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Liquid Crystals

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Crystal structure of 4′-pentyl-4-cyanobiphenyl (5CB)

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The crystal structure and the molecular arrangement of 4′-pentyl-4-cyanobiphenyl (5CB) at 253 K are described. At 253 K the compound crystallized from pure ethanol as plates, as well as fine needles, both colourless. The crystal data for both crystal habits are within experimental error identical. The data for the plates were measured as: $a = 8{\cdot}249(5)$ Å, $b = 16{\cdot}022(4)$ Å, $c = 10{\cdot}935(3)$ Å $\beta = 95{\cdot}09(3)^{\circ}$, space group $P2_1/a$. Considering 2014 independent reflections, the structure was refined to a final R value of 0·0588. In the case of the needles, with 1892 independent reflections, R converged to 0·0503. The torsion angle between the normals of the benzene rings in the biphenyl moiety was $-26{\cdot}3(3)^{\circ}$. Within the aliphatic chain an all-*trans* conformation was given, but the orientation of the pentyl group relative to the plane of the attached aromatic ring was nearly vertical ($-90{\cdot}5(3)^{\circ}$). The structure obtained is discussed in comparison with the lower homologues 1CB up to 4CB.

1. Introduction

4′-Pentyl-4-cyanobiphenyl (5CB) has been one of the most investigated liquid crystal materials due to its readily accessible nematic range around room temperature which allows for its use as a suitable model compound for studying the physical behaviour of simple nematics [1–3]. The polar structure containing a cyano group attached to one benzene ring gives rise to a strong dipolar association and dimer formation in the mesophase which can be determined using X-ray measurements, magnetic resonance techniques and—for the higher homologues 7CB–12CB—scanning tunnelling microscopy [4–6]. The crystal structures of the lower homologues (1CB–4CB) are known [7–9], one of them showing solid state polymorphism. The aim of this work was the clarification of the phase behaviour and the structure determination of solid 5CB.

2. Experimental

5CB, first synthesized and reported by Gray, Harrison and Nash in 1973 [10], was obtained from E. Merck, Darmstadt. It was used without further purification and dissolved in pure ethanol. The solution was stored at 253 K in a refrigerator and after a short time fine needles formed. Holding the mixture for a longer period at this temperature, the needles grew, forming large plates. DSC measurements (Dupont Thermal Analyser 990) and polarizing thermomicroscopy (Leitz Orthoplan Pol, Mettler FP 800), yielded the following phase behaviour for the investigated batch of 5CB: Cr 294·0 N 306·7 I [K].

After quenching the isotropic phase with liquid nitrogen down to 173 K and reheating again to ambient temperature, an unstable metaphase appeared with an exothermal peak at 232 K. Moderate cooling rates suppressed the formation of the metaphase.

A colourless plate with the dimensions $1{\cdot}00 \times 1{\cdot}00 \times 0{\cdot}20$ mm was taken to determine the crystal structure at 253 K. To avoid partial melting, any kind of sample preparation had to be carried out at 253 K under a CO_2 atmosphere, and the temperature during the measurements was controlled by a continuous flux of cooled nitrogen. For comparison, a freshly crystallized, small, colourless needle ($1{\cdot}15 \times 0{\cdot}30 \times 0{\cdot}20$ mm) was examined under the same conditions. X-ray diffraction (Enraf–Nonius CAD4, Stoe Stadi 4), using MoK_{α} radiation at a wavelength of 0·71069 Å, was performed to characterize the solid state phase. The program packages SHELXS-86 and SHELXL-93 allowed structure solution and refinement [11, 12], and the hydrogen atom positions were calculated. The refinement procedures converged at $R = 0{\cdot}0588$ (plate) and 0·0503 (needle), respectively. In the following text, only the results for the plate habit are

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Table 1. Basic crystal data and structure refinement.

