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The Crystal and Molecular Structures of a Second Crystalline Modification of the Mesogenic trans-4-n-octyl-(4′-cyanophenyl)- cyclohexane (PCH8B) and of Two Crystalline Modifications of the Mesogenic trans-4-n-nonyl-(4′-cyanophenyl)- cyclohexanes (PCH9A, PCH9B)

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The Crystal and Molecular Structures of a Second Crystalline Modification of the Mesogenic trans-4-*n*-octyl-(4′-cyanophenyl)-cyclohexane (PCH8B) and of Two Crystalline Modifications of the Mesogenic trans-4-*n*-nonyl-(4′-cyanophenyl)-cyclohexanes (PCH9A, PCH9B)

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The crystal and molecular structures of a new crystalline modification of the mesogenic PCH8 and of two solid modifications of PCH9 are described: PCH8B: Triclinic, space group $P\bar{1}$, a = 6.369 (2), b = 11.907 (3), c = 13.119 (3) Å, α = 77.39 (1), β = 78.48 (1), γ = 77.68 (1)°; Z = 2; PCH9A: Monoclinic, space group $P2_1/c$, a = 21.562 (4), b = 5.158 (1), c = 19.326 (4) Å, β = 112.99 (1)°, Z = 4; PCH9B: Triclinic, space group $P\bar{1}$, a = 7.622 (2), b = 11.372 (3), c = 23.574 (6) Å, α = 94.20 (1), β = 95.68 (1), γ = 97.01 (1)°, Z = 4. PCH9A is isostructural with PCH8A (Paulus and Haase),[2] showing overlapping of the cyanophenyl groups in a head to tail manner. PCH8B and PCH9B are different from the A-modification and different from each other. PCH8B shows antiparallel CN—CN correlation interpreted as dimers of infinite stackings, for PCH9B four molecules are showing antiparallel CN—CN clustering in form of an island. In all of the described modifications the alkylcyclohexyl groups are unflexible whereas the angle between the phenyl and the cyclohexyl groups is more flexible.

Keywords: Crystal structures, molecular structures, solid state polymorphism, PCH8, PCH9

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INTRODUCTION

The title compounds (PCH8B, PCH9A, PCH9B) are members of the series of the trans-4-*n*-alkyl-(4′-cyanophenyl)cyclohexanes (PCH's), first described by Eidenschink *et al.*[1] The crystal and molecular structure of the A-modification of PCH8 was published by Paulus and Haase.[2] The structures of the B-modification of PCH8 and the modifications of PCH9 will be discussed in relation to the PCH8A and other similar compounds. It was found by DSC-experiments that PCH3 shows three different solid modifications and PCH7 even four, whereas no solid state polymorphism could be observed for PCH5.[3] The structure of one of the solid phases of PCH3 was published by Foitzik *et al.*[4]

EXPERIMENTAL

Crystals suitable for x-ray examination were obtained by evaporation of the solutions of the respective chemical compound in methanol as described in the following: plates (PCH8B) and needles (PCH9B) grow as a first precipitate by temperatures of 280 K; needles (PCH8A) and prisms (PCH9A) grow during very slow evaporation by temperatures of 296 K.

The x-ray measurements were made on a Stoe-4-circle diffractometer with Mo Kα-radiation ($\lambda = 0.71069$ Å), graphite monochromated. The basic crystallographic data and experimental details are presented in Table I. The number of reflections used for lattice parameters refinement was 20 for PCH8B, 48 for PCH9A and 60

