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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE MESOGENIC trans-4-n-OCTYL-(4'-CYANOPHENYL)CYCLOHEXANE (PCH 8)

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ABSTRACT

The lattice dimensions are a = 20.975 (6), b = 5.173 (2), c = 19.332(5) Å, ß = 115.97(1)°. The space group is $P2_1/c$ with 4 molecules in the elementary cell. The octyl chain is fully extended. The molecules are packed parallel in a head-to-tail manner with an overlapping of the octylcyclohexyl groups and an overlapping of the cyanophenyl groups, respectively.

INTRODUCTION

The title compound (PCH 8) is a member of the trans-4-n-Alkyl-(4'-cyanophenyl)cyclohexanes (PCH), first described by Eidenschink et al. [1]. PCH 8 is a nematic liquid crystal in the range from 37°C (melting point) to 55°C (clearing point) [2,3].

Recently the molecular structures of a number of similar mesogenic compounds in the crystalline state, e.g. trans, trans-4'-Alkyl-cyclohexyl-4-carbonitrile (CCH with CCH 3, CCH 5 and CCH 7 [4]), 4-Cyano-4'-alkyl-biphenyl (CB with (CB 3 [5], CB 4 [6]) and trans-4-n-Alkyl-(4'-cyanobiphenyl)-cyclohexane (BCH with BCH 3O and BCH 5CN [7]) were reported. The results of PCH 8 will be discussed in relation to the above cited compounds.

EXPERIMENTAL

Crystals suitable for x-ray examinations were obtained by slow evaporation of a solution of PCH 8 in methanol. The lattice constants were determined from the angles of 44 strong reflections of a needle-shaped crystal extended along b with a diameter of approx. 0.2 mm.

The x-ray measurements were made on a STOE-4-circle diffractometer with MoKα -radiation (μ = 0.30). The intensities of 2473 symmetry independent reflections were measured of which 1773 had $F_o \geq 26(F_o)$. These were included in the subsequent calculations. After applying usual intensity corrections, the structure was solved by direct methods. The least-squares refinement of the atomic parameters lead to R = 0.063, R_w = 0.045, whereby thermal anisotropy in all non-hydrogen atoms was accounted for. The positional parameters of the hydrogen atoms were calculated from the parameters of the neighbouring carbon atoms and were not refined independently; the C-H-distance was fixed at 0.96 Å.

The atomic parameters are presented in Table 1. Lists of the F_o/F_c data and the anisotropic thermal parameters can be received from the authors on request.

MOLECULAR STRUCTURE

The PCH 8 molecule is depicted in Fig. 1. The octyl chain is fully extended in a trans conformation. The torsion angles between the best planes (plane 1 : C(2) to C(7); plane 2 : C(9), C(10), C(12), C(13); plane 3 : C(14) to C(21) are 1/2 : 64.9°; 1/3 : 98.1°; 2/3 : 33.3°. Analogously data for the angle 1/2 in the BCH-compounds are [7] BCH 30 : 75.8° and BCH 5CN : 81.7°. Thus the octyl chain lies in a plane which is nearly perpendicular to the plane of the phenyl ring. Furthermore the bonds between the atoms C(11) to C(14), C(15) to C(16), C(17) to C(18) as well as C(19) to C(20) are nearly parallel to the plane through the phenyl group. The largest distance from this plane shows the last atom of the octyl group, C(21), with 5.75 Å.

The largest extension of the molecule from N(1) to C(21) including the covalent radius of 0.55 Å for nitrogen, is 19.90 Å. Similarly, the extension between N(1) and the hydrogen H(211), including the covalent radii for nitrogen and analogously for hydrogen with 0.30 Å, is 21.08 Å. The distances from N(1) to the middle of the bonds C(5) - C(8) and C(11) - C(14), including the covalent radius for nitrogen, are found to be 6.68 Å and 10.93 Å, respectively.

TABLE 1 : Atomic parameters

	x/a	y/b	z/c	U_{eq}^{*}
Cyano group				
N(1)	0.6474(1)	0.1005(7)	1.0288(1)	0.104(2)
C(1)	0.6008(2)	0.2050(7)	0.9829(2)	0.076(2)
Phenyl group				
C(2)	0.5394(1)	0.3298(7)	0.9237(2)	0.065(2)
C(3)	0.5454(2)	0.5277(7)	0.8801(2)	0.080(3)
C(4)	0.4861(1)	0.6386(6)	0.8238(2)	0.075(2)
C(5)	0.4186(1)	0.5612(5)	0.8087(1)	0.058(2)
C(6)	0.4138(1)	0.3623(7)	0.8532(2)	0.086(3)
C(7)	0.4727(1)	0.2483(7)	0.9092(2)	0.089(2)
Cyclohexyl group				
C(8)	0.3540(1)	0.6805(6)	0.7457(1)	0.061(2)
C(9)	0.2912(1)	0.7056(6)	0.7652(1)	0.073(2)
C(10)	0.2262(1)	0.8195(6)	0.6998(2)	0.074(2)
C(11)	0.2034(1)	0.6712(6)	0.6257(1)	0.058(2)
C(12)	0.2652(1)	0.6498(6)	0.6048(1)	0.068(2)
C(13)	0.3312(1)	0.5365(6)	0.6698(1)	0.065(2)
Octyl group				
C(14)	0.1366(1)	0.7863(6)	0.5621(1)	0.068(2)
C(15)	0.1018(1)	0.6350(6)	0.4883(1)	0.069(2)
C(16)	0.0328(1)	0.7515(6)	0.4307(1)	0.070(2)
C(17)	-0.0023(1)	0.6119(6)	0.3549(2)	0.070(2)
C(18)	-0.0703(1)	0.7369(6)	0.2980(1)	0.067(2)
C(19)	-0.1059(1)	0.6093(6)	0.2203(2)	0.071(2)
C(20)	-0.1731(1)	0.7387(6)	0.1639(2)	0.073(2)
C(21)	-0.2096(1)	0.6047(7)	0.0876(2)	0.099(3)

