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

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To cite this article: I. H. Ibrahim, H. Paulus, M. Mokhles & W. Haase (1997): Structure of Pch4, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 497-501

To link to this article: http://dx.doi.org/10.1080/10587259708042033

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 497–501
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STRUCTURE OF PCH4

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Abstract The crystal and molecular structure of the mesogenic trans-4-n-butyl-(4′-cyanophenyl)-cyclohexane (PCH4) has been determined using single crystal X-ray diffraction data. The crystals belong to the monoclinic system with space group $P2_1/c$, a=17.006(6), b=5.764(2), c=15.526(5)Å, ß=96.73(1)°, Z=4. The structure of PCH4 has been solved by direct methods and refined to R-value of 0.0484 for 1779 observed reflections. All the molecules occur in their extended form. The crystal packing involves a centrosymmetric head-to-tail pairing of molecules , so that individual molecular dipoles are opposed. A cyano-cyano weak interaction is indicated.

INTRODUCTION

As part of a study of the intermolecular contacts in the crystalline state of mesogenic compounds we have looked for examples of cyano-cyano and cyano-phenyl contacts in some members of the series of the trans-4-n-alkyl-(4′-cyanophenyl) cyclohexanes PCH3,PCH8 and PCH9 [1-3]. We report here the crystal structure of another member PCH4 of this series. This compound exhibits a nematic phase(40°C - 71°C).

EXPERIMENTAL

The PCH4 compound was provided by E.Merck, Darmstadt,Germany. The single crystals used in the X-ray analysis were obtained by recrystallization from methanol at room temperature. Crystal size 0.2x0.5x4.6 mm, was mounted along $[0\bar{1}0]$ on a STOE-STADI-4 diffractometer. Cell dimensions were determined from the setting angles of 46 reflections in the range $37.6 < 2\theta < 42.8^\circ$ using ω scans. Intensity data were measured with graphite-monochromated MoKα radiation(λ = 0.71073 Å).3864 reflections were scanned by $\omega/2\theta$(= 1/1) scans having $3 < 2\theta < 45^\circ$, $-18 \leq h \leq 18$, $-6 \leq k \leq 6$, $0 \leq \ell \leq 16$, of which 1968 were unique (R_{int} = 0.0164). 1779 ($F_o > 2\sigma(F_o)$) reflections were considered observed and used in the analysis. Three standard reflections $(314, \bar{3}11, \bar{3}\,\bar{1}1)$ measured every 2h showed 1% increase in intensity. Lorentz and polarization corrections but no absorption corrections were performed. A correction was made for secondary extinction $[F_o^* = F_o(1 - x.F_o^2/\sin\theta)$, with $x = 21.8\times10^{-8}(1.4\times10^{-8})]$.

The basic crystal data are listed in Table I.

TABLE I Crystal data of PCH4.

Chemical formula	$C_{17}H_{23}N$
M_r(g mol^{-1})	241.38
Crystal system	monoclinic
Space group (No.in int.Tables)	$P2_1/c$ (14)
a(Å)	17.006(6)
b(Å)	5.764(2)
c(Å)	15.526(5)
β(°)	96.73(1)
V(Å^3)	1511.4
Z	4
D_x(g cm^{-3})	1.06
μ[MoKα](cm^{-1})	0.57
F(000)	528
Number of reflections measured	3864
Number of unique reflections	1968
R_{int}	0.0164
Number of reflections used	1779
Criterion for reflections used	$F_o>2\sigma(F_o)$
R	0.0484
R_w [$w=3.2648/\sigma^2(F_o)$]	0.0437

The structure was solved by direct methods, using SHELXS86[4] and SHELX76[5], and refined by least squares using anisotropic thermal parameters for the non-hydrogen atoms. H atoms were included in geometrically idealized positions, riding on their respective bonded atoms(C–H=0.96 Å),and given isotropic thermal factors fixed at 1.1 times that of the connecting carbon atoms. The refinements was carried out on F values and converged to R=0.0484 and R_w =0.0437($w=3.2648/\sigma^2$ (F_o))with maximum shift/e.s.d.ratio<0.01.The maximum and minimum peaks shown in the final difference Fourier map were 0.115 and -0.126 e/ Å^3,respectively. The final atomic parameters and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table II. Lists of structure factors, anisotropic thermal parameters, torsion angles, and calculated H-atoms positions are available from the authors on request.