TABLE I

Basic crystal data and experimental details

	PCH8B	PCH9A	PCH9B
Molecular formula	$C_{21}H_{31}N$	$C_{22}H_{33}N$	$C_{22}H_{33}N$
Formula weight ($g \cdot mol^{-1}$)	297.48	311.52	311.52
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a[Å]	6.369(2)	21.562(4)	7.622(2)
b[Å]	11.907(3)	5.158(1)	11.372(3)
c[Å]	13.119(3)	19.326(4)	23.574(6)
α[°]	77.39(1)		94.20(1)
β[°]	78.48(1)	112.99	95.68(1)
ϑ[°]	77.68(1)		97.01(1)
V[Å^3]	936.22	1978.43	2010.56
Z	2	4	4
D_x[$g \cdot cm^{-3}$]	1.055	1.046	1.029
$\mu_{Mo\text{-}K\alpha}$[cm^{-1}]	0.30	0.29	0.29
Number of reflections measured	2436	2745	5251
Number of independent reflections	2436	2609	5250
Merging R		0.015	
Number of unobserved reflection ($F_0 < 2\sigma(F_0)$)	441	683	2107
R	0.051	0.055	0.076
$R_w(W = 1/\sigma^2(F_0))$	0.047	0.040	0.053

TABLE II

Positional parameters with estimated standard deviations and equivalent temperature factors (U_{eq} = 1000/3 ($\Sigma\Sigma_{ij} U_{ij} \cdot a_i^* \cdot a_j^* \cdot (a_i \cdot a_j)$/Å^2)

	x/a	y/b	z/c	U_{eq}
N*	0.7409(3)	0.9915(2)	1.0721(5)	78(1)
	0.6339(1)	0.1260(5)	1.0164(1)	117(2)
	−0.1128(4)	1.0984(3)	0.0367(1)	99(3)
	−0.8249(4)	0.6486(3)	−0.1274(1)	111(3)
C(1)	0.7641(4)	0.9189(2)	1.0242(2)	60(1)
	0.5902(1)	0.2343(6)	0.9731(1)	85(2)
	0.0132(5)	1.1075(3)	0.0677(1)	76(3)
	−0.7035(5)	0.6651(4)	−0.0942(2)	89(3)
C(2)	0.7916(3)	0.8253(2)	0.9662(2)	49(1)
	0.5325(1)	0.3628(5)	0.9179(1)	71(2)
	0.1738(4)	1.1153(3)	0.1069(1)	66(2)
	−0.5483(5)	0.6820(4)	−0.0527(2)	77(3)
C(3)	0.9836(4)	0.7974(2)	0.8989(2)	55(1)
	0.5399(1)	0.5663(5)	0.8755(1)	83(2)
	0.2850(4)	1.0301(3)	0.1005(1)	78(2)
	−0.4331(6)	0.6005(4)	−0.0507(2)	133(4)
C(4)	1.0070(3)	0.7069(2)	0.8450(2)	53(1)
	0.4841(1)	0.6835(5)	0.8227(1)	76(2)
	0.4355(4)	1.0337(3)	0.1386(1)	75(2)
	−0.2844(5)	0.6166(4)	−0.0113(2)	122(3)
C(5)	0.8433(3)	0.6423(1)	0.8560(1)	42(1)
	0.4194(1)	0.6062(4)	0.8106(1)	61(2)
	0.4788(4)	1.1211(3)	0.1829(1)	63(2)
	−0.2456(4)	0.7140(3)	0.0274(2)	70(2)
C(6)	0.6526(3)	0.6732(2)	0.9237(1)	50(1)
	0.4132(1)	0.4022(5)	0.8541(1)	83(2)
	0.3664(5)	1.2068(3)	0.1873(1)	83(3)
	−0.3635(5)	0.7964(3)	0.0239(2)	82(3)
C(7)	0.6257(3)	0.7632(2)	0.9778(2)	54(1)
	0.4684(1)	0.2825(5)	0.9065(1)	86(2)
	0.2148(4)	1.2049(3)	0.1500(2)	83(3)
	−0.5120(4)	0.7807(4)	−0.0151(2)	81(3)
C(8)	0.8803(3)	0.5427(1)	0.7959(1)	43(1)
	0.3590(1)	0.7345(4)	0.7526(1)	65(2)
	0.6370(4)	1.1249(3)	0.2276(1)	65(2)
	−0.0852(4)	0.7344(3)	0.0714(1)	69(2)
C(9)	1.0639(3)	0.4454(2)	0.8305(2)	51(1)
	0.2998(1)	0.7633(5)	0.7763(1)	76(2)
	0.7788(4)	1.0506(3)	0.2103(1)	78(2)
	0.0557(4)	0.6521(3)	0.0620(1)	82(2)
C(10)	1.1090(3)	0.3474(2)	0.7669(2)	52(1)
	0.2395(1)	0.8916(5)	0.7163(1)	76(2)
	0.9336(4)	1.0567(3)	0.2575(1)	80(2)
	0.2145(4)	0.6776(3)	0.1081(1)	82(2)
C(11)	0.9089(3)	0.2951(1)	0.7720(1)	46(1)
	0.2156(1)	0.7525(4)	0.6416(1)	64(2)
	0.8714(4)	1.0181(3)	0.3131(1)	72(2)
	0.1606(4)	0.6676(3)	0.1682(1)	72(2)
C(12)	0.7256(3)	0.3926(2)	0.7381(2)	55(1)
	0.2743(1)	0.7224(4)	0.6169(1)	74(2)
	0.7313(4)	1.0936(3)	0.3305(1)	83(2)
	0.0208(4)	0.7504(3)	0.1774(1)	86(3)

