 K.

2. Experimental

White needle shaped crystals of 9CB were obtained from a solution in acetone. Crystals with the approximate size of $0{\cdot}15\times0{\cdot}23\times0{\cdot}32$ mm were mounted on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite-monochromated CuK$_\alpha$ X-ray source ($\lambda=1{\cdot}5418$ Å). The unit-cell parameters were obtained using the method of short vectors followed by least-squares refinement of 25 reflections. All 25 reflections could be indexed with respect to a triclinic unit. Lorentz and polarization corrections were applied. The crystal structure was solved by SHELXS-86 [4]. The structure solution did not yield a meaningful E-map in the space group $P\bar{1}$ even though the E-statistics showed better zonal agreements and all data with the centrosymmetric system. Subsequently, the structure was solved in the space group $P1$ assuming four molecules in the asymmetric unit. The solved structure showed a centre of inversion. The origin was shifted to the centre of inversion and the structure was refined with two partial molecules in the asymmetric unit. The subsequent difference Fourier map showed the positions of all missing non-hydrogen atoms. The structure was refined by a full-matrix least-squares method using SHELXL-93 [5] [3248 unique reflections with $I>2\sigma(I)$]. All the hydrogen atoms located through the difference mapping were least-squares refined with isotropic thermal parameters assigned to them. Six hundred and thirty two parameters have been refined using 3248 unique reflections to $R=0{\cdot}0523$ and $wR2=0{\cdot}1559$. In the final difference map $(\Delta\sigma)_{max}=-0{\cdot}036$ and $(\Delta\rho)_{min}=-0{\cdot}179$, $(\Delta\rho)_{max}=0{\cdot}183$e Å^{-3}. All calculations were performed on a MicroVax 3100 computer.

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) with e.s.d.s in parentheses for the non-hydrogen atoms. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
N(1)	−14 784(3)	16 888(3)	11 380(2)	123(1)
C(1)	−14 075(3)	16 258(3)	10 909(2)	89(1)
C(2)	−13 170(3)	15 453(2)	10 313(2)	71(1)
C(3)	−11 854(3)	14 634(2)	10 444(1)	75(1)
C(4)	−11 006(3)	13 873(2)	9873(1)	72(1)
C(5)	−11 435(2)	13 923(2)	9161(1)	59(1)
C(6)	−10 512(2)	13 080(2)	8561(1)	62(1)
C(7)	−12 768(3)	14 761(2)	9044(1)	68(1)
C(8)	−13 628(3)	15 529(2)	9611(2)	73(1)
C(9)	−8999(3)	12 730(2)	8486(1)	76(1)
C(10)	−8141(3)	11 918(3)	7954(2)	78(1)
C(11)	−8735(3)	11 386(2)	7469(1)	65(1)
C(12)	−7729(3)	10 453(2)	6914(1)	76(1)
C(13)	−10 232(3)	11 747(2)	7532(1)	70(1)
C(14)	−11 119(2)	12 577(2)	8063(1)	66(1)
C(15)	−8445(3)	9881(2)	6406(1)	72(1)
C(16)	−7343(3)	8932(2)	5892(1)	73(1)
C(17)	−8037(3)	8307(2)	5402(1)	77(1)
C(18)	−6933(3)	7358(2)	4888(1)	76(1)
C(19)	−7610(3)	6712(2)	4401(1)	77(1)
C(20)	−6493(3)	5766(2)	3890(1)	77(1)
C(21)	−7151(3)	5055(2)	3440(1)	78(1)
C(22)	−5993(3)	4120(3)	2940(2)	93(1)
N(2	−4531(3)	1847(2)	1482(2)	105(1)
C(23)	−3906(3)	1223(3)	995(2)	81(1)
C(24)	−3120(3)	446(2)	373(1)	68(1)
C(25)	−3375(2)	−665(2)	293(1)	68(1)
C(26)	−2603(2)	−1402(2)	−297(1)	65(1)
C(27)	−1555(3)	−1091(2)	−820(1)	61(1)
C(28)	−668(3)	−1938(2)	−1425(1)	63(1)
C(29)	−1337(3)	36(2)	−733(1)	81(1)
C(30)	−2105(3)	787(2)	−150(2)	85(1)
C(31)	−1204(3)	−2776(2)	−1715(1)	74(1)
C(32)	−336(3)	−3619(2)	−2239(1)	77(1)
C(33)	1092(3)	−3674(2)	−2501(1)	67(1)
C(34)	2108(3)	−4638(2)	−3040(1)	79(1)
C(35)	1612(3)	−2822(2)	−2224(1)	74(1)
C(36)	755(3)	−1970(2)	−1700(1)	72(1)
C(37)	1392(3)	−5246(2)	−3523(1)	75(1)
C(38)	2509(3)	−6169(2)	−4057(1)	75(1)
C(39)	1815(3)	−6758(2)	−4565(1)	74(1)
C(40)	2908(3)	−7689(2)	−5101(1)	72(1)
C(41)	2207(3)	−8231(2)	−5631(1)	76(1)
C(42)	3282(3)	−9143(2)	−6178(1)	78(1)
C(43)	2578(3)	−9707(3)	−6693(2)	85(1)
C(44)	3670(4)	−10 561(3)	−7256(2)	120(1)