	5CB-Plate
Empirical formula	$C_{18}H_{19}N$
Formula weight/g mol^{-1}	249·34
Temperature/K	253
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	8·249(5)
b/Å	16·022(4)
c/Å	10·935(3)
β/°	95·09(3)
V/Å^3	1439·5(10)
Z	4
Calculated density/g cm^{-3}	1·150
Crystal size/mm	1·00 × 1·00 × 0·20
Absorption coefficient μ_{MoK_α}/cm^{-1}	0·66
F(000)	536
Number of measured reflections	2413
Number of independent reflections	2014
Final R index [$I_{obs.} > 2\sigma(I)$]	0·0588
Final R_W index	0·1514
S	1·081

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/Å	y/Å	z/Å	U(eq)
N(1)	−6040(3)	8759(2)	3059(2)	91(1)
C(1)	−4777(4)	8777(2)	3583(3)	67(1)
C(2)	−3206(3)	8807(2)	4260(2)	56(1)
C(3)	−1862(3)	8433(2)	3815(2)	61(1)
C(4)	−375(3)	8467(1)	4477(2)	58(1)
C(5)	−160(3)	8862(1)	5618(2)	49(1)
C(6)	−1526(3)	9242(1)	6036(2)	57(1)
C(7)	−3017(3)	9220(2)	5378(2)	59(1)
C(8)	1421(3)	8891(1)	6370(2)	49(1)
C(9)	2567(3)	8234(2)	6273(2)	57(1)
C(10)	4019(3)	8228(2)	6999(2)	61(1)
C(11)	4413(3)	8846(1)	7861(2)	55(1)
C(12)	3280(3)	9472(2)	7953(2)	60(1)
C(13)	1828(3)	9481(1)	7235(2)	58(1)
C(14)	5979(3)	8834(2)	8674(2)	66(1)
C(15)	5864(3)	8382(2)	9880(2)	64(1)
C(16)	5680(3)	7438(2)	9719(2)	70(1)
C(17)	5794(4)	6967(2)	10888(3)	79(1)
C(18)	5656(4)	6037(2)	10729(3)	83(1)

presented; the basic crystal data are listed in table 1, and the atomic coordinates and displacement parameters in table 2.

3. Results and discussion

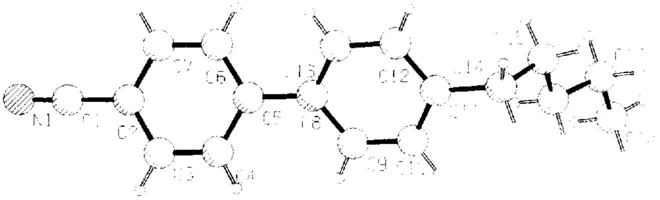

Figure 1. Perspective view of 5CB, indicating the numbering scheme, projection on the benzene ring with carbon atoms C2 to C7.

The structure and the labelling used for a single molecule of 5CB are given in figure 1. In contrast to most analogous molecules, the aliphatic chain is oriented approximately perpendicular to the plane of the attached benzene ring (torsion angle: C10–C11–C14–C15: − 90·3(3)°). The conformation within the pentyl chain is all-*trans*, but due to the aromatic ring on one side, a *gauche* conformation of the planes defined by the bonds C11–C14 and C15–C16 with a dihedral angle of − 70·4(3)° was found. The torsion angle between the normals of the two benzene amounted to − 26·3(3)°, quite similar to the value obtained for pure biphenyl obtained from SCF-LCAO-MO and force field calculations ($\varphi \approx 26°$) [13]. Following deuteron NMR studies on the nematic phase of 5CB, the torsion angle was found to be 32° [4].

Table 3 compares the first homologues 1CB–4CB of the series with 5CB, all in the solid state. Generally speaking, the basic crystallographic data for the homologues are rather similar. With the exception of the high temperature phase of 2CB, all crystallize monoclinic in a centrosymmetric space group, with the monoclinic β angle close to 95°, except in the case of 3CB and 4CB for which the β values were larger at 103·39(2)° and 123·4(3)°, respectively [8, 9]. The volume of the elementary cell divided by the number of contained molecules increased with increasing length of the aliphatic chain. Within the range of five homologues, no systematic change in the torsion angle between the aromatic moieties was observed, and in the case of the two solid state phases of 2CB, the aromatic rings of the biphenyl group were approximately coplanar, with negligible twist angles of 0·7° and 1·5°, due to packing effects in the lattice.