TABLE II (*continued*)

	x/a	*y/b*	*z/c*	U_{eq}
C(13)	0.6788(3)	0.4903(2)	0.8019(2)	51(1)
	0.3359(1)	0.5955(5)	0.6767(1)	71(2)
	0.5762(4)	1.0885(3)	0.2837(1)	82(2)
	−0.1393(4)	0.7252(3)	0.1319(1)	81(2)
C(14)	0.9559(3)	0.1971(2)	0.7082(2)	53(1)
	0.1545(1)	0.8856(5)	0.5835(1)	76(2)
	1.0241(4)	1.0238(3)	0.3610(1)	81(3)
	0.3180(4)	0.6927(3)	0.2143(1)	82(2)
C(15)	0.7752(3)	0.1268(2)	0.7238(2)	56(1)
	0.1184(1)	0.7415(4)	0.5108(1)	76(2)
	1.1490(4)	0.9313(3)	0.3539(1)	84(3)
	0.4441(4)	0.5989(3)	0.2150(1)	83(3)
C(16)	0.8245(3)	0.0325(2)	0.6573(2)	55(1)
	0.0540(1)	0.8725(5)	0.4588(1)	76(2)
	1.3000(4)	0.9415(3)	0.4021(1)	83(2)
	0.5990(4)	0.6220(3)	0.2618(1)	81(2)
C(17)	0.6427(3)	−0.0356(2)	0.6702(2)	56(1)
	0.0190(1)	0.7395(4)	0.3842(1)	74(2)
	1.4226(4)	0.8471(3)	0.3970(1)	88(3)
	0.7209(4)	0.5262(3)	0.2624(1)	83(3)
C(18)	0.6876(3)	−0.1258(2)	0.5999(2)	55(1)
	−0.0449(1)	0.8696(5)	0.3316(1)	74(2)
	1.5742(4)	0.8595(3)	0.4450(1)	85(3)
	0.8776(4)	0.5485(3)	0.3079(1)	85(3)
C(19)	0.5060(3)	−0.1934(2)	0.6120(2)	56(1)
	−0.0778(1)	0.7407(5)	0.2562(1)	74(2)
	1.7001(4)	0.7682(3)	0.4388(1)	95(3)
	1.0010(4)	0.4548(3)	0.3066(1)	86(3)
C(20)	0.5465(4)	−0.2807(2)	0.5389(2)	62(1)
	−0.1415(1)	0.8667(5)	0.2030(1)	74(2)
	1.8557(5)	0.7801(3)	0.4846(1)	91(3)
	1.1608(5)	0.4751(3)	0.3510(2)	91(3)
C(21)	0.3621(4)	−0.3468(2)	0.5512(2)	74(2)
	−0.1749(1)	0.7340(5)	0.1283(1)	92(2)
	1.9783(5)	0.6878(4)	0.4779(2)	117(3)
	1.2805(5)	0.3819(3)	0.3506(2)	116(3)
C(22)**	−0.2377(1)	0.8599(6)	0.0749(1)	113(2)
	2.1351(5)	0.6978(4)	0.5227(2)	132(3)
	1.4381(5)	0.3990(4)	0.3955(2)	141(4)