TABLE II Atomic parameters with e.s.d.'s in parentheses.

Atom	x/a	y/b	z/c	$U_{eq}^{\star}$ (Å^2)
N1	0.5593(1)	0.2505(3)	0.0300(1)	0.0845(8)
C1	0.5094(1)	0.2615(4)	0.0731(1)	0.0669(9)
C2	0.4488(1)	0.2741(4)	0.1300(1)	0.0602(8)
C3	0.3952(1)	0.0956(4)	0.1344(1)	0.0685(9)
C4	0.3387(1)	0.1106(4)	0.1906(1)	0.0677(9)
C5	0.3328(1)	0.3015(3)	0.2440(1)	0.0593(8)
C6	0.3872(1)	0.4782(4)	0.2384(1)	0.0715(9)
C7	0.4440(1)	0.4675(4)	0.1824(1)	0.0720(9)
C8	0.2721(1)	0.3068(3)	0.3072(1)	0.0628(8)
C9	0.3064(1)	0.2151(3)	0.3955(1)	0.0700(9)
C10	0.2449(1)	0.2098(3)	0.4594(1)	0.0748(9)
C11	0.2072(1)	0.4466(4)	0.4701(1)	0.0648(8)
C12	0.1731(1)	0.5378(4)	0.3818(1)	0.0734(9)
C13	0.2352(1)	0.5454(4)	0.3181(1)	0.0711(9)
C14	0.1470(1)	0.4378(4)	0.5355(1)	0.0763(10)
C15	0.1161(1)	0.6706(4)	0.5616(1)	0.0832(10)
C16	0.0650(1)	0.6589(4)	0.6348(2)	0.0899(11)
C17	0.0302(2)	0.8911(5)	0.6565(2)	0.1108(13)

★ $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

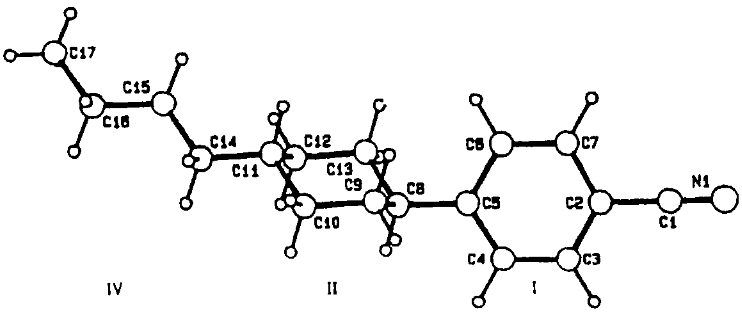

FIGURE 1 PCH4 molecule.

DISCUSSION

Figure 1 illustrates the molecule and the numbering scheme as projection perpendicular to the atoms C3,C5,and C7. The molecule occurs in its fully extended form. Bond lengths and bond angles are listed in Table III. All these values are of normal magnitudes compared with the corresponding values for PCH3[1], PCH8A[2], PCH8B[3],PCH9A[3],and PCH9B[3]. There is no indication of disordered structure, although the data collection took place at about 15 C° below the melting temperature.

TABLE III Bond lengths (Å) and angles (°).