The molecular packing of 5CB in the crystalline state is shown in figures 2, 3, and 4 with projections along the a, b, and c axes of the elementary cell. At first sight, the molecular arrangement estimated from the images (see figures 2–4) seemed not to be unique. Following the projections along the a and b axes, a layered structure could be assumed, quite similar to that in the STM-images of higher homologues [5]. Figure 2 suggests an alternating arrangement of bilayers, with two parallel oriented molecules within one layer, the orientation of two neighbouring bilayers seeming to be antiparallel. Figure 3, with the projection along the b axis, indicates a strong parallel orientation within and between the different layers. Figure 4, with the projection along the c axis does

Table 3. Comparison of 5CB with the homologues 1CB-4CB; 2CB shows solid state polymorphism. The numbering scheme used is as in figures 1, 2 and 4 (′: next neighbour molecule).

	1CB [7]	2CB [7]		3CB [8]	4CB [9]	5CB, this work
Space group	$P2_1/n$	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/a$
Z	8	4	2	4	4	4
T/K	296	223	298	298	298	253
a/Å	15·71(8)	8·24(1)	8·589(2)	6·259(3)	12·198(9)	8·249(2)
b/Å	14·38(8)	5·94(1)	5·864(1)	19·1216(9)	9·204(8)	16·022(4)
c/Å	9·61(6)	23·15(2)	11·835(3)	11·0473(5)	14·746(9)	10·935(3)
β/°	95·0(2)	92·93(1)	92·41(1)	103·39(2)	123·4(3)	95·09(3)
V/Å^3	2171·0	1156·3	595·55	1286·2	1382·5	1439·5(1)
d/g cm^{-3}	1·188	1·191	1·156	1·142	1·130	1·150
Twist angle /°	—	0·7	1·5	42·8	40·5	−26·3
Selected distances/Å	—	3·35, 3·57 2×(N1C1′)	3·55 (N1C1′)	4·19 (C1C3′) 3·95 (C1C4′)	3·45 (N1C1′) 3·55 (N1C13′)	antiparallel: 3·55 (C1C12′) 3·86 (C1C13′) parallel: 3·95 (C1C3′) 3·77 (C1C4′)

not allow for an unequivocal description, and again, as in figure 2, two antiparallel oriented bilayers are present in the elementary cell.

Other cyanobiphenyl homologues (2CB [7] and 4CB [9]) show a tendency to form associates with an antiparallel arrangement and a small cyano–cyano distance around 3·5 Å (see table 3). A more careful analysis of the X-ray data yielded the following measured intermolecular distances between one cyano group and the closest benzene ring in the next layer: in the case of antiparallel oriented molecules, the neighbouring carbon atoms (C12′ and C13′) of the aromatic ring attached to the pentyl chain were 3·55 Å and 3·86 Å apart (see table 3: C1C12′ and C1C13′). The corresponding values for parallel packed molecules were 3·95 Å and 3·77 Å, considering the distance to the aromatic ring attached to the cyano group (see table 3: C1C3′ and C1C4′); all notations follow the scheme used in figures 1, 2 and 4, the prime on the atom number representing the next neighbouring molecule. Hence the next antiparallel oriented layer is slightly closer than the parallel oriented layer in the given lattice at 253 K, and therefore 5CB has an analogous behaviour to that of the higher homologues.