*line 1: PCH8B, line 2: PCH9A, line 3: PCH9B I, line 4: PCH9B II.
**line 1: PCH9A, line 2: PCH9B I, line 3: PCH9B II.

for PCH9B, respectively, the amount of reflections for structure determination was 1995 for PCH8B, 1926 for PCH9A and 3143 for PCH9B, respectively. The structures were solved by direct methods. The least-squares refinement was performed with anisotropic thermal parameters for non-H atoms and hydrogen atoms in geometrically idealized positions (C—H = 0.96 Å) using the program SHELX 76.[5] The atomic coordinates and thermal parameters U_{eq} of non-H atoms are listed in Table II. Lists of F_0, F_c data, anisotropic thermal parameters of non-H atoms and H atoms coordinates are available from the authors on request. Selected bond distances and the N—C1—C2 angles are given in Table III.

Clearing point temperatures were determined using a polarizing microscope (Leitz Orthoplan Pol) equipped with a Mettler Hotstage FP-82. The tolerance for tran-

TABLE III

Selected bond distances [Å] and angles [°]

	PCH8B	PCH9A	PCH9B I	PCH9B II
N—C(1)	1.144(3)	1.134(4)	1.137(5)	1.139(5)
C(1)—C(2)	1.445(3)	1.445(4)	1.449(5)	1.443(5)
(C—C)phenyl	1.382(9)	1.379(12)	1.375(10)	1.367(21)
C(5)—C(8)	1.516(2)	1.499(3)	1.514(4)	1.508(5)
(C—C)cyclohexyl	1.523(6)	1.522(15)	1.521(16)	1.528(8)
C(11)—C(14)	1.526(2)	1.520(3)	1.532(4)	1.520(4)
C(14)—C(15)	1.520(3)	1.510(3)	1.513(5)	1.520(5)
C(15)—C(16)	1.512(2)	1.519(3)	1.524(4)	1.518(4)
C(16)—C(17)	1.513(3)	1.506(3)	1.512(5)	1.516(5)
C(17)—C(18)	1.511(2)	1.513(3)	1.521(4)	1.508(4)
C(18)—C(19)	1.510(3)	1.504(3)	1.506(5)	1.505(5)
C(19)—C(20)	1.512(3)	1.504(3)	1.510(4)	1.509(4)
C(20)—C(21)	1.513(3)	1.503(3)	1.498(5)	1.481(5)
C(21)—C(22)		1.493(3)	1.502(5)	1.504(5)
N—C(1)—C(2)	177.6(5.6)	178.6(11.9)	176.7(6.7)	177.2(8.7)