N1—C1	1.144(2)	C11—C14	1.524(2)
C1—C2	1.435(3)	C14—C15	1.514(3)
($\overline{C-C}$)phenyl	1.382(1)	C15—C16	1.511(3)
C5—C8	1.507(3)	C16—C17	1.517(3)
($\overline{C-C}$)cyclohexyl	1.525(1)		

N1—C1—C2	177.9(0.2)	C8—C9—C10	111.9(0.2)
C1—C2—C7	119.8(0.2)	C9—C10—C11	112.5(0.2)
C2—C7—C6	120.0(0.2)	C10—C11—C12	109.4(0.2)
C7—C6—C5	122.0(0.2)	C11—C14—C15	115.5(0.2)
C6—C5—C4	116.8(0.2)	C14—C15—C16	114.2(0.2)
C5—C8—C9	111.1(0.2)	C15—C16—C17	113.7(0.2)

Table IV shows that the dihedral angle between the cyclohexyl group and the butyl group is 32.6°. This indicates that the geometry of the alkylcyclohexyl part is almost identical for the PCH series[1-3],and is concerned as the fixed part of the molecule to which the phenyl group is flexible.

TABLE IV Dihedral angles between best planes defined in Figure 1 ; plane III is defined through the atoms C8,C9, C12,and C13.

Planes	I/II	I/III	I/IV	II/III	II/IV	III/IV
Angle(°)	68.6	66.3	36.0	18.0	32.6	32.9

The packing of PCH4 molecules in the solid crystalline state is shown in Figure 2.It is arranged in such a manner that the molecules are extended parallel to each other and lie perpendicular to [010] alternating in a head-to-tail configuration. Each cyanophenyl group overlaps more or less with a cyanophenyl group of a neighboring molecule related by a centre of symmetry to the former. Moreover,one can recognize that around the 2_1 axis parallel to the crystallographic b axis the cyano groups form an infinite stacking parallel to this axis, showing short

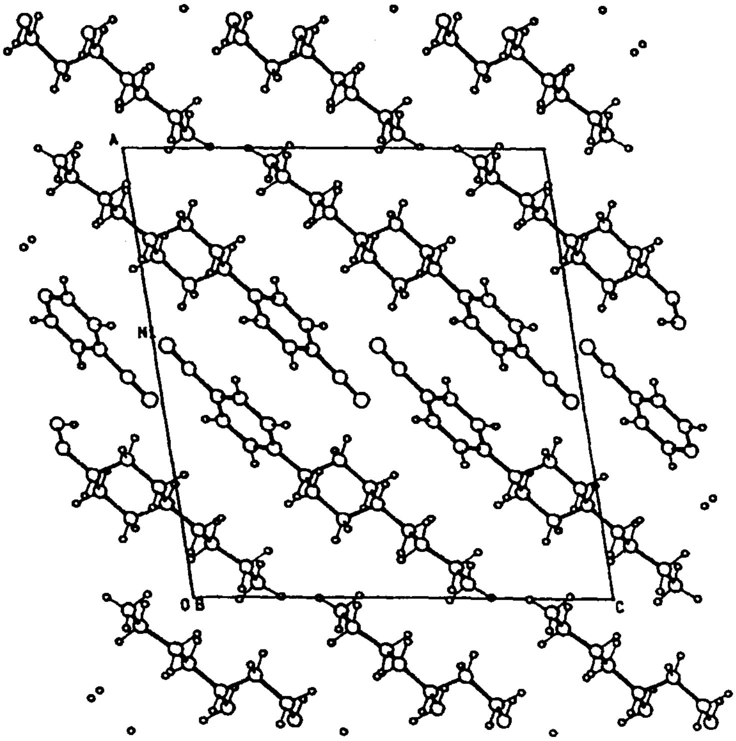

FIGURE 2 View of the crystal structure along the [010].

intermolecular distances: N1...N1′=3.573 Å, and, N1...C1′=3.377 Å,and C1...C1′=3.557 Å. Similar dipole-dipole contacts were found,for example,in PCH8B[3],PCH9B[3],BCH5CN[6] ,5SCN[7] ,and CPBOB[8].

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