Table 2. Anisotropic displacement parameters ($Å^2 \times 10^3$) for non-hydrogen atoms with e.s.d.s in parentheses. The anisotropic displacement factor exponent takes the form: $-2\Pi^2[h^2a^{*2}U11 + \ldots + 2hka^*b^*U12]$.

Atom	U11	U22	U33	U23	U13	U12
N(1)	102(2)	124(2)	148(2)	−78(2)	19(2)	−42(2)
C(1)	85(2)	85(2)	107(2)	−33(2)	3(2)	−43(2)
C(2)	78(2)	56(2)	86(2)	−15(1)	3(1)	−34(1)
C(3)	93(2)	63(2)	74(2)	−12(1)	−13(1)	−26(2)
C(4)	82(2)	58(2)	74(2)	−8(1)	−19(1)	−15(1)
C(5)	71(2)	47(1)	65(1)	−2(1)	−9(1)	−27(1)
C(6)	69(2)	55(2)	63(1)	0(1)	−11(1)	−22(1)
C(7)	71(2)	64(2)	74(2)	0(1)	−14(1)	−25(1)
C(8)	68(2)	59(2)	93(2)	−4(1)	−11(1)	−22(1)
C(9)	75(2)	77(2)	85(2)	−21(1)	−18(1)	−28(1)
C(10)	62(1)	88(2)	84(2)	−22(2)	−11(1)	−17(1)
C(11)	71(2)	64(2)	62(1)	−7(1)	−10(1)	−26(1)
C(12)	70(2)	84(2)	72(2)	−18(1)	−8(1)	−19(1)
C(13)	74(2)	76(2)	65(1)	−13(1)	−12(1)	−27(1)
C(14)	69(1)	66(2)	67(1)	−5(1)	−14(1)	−23(1)
C(15)	76(2)	71(2)	72(2)	−11(1)	−9(1)	−23(1)
C(16)	70(2)	72(2)	77(2)	−15(1)	−11(1)	−18(1)
C(17)	74(2)	73(2)	83(2)	−17(1)	−12(1)	−17(1)
C(18)	69(2)	78(2)	81(2)	−22(1)	−8(1)	−20(1)
C(19)	74(2)	72(2)	87(2)	−17(1)	−14(1)	−21(1)
C(20)	77(2)	75(2)	81(2)	−17(1)	−10(1)	−25(1)
C(21)	86(2)	65(2)	87(2)	−13(1)	−24(1)	−21(1)
C(22)	104(2)	87(2)	92(2)	−27(2)	−15(2)	−28(2)
N(2)	109(2)	93(2)	111(2)	−45(2)	1(2)	−28(2)
C(23)	87(2)	71(2)	86(2)	−20(2)	−9(2)	−23(2)
C(24)	76(2)	52(2)	75(2)	−10(1)	−11(1)	−17(1)
C(25)	67(1)	60(2)	76(2)	−9(1)	−4(1)	−22(1)
C(26)	69(1)	49(1)	82(2)	−10(1)	−8(1)	−25(1)
C(27)	76(2)	49(2)	62(1)	−4(1)	−11(1)	−23(1)
C(28)	74(2)	54(2)	66(1)	−1(1)	−9(1)	−27(1)
C(29)	114(2)	57(2)	76(2)	−7(1)	10(2)	−41(2)
C(30)	114(2)	56(2)	93(2)	−16(1)	−1(2)	−39(2)
C(31)	67(2)	71(2)	86(2)	−21(1)	−4(1)	−27(1)
C(32)	73(2)	76(2)	89(2)	−27(2)	−2(1)	−32(1)
C(33)	75(2)	63(2)	68(1)	−12(1)	−4(1)	−27(1)
C(34)	77(2)	82(2)	84(2)	−26(1)	0(1)	−31(1)
C(35)	75(2)	76(2)	77(2)	−13(1)	6(1)	−36(1)
C(36)	86(2)	67(2)	75(2)	−13(1)	0(1)	−42(1)
C(37)	76(2)	72(2)	78(2)	−15(1)	−2(1)	−26(1)
C(38)	71(2)	77(2)	78(2)	−22(1)	−2(1)	−25(1)
C(39)	70(2)	74(2)	81(2)	−18(1)	−1(1)	−26(1)
C(40)	72(1)	68(2)	76(2)	−16(1)	−6(1)	−23(1)
C(41)	70(2)	79(2)	82(2)	−17(1)	−8(1)	−27(1)
C(42)	80(2)	80(2)	82(2)	−20(1)	−2(1)	−35(1)
C(43)	88(2)	92(2)	87(2)	−26(2)	−11(1)	−39(2)
C(44)	132(3)	141(3)	105(2)	−57(2)	0(2)	−62(2)