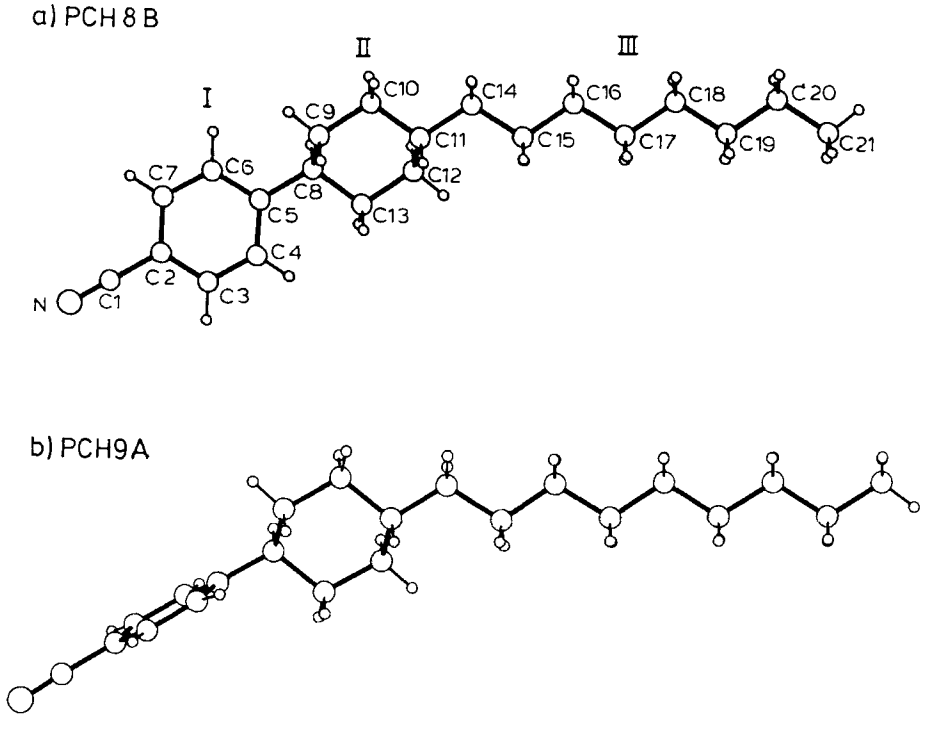

FIGURE 1 Molecular structures of PCH8B and PCH9A with the numbering of atoms and with definition of the planes used in Table IV.

sition temperatures is about ±0.2°C. The calorimetric investigations were done by a Du Pont 990-DSC-Cell equipment. The mass of samples encapsulated in sealed aluminium pons ranged between 5 and 9 mg. The accuracy of the balance was ± 0.1 mg.

DESCRIPTION OF THE STRUCTURES

Figure 1 shows the molecular structures of PCH8B and PCH9A with the numbering of atoms as projection perpendicular to the atoms C2, C4, C6 (PCH8B) and per-

TABLE IV

Angles (°) between best planes defined in Figure 1. (Data for PCH8A are calculated using the parameters given in Reference 2)

	I/II	I/III	II/III
PCH8A	64.9	98.1	33.3
8B	36.5	4.1	38.5
9A	65.9	99.1	33.4
9B I	45.9	3.7	43.7
9B II	41.3	2.1	40.1

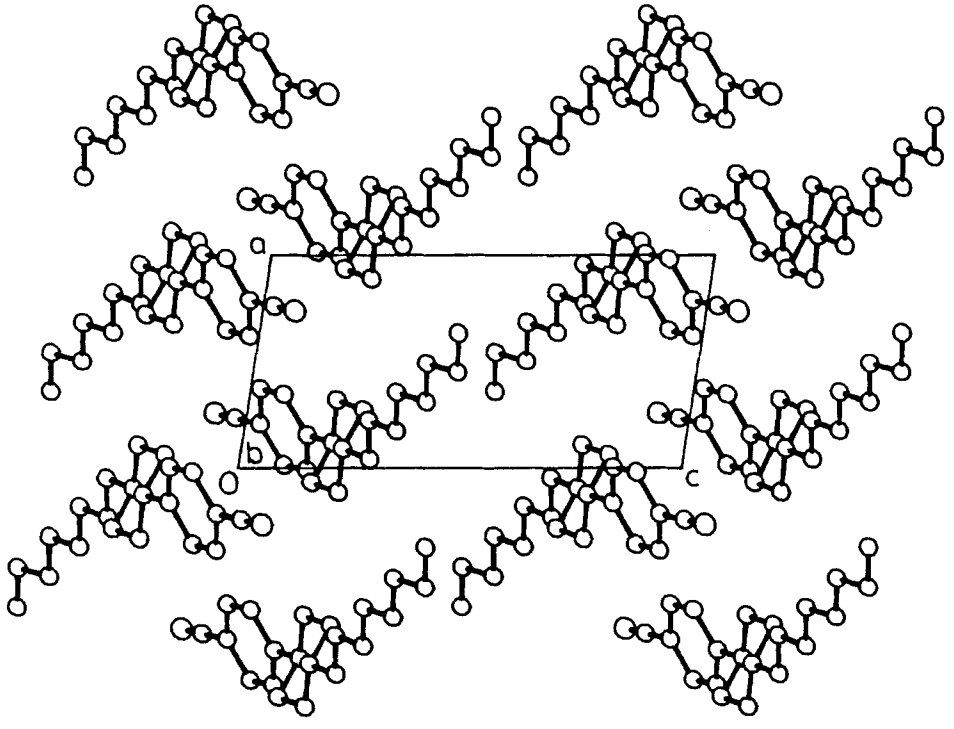

FIGURE 2 Crystal packing in PCH8B (view along [010])