$$U_{eq}^{*} = \frac{1}{3}\,(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$$

These values are also in agreement with the values for CCH 3 and CCH 5, calculated from data given by [4].

The bond distances (depicted in Fig. 1) are of normal magnitude. The same can also be said of the bond angles.

Taking into account the relatively low melting point of the substance and the temperature of 23°C during the measure-

ment, the thermal amplitudes of the atoms - especially those of the octyl group - are comparatively small. There was no indication of a disordered structure or partial occupancy.

CRYSTAL PACKING

In Fig. 2 a projection along the short crystallographic b-axis is given.. The molecules are arranged in a head-to-tail manner parallel to each other with an overlapping of the octylcyclohexyl groups of the molecules. Additionally each cyanophenyl group overlaps with a cyanophenyl group of a neighbouring molecule related by a centre of symmetry to the former.This overlapping, not interpreted as dipole-dipole contact but as a precursor [8] to the nematic state, is rather similar to the arrangement in the higher melting crystalline form of CB 3 [5]. The mean distance N(1) - C'phenyl is 4.80 Å, the mean distance C(1) - C'phenyl = 4.54 Å, with the 'positions being, $x' = 1 - x$, $y' = 1 - y$ and $z' = 2 - z$. In comparison with CB 3, the normal to the C(1)' - C(2)' bond in the direction of the overlapped phenyl ring in PCH 8 crosses the C(6) - C(7) bond and is unlike CB 3 displaced off-centre relative to this phenylring.This deviation could be due to the more voluminous cyclohexyl unit.

X-RAY DATA OF THE NEMATIC STATE

In the nematic state, i.e. within the temperature range of 40° to 48°C $d_{\parallel}$ and $d_{\perp}$ were found to be 32.1 Å and 5.3 Å, respectively. These observations indicate a semibilayer molecular arrangement in the nematic phase.

THERMAL PROPERTIES

Crystals with the described structure melt at 37°C[2,3]. This evidence comes from DSC and thermal microscopy. Solid state polymorphism is indicated by different cooling procedures from the nematic state. This will be reported later [9].

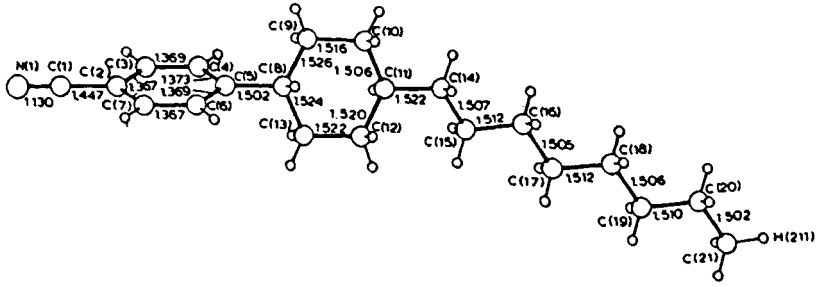

Fig. 1 PCH 8 molecule projected perpendicular to the plane through the atoms C(9), C(10),C(12),C(13). Standard deviations are 4 in the last figure.

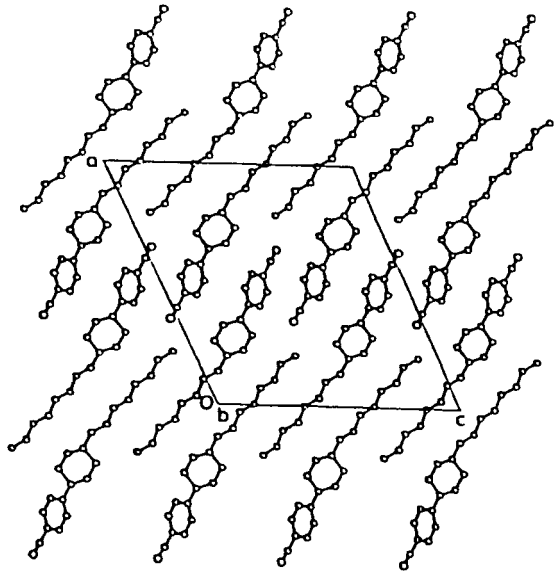

Fig. 2 Projection along the monoclinic b-axis

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