3. Results and discussion

The final atomic coordinates with equivalent isotropic temperature factors for non-hydrogen atoms are given in table 1. Anisotropic parameters (U_{ij}) for the non-hydrogen atoms are listed in table 2. Table 3 gives the bond distances and angles of non-hydrogen atoms. Figure 1 represents the ORTEP [6] diagram of the molecule with thermal ellipsoids at 50 per cent probability and figure 2 shows the packing of molecules in the unit cell. The molecules are projected on to the *bc* plane. Figure 3 shows the imbricated arrangement of the molecules.

Table 3. Bond lengths [Å] and angles [deg] involving non-hydrogen atoms with e.s.d.s in parentheses.

Bond	Data	Bond	Data
N(1)–C(1)	1·142(3)	C(2)–C(3)–C(4)	119·3(2)
C(1)–C(2)	1·452(4)	C(3)–C(4)–C(5)	121·9(2)
C(2)–C(3)	1·374(3)	C(7)–C(5)–C(4)	117·5(2)
C(2)–C(8)	1·382(3)	C(7)–C(5)–C(6)	121·8(2)
C(3)–C(4)	1·379(3)	C(4)–C(5)–C(6)	120·7(2)
C(4)–C(5)	1·392(3)	C(9)–C(6)–C(14)	117·0(2)
C(5)–C(7)	1·387(3)	C(9)–C(6)–C(5)	121·4(2)
C(5)–C(6)	1·483(3)	C(14)–C(6)–C(5)	121·6(2)
C(6)–C(9)	1·391(3)	C(8)–C(7)–C(5)	121·2(2)
C(6)–C(14)	1·393(3)	C(7)–C(8)–C(2)	119·8(2)
C(7)–C(8)	1·382(3)	C(10)–C(9)–C(6)	121·7(2)
C(9)–C(10)	1·366(3)	C(9)–C(10)–C(11)	121·7(2)
C(10)–C(11)	1·387(3)	C(13)–C(11)–C(10)	116·8(2)
C(11)–C(13)	1·377(3)	C(13)–C(11)–C(12)	124·0(2)
C(11)–C(12)	1·513(3)	C(10)–C(11)–C(12)	119·2(2)
C(12)–C(15)	1·525(3)	C(11)–C(12)–C(15)	116·9(2)
C(13)–C(14)	1·384(3)	C(11)–C(13)–C(14)	122·3(2)
C(15)–C(16)	1·513(3)	C(13)–C(14)–C(6)	120·5(2)
C(16)–C(17)	1·527(3)	C(16)–C(15)–C(12)	112·5(2)
C(17)–C(18)	1·514(3)	C(15)–C(16)–C(17)	113·4(2)
C(18)–C(19)	1·529(3)	C(18)–C(17)–C(16)	113·4(2)