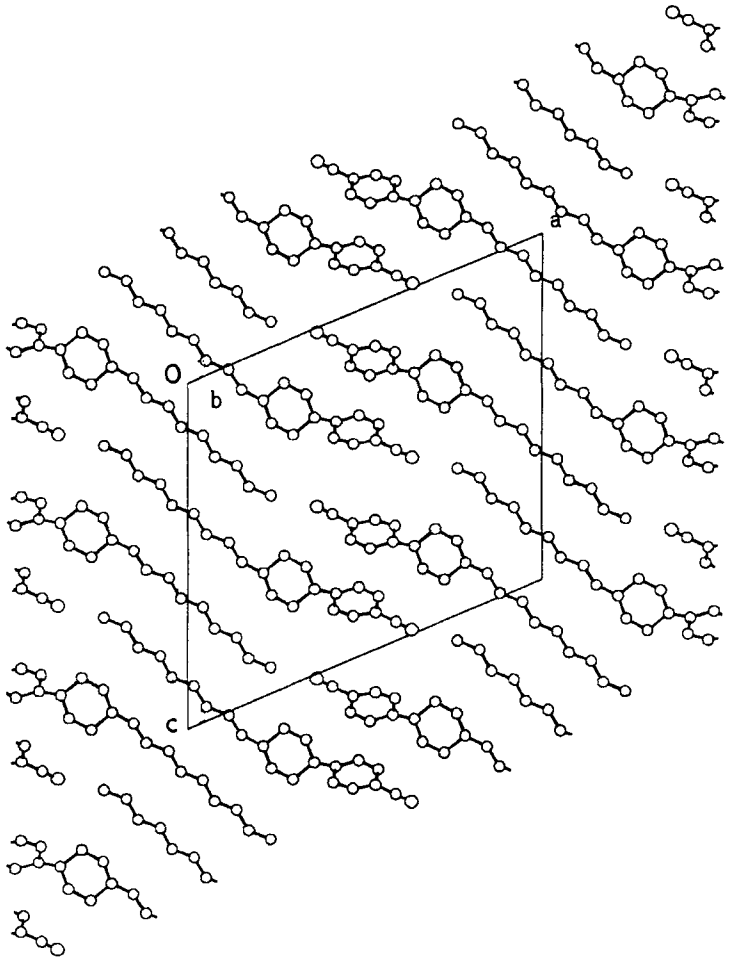

FIGURE 3 Crystal packing in PCH9A (view along [010])

pendicular to the atoms C17, C18, C19 (PCH9A). The Roman numbers define the molecular subunits used in Table IV in which the angles between the best planes through these subunits are presented (plane I: C2 to C7, plane II: C9, C10, C12, C13, plane III: C14 to C21 or C22). The N—C1 bond distances and the angles N—C1—C2 are normal compared with the data given for PCH8A[2] and the trans-4′-alkyl-trans-4-(1,1′-bicyclohexyl)-carbonitril's (CCH's)[6] or trans,trans-4,4′-di-alkyl-)1α,1′-bicyclohexyl)-4β-carbonitril's (CCN's),[7] respectively. Also all bond distances and angles are normal (Table III). Table IV and Figure 1 reveal immediately the principal differences in the molecular structures of the modifications crystallizing in the monoclinic (PCH8A, PCH9A) and triclinic space groups (PCH8B, PCH9B). In the A-modifications the alkyl chain III lies in a plane which is nearly perpendicular to the plane I through the phenyl ring, in the B-modifications the alkyl chain III is nearly coplanar with the phenyl ring. This is a consequence of