The intermolecular distances in 5CB are in the range of real dipole–dipole contact, so that the given lattice with the layered structure could be treated as a precursor state to the nematic phase, as for the other homologues and simulated by Luckhurst *et al.*, on the basis of the

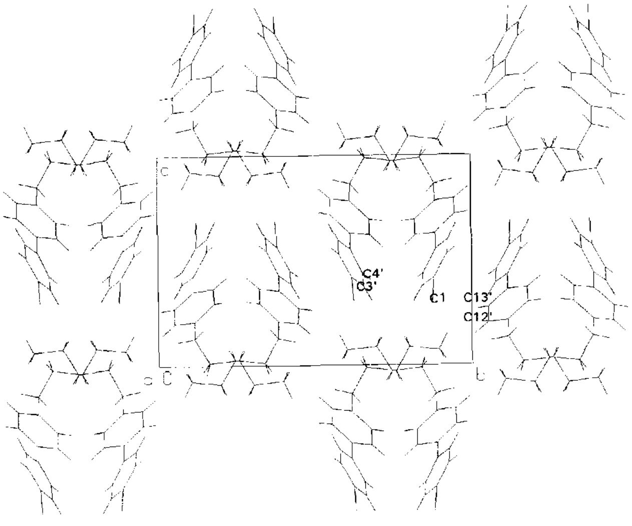

Figure 2. Crystal structure of 5CB; projection along [1 0 0].

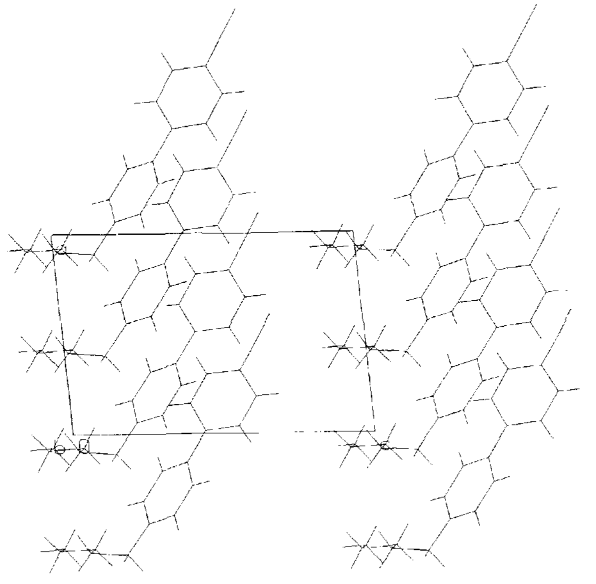

Figure 3. Crystal structure of 5CB; projection along [0 1 0], with half height for better clearness.

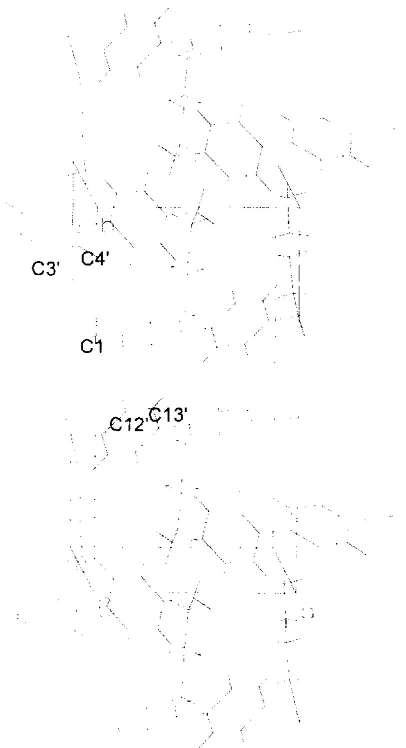

Figure 4. Crystal structure of 5CB; projection along [0 0 1].

Gay–Berne potential including attractive, as well as repulsive forces between the molecular dipoles [14]. These authors considered that in the case of the crystalline state a perfect order of the elongated molecules would exist, with a calculated orientational order of 0·98, and obtained for the nematic phase 0·41. In the case here, the structure of 5CB has been folded, but a layer structure as a potential mesogenic arrangement is still present. Therefore the results are in agreement with the simulation studies and the other CBs, despite the unusual orientation of the pentyl group with respect to the aromatic part.

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