C(19)–C(20)	1·514(3)	C(17)–C(18)–C(19)	114·0(2)
C(20)–C(21)	1·524(3)	C(20)–C(19)–C(18)	113·4(2)
C(21)–C(22)	1·514(3)	C(19)–C(20)–C(21)	114·0(2)
N(2)–C(23)	1·138(3)	C(22)–C(21)–C(20)	112·0(2)
C(23)–C(24)	1·439(4)	N(2)–C(23)–C(24)	179·3(3)
C(24)–C(30)	1·378(3)	C(30)–C(24)–C(25)	119·2(2)
C(24)–C(25)	1·394(3)	C(30)–C(24)–C(23)	120·6(2)
C(25)–C(26)	1·371(3)	C(25)–C(24)–C(23)	120·3(2)
C(26)–C(27)	1·386(3)	C(26)–C(25)–C(24)	119·5(2)
C(27)–C(29)	1·398(3)	C(25)–C(26)–C(27)	122·4(2)
C(27)–C(28)	1·482(3)	C(26)–C(27)–C(29)	116·8(2)
C(28)–C(36)	1·388(3)	C(26)–C(27)–C(28)	121·5(2)
C(28)–C(31)	1·394(3)	C(29)–C(27)–C(28)	121·7(2)
C(29)–C(30)	1·369(3)	C(36)–C(28)–C(31)	117·3(2)
C(31)–C(32)	1·380(3)	C(36)–C(28)–C(27)	121·3(2)
C(32)–C(33)	1·381(3)	C(31)–C(28)–C(27)	121·4(2)
C(33)–C(35)	1·388(3)	C(30)–C(29)–C(27)	121·5(2)
C(33)–C(34)	1·518(3)	C(29)–C(30)–C(24)	120·6(2)
C(34)–C(37)	1·520(3)	C(32)–C(31)–C(28)	121·0(2)
C(35)–C(36)	1·382(3)	C(31)–C(32)–C(33)	122·0(2)
C(37)–C(38)	1·523(3)	C(32)–C(33)–C(35)	116·9(2)
C(38)–C(39)	1·523(3)	C(32)–C(33)–C(34)	123·5(2)
C(39)–C(40)	1·520(3)	C(35)–C(33)–C(34)	119·6(2)
C(40)–C(41)	1·524(3)	C(33)–C(34)–C(37)	116·5(2)
C(41)–C(42)	1·514(3)	C(36)–C(35)–C(33)	121·8(2)
C(42)–C(43)	1·520(3)	C(35)–C(36)–C(28)	121·1(2)
C(43)–C(44)	1·504(4)	C(34)–C(37)–C(38)	112·1(2)
		C(39)–C(38)–C(37)	113·0(2)
		C(40)–C(39)–C(38)	114·0(2)
N(1)–C(1)–C(2)	179·8(3)	C(39)–C(40)–C(41)	113·7(2)
C(3)–C(2)–C(8)	120·3(2)	C(42)–C(41)–C(40)	114·4(2)
C(3)–C(2)–C(1)	119·9(2)	C(41)–C(42)–C(43)	114·2(2)
C(8)–C(2)–C(1)	119·8(2)	C(44)–C(43)–C(42)	113·1(2)

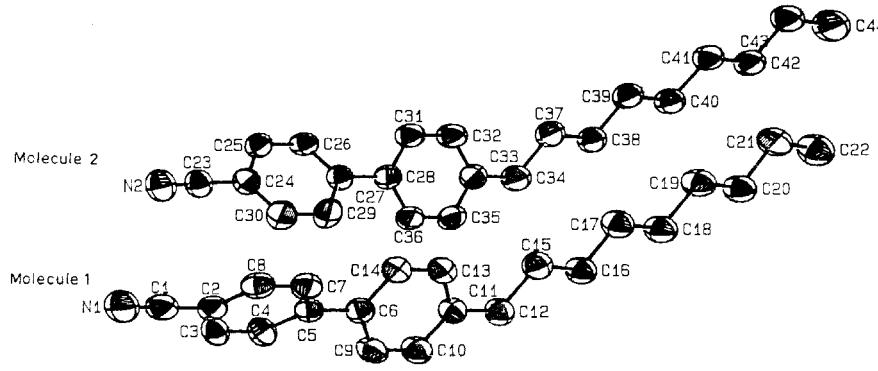

Figure 1. ORTEP diagram of the molecules.