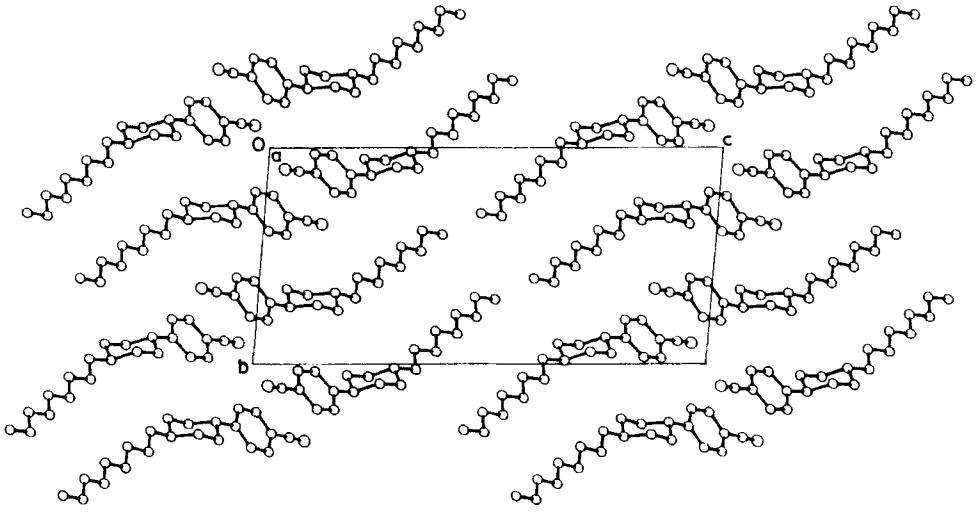

FIGURE 4 Crystal packing in PCH9B (view along [100])

TABLE V

Transition temperatures T (°C) and enthalpies ΔH (kJ/mol) for PCH8 and PCH9 compounds

	PCH8A,B		PCH9A,B	
Transition	T	ΔH	T	ΔH
$C_A \rightarrow N$	35(1)	37(1)	43(1)	34.9(3)
$C_B \rightarrow N$	32(1)	32(1)	40(1)	32.8(9)
$N \rightarrow I$	54.7(3)	1.0(4)	60.0(3)	1.4(3)

different structural relations between the groups described through plane I and II (Table IV).

A comparison of the data for PCH3[4] (monoclinic, angles I/II = 81.5, I/III = 115.6 and II/III = 34.1°) and PCH8, PCH9 leads to the conclusion, that the geometry of the alkylcyclohexyl part (II/III) is almost identical and the angles are in the expected range (33–44°) for such systems. The inspection of the data of the known molecular structures with an alkylcyclohexyl fragment (PCH3[4], PCH8[2], CCH's,[6] CCN's[7] and this work) shows that these groups are the almost fixed part of a molecule whereas the angle between the neighbouring phenyl or cyclohexyl group is flexible.[6,7,8]

The largest extension of the PCH8B molecule from N to H211 including the covalent radii of N (0.55 Å) and H (0.30 Å) is 21.1 Å (in PCH8A molecule it is 21.1 Å). The analogous values of PCH9A and PCH9B are 22.2 and 22.3 Å.

CRYSTAL PACKING

In Figures 2, 3 and 4 projections of the crystal structures are given. The modifications PCH8A and PCH9A are isostructural, having the same space group and

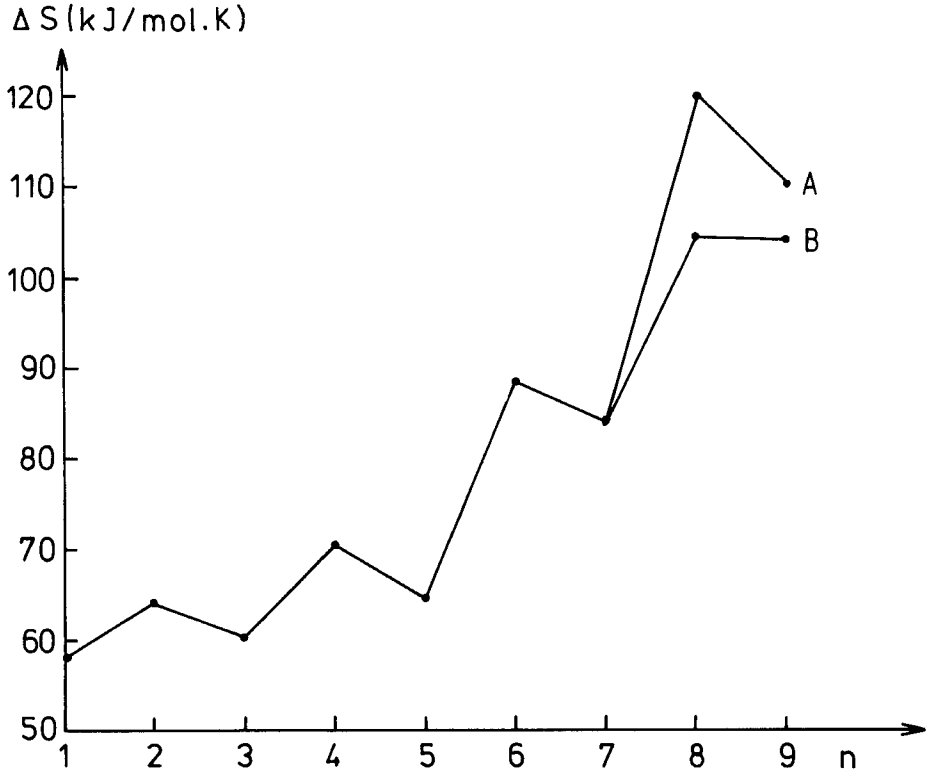

FIGURE 5 The molar transition entropies ΔS (kJ/mol. K) for the transitions crystalline-nematic (for n = 1,2 crystalline-isotropic, n is the number of C-atoms in the alkyl groups).

similar lattice constants (the differences of equivalent constants Δ = PCH8A-PCH9A are Δa = −0.587, Δb = −0.015, Δc = 0.006 Å and Δβ = 2.98°). Also the calculated densities D_c are practically the same (1.047 and 1.046 g. cm^{-3}). The molecular long axes are parallel to [304]. The molecules are arranged in a head-to-tail manner parallel to each other with an overlapping of the alkylcyclohexyl 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. The mean distance N—C^{i} phenyl is 4.80 for PCH8A and 4.51 Å for PCH9A, the mean distance C1—C^{i} phenyl = 4.54 and 4.31 Å, with the symmetry code i = $1-x, 1-y, 2-z$. It should be noted that the similar arrangement is observed in the 4-cyano-4′-propylbiphenyl (Haase *et al.*)[9] and some other 4-cyano-4′-alkoxybiphenyls (Walz *et al.*).[10]

The molecules of PCH8B are arranged along the direction [211] showing an overlapping of the cyano groups, with the distances N—N^{ii} = 3.48, N—C1^{ii} = 3.45 and C1—C1^{ii} = 3.79 Å, (ii = $2-x, 2-y, 2-z$) and N—N^{iii} = 3.86, N—C1^{iii} = 3.55 and C1—C1^{iii} = 3.60 Å, (iii = $1-x, 2-y, 2-z$). The cyano groups build the infinite chains along the direction [100].

The molecules of PCH9B are arranged parallel [011]. The molecules I form the

centrosymmetric dimers with the antiparallel overlapping of the cyano-cyano groups with the distances NI—NI^{iv} = 3.45, NI—C1I^{iv} = 3.47 Å C1I—C1I^{iv} = 3.85 Å (iv = x, 2 − y, z). Likewise each molecule I forms with the neighboured molecule II a dimer by antiparallel cyano-cyano overlapping with the distances NI—NII^{v} = 3.56, NI—C1II^{v} = 3.43, C1I—NII^{v} = 3.54 and C1I—C1II^{v} = 3.77 Å (v = −1 − x, 2 − y, z). As a result of this a clustering of four molecules (for example II^{v}—I—I^{iv}—II^{vi}, vi = 1 + x, y, z) through cyano-cyano contacts in form of an island can be considered.

THERMAL PROPERTIES

The transition temperatures[11] and the molar transition enthalpies are summarized in Table V. The molar transition entropies calculated from these data fit well into the series of PCH derivatives as can be seen in Figure 5. Data for PCH1, 2, 6 are taken from specification of the products of the E. MERCK Company, Darmstadt and for PCH3, 5, 7 from Reference 3. Looking at the data of entropies ΔS, one can see that the compounds with the odd number n of C-atoms have the smaller values of entropies than the compounds with the even number. This reflects the well known odd-even effect.

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