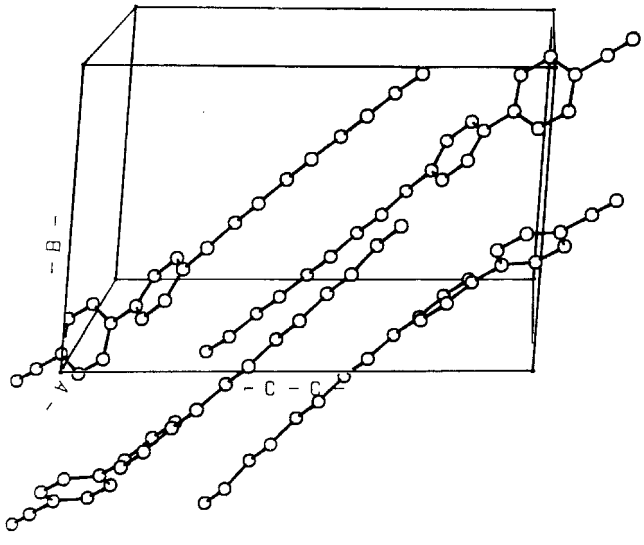

Figure 2. Packing of the molecules on the *ab* plane.

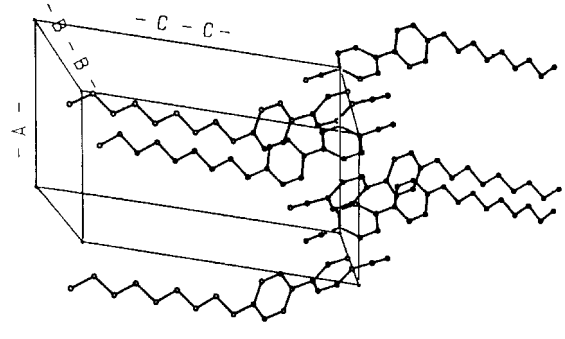

Figure 3. Imbricated arrangement of the molecules.

The dihedral angle between the phenyl rings in molecule **1** of the asymmetric unit is 35·97(0·08)°, while the dihedral angle between the corresponding rings in molecule **2** of the asymmetric unit is 29·83(0·08)°. This shows that the two molecules in the asymmetric unit have slightly different conformations. As can be seen from the packing diagram, pairs of molecules form an antiparallel arrangement. Overlapping of the diphenyl part has been observed in the packing. Atoms C(1)–N(1) and C(23)–N(2) lie within the plane of the phenyl ring. The torsion angle between the linear chain and the benzene ring is quite significant. They are 178·89(0·23)° about C(10)–C(11)–C(12)–C(15) for molecule **1** and 159·98(0·24)° about C(35)–C(33)–C(34)–C(37) for molecule **2**. It is clear from the packing diagram (figure 2) that the two molecules of the asymmetric unit are bent at C(12) and C(34). Atoms C(11) to C(22) and C(33) to C(44) form chains with an extended conformation.

The N(1) terminal dipole of molecule **1** in the asymmetric unit interacts through C(25) of molecule **2**. The N(2) terminal dipole of molecule **2** interacts through C(8) of the inverted molecule **1**. Also the N(1) terminal dipole of molecule **1** interacts with C(7) of the inverted molecule **1**. These dipole interactions are evident from figure 3. The packing shows imbrication of the molecules by the dipole connected chain along the *a* axis and layering down the other axes. The distance between the terminal CH_3 groups of opposing molecules turns out to be 31·9 Å, and compares well with the value given by $d \cong 1{\cdot}4l$, which is equal to 32·3 Å.

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