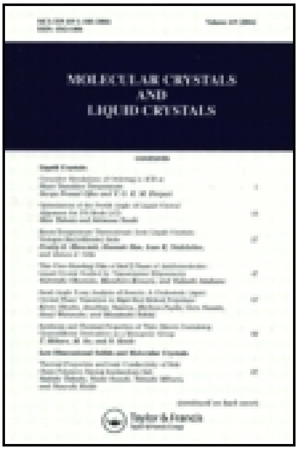

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An X-Ray Study of Cyanophenylpyrimidines Part III. Crystal Structure of 5-(trans-4-Heptylcyclohexyl)-2-(4-Cyanophenyl) Pyrimidine

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An X-Ray Study of Cyanophenylpyrimidines Part III. Crystal Structure of 5-(*trans*-4-Heptylcyclohexyl)-2-(4-Cyanophenyl)Pyrimidine

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The compound $C_{24}H_{31}N_3$ at higher temperatures shows a smectic liquid crystal phase followed by a nematic phase. The crystals belong to space group $P2_1/c$, with a = 13.0422(6), b = 17.7464(11) and c = 9.5950(5) Å, β = 107.170(1)°, Z = 4. The structure has been solved by the direct method program system SIMPEL83 and refined to an R-value of 0.041. Molecules are packed in associated pairs running parallel to the a axis. An X-ray study at higher temperatures shows that the smectic phase is also built up from similar pairs of molecules.

1. INTRODUCTION

In this paper we report the results of a crystal structure analysis of the compound 5-(*trans*-4-heptylcyclohexyl)-2-(4-cyanophenyl)pyrimidine (HCCPP). This is part of our program of structure determinations for a series of homologous compounds having liquid crystal phases. The crystal and molecular structures of the related propyl and ethyl compounds have already been reported.[1,2]

In homologous series of thermotropic mesogens containing alkyl chains, the type of liquid crystalline phase depends on the chain length. The two lower homologues mentioned above have nematic phases only, while the present heptyl compound (HCCPP) has a smectic phase followed by a nematic phase. Its expanded molecular formula is $C_7H_{15}(C_6H_{10})(C_4N_2H_2)(C_6H_4)CN$. The transition temperatures for the compound have been determined by X-ray diffraction, texture studies and density measurements with the following results:

$$\text{Crystalline Solid} \underset{57°\text{C}}{\overset{82°\text{C}}{\rightleftarrows}} \text{Sm} \overset{158°\text{C}}{\rightleftarrows} \text{N} \overset{223°\text{C}}{\rightleftarrows} \text{Isotropic}$$

2. EXPERIMENTAL

Transparent plate-like monoclinic crystals were obtained by slow evaporation from a solution in acetone. Systematic absences occur for *hol* reflections with $l = 2n + 1$ and *oko* reflections with $k = 2n + 1$ indicating the space group $P2_1/c$. Accurate cell parameters were determined by a least-squares fit of sinθ values of 24 reflections having θ values $45° < \theta < 48°$, measured on an Enraf Nonius CAD-4 diffractometer, using CuK_α radiation monochromatized by a graphite monochromator. A crystal of dimensions 0.4 × 0.4 × 0.3 mm was used for intensity data collection. A total of 4012 reflections were collected in the ω-2θ scan mode, of which 2951 were above the zero level of 2.5σ(I). The data were corrected for Lorentz and polarization factors and no absorption correction was necessary. The crystallographic data are given in Table I.

3. STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by means of the direct methods program SIMPEL83 of Kiers and Schenk,[3] using all reflections in order to employ positive and negative quartet relationships, sigma 1 reflections and special two dimensional quartets, apart from the triplets. The strongest 500 reflections were phased using three symbols. Two out of eight solutions had appreciably better combined figures of merit. The E-map with highest combined figure of merit could not solve the structure and showed instead a superposition of two structures. The other one revealed the structure completely.

The structure was refined by block diagonal least-squares calculations to a final $R = 0.041$. In the course of the refinement the hydrogen atoms were located and

TABLE I

Summary of Crystallographic Data

Molecular formula	$C_{24}H_{31}N_3$	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Form/habit	Plate shaped.	
$a = 13.0422(6)$	$b = 17.7464(11)$	$c = 9.5950(5)$ Å
$\beta = 107.170(1)°$	$V_c = 2121.8$ Å^3	$D_c = 1.13$ g cm^{-3}
$D_0 = 1.12$ g cm^{-3}	$Z = 4$	
Number of independent reflections 4012		
Number of observed reflections 2951		

refined isotropically. A weighting scheme $w = (7.9 + F_{obs} + .0049\ F^2_{obs})^{-1}$ was applied and extinction was taken into account. All calculations were carried out with X-ray76 program of Stewart[4] using scattering factors from Cromer and Mann.[5]

4. RESULTS AND DISCUSSIONS

4.1 Molecular conformation

Final positions and thermal parameters of the atoms are listed in Tables II–IV using the atom numbering of Figure 1. Bond lengths and bond angles are given in Tables V and VI. The perspective drawing of the molecule viewed normal to its least squares plane is shown in Figure 1.

The average C—C bond length in the phenyl ring is 1.385(2) Å. In the pyrimidine ring the average C—C bond length is 1.386(2) Å, and the C—N bond length is 1.335(2) Å. The average C—C bond length in the cyclohexane ring is 1.524(2) Å. All lengths are consistent with our previous observations[1,2] and have expected values.[6] The average C—C bond length in the alkyl chain is 1.518(2) Å and is apparently influenced by thermal vibrations. For the same reason, the average bond angle in the alkyl chain is 114.03°. The bond length of C24—N3 is 1.141(2) Å, close to the value found in other mesogenic compounds.[7,8]

TABLE II

Fractional co-ordinates of the non-hydrogen atoms and equivalent isotropic thermal parameters.

	X	Y	Z	Ueq
C(1)	1.4855(2)	0.1849(2)	−0.2097(3)	0.094(2)
C(2)	1.3837(2)	0.1515(1)	−0.1916(2)	0.076(1)
C(3)	1.3414(1)	0.1899(1)	−0.0794(2)	0.064(1)
C(4)	1.2392(1)	0.1545(1)	−0.0645(2)	0.066(1)
C(5)	1.1889(1)	0.1956(1)	0.0369(2)	0.063(1)
C(6)	1.0834(1)	0.1612(1)	0.0432(2)	0.063(1)
C(7)	1.0267(1)	0.2074(1)	0.1319(2)	0.063(1)
C(8)	0.9146(1)	0.17944(9)	0.1271(2)	0.0525(9)
C(9)	0.9169(1)	0.1018(1)	0.1954(2)	0.062(1)
C(10)	0.8578(2)	0.2351(1)	0.1999(2)	0.066(1)
C(11)	0.7469(1)	0.2085(1)	0.2014(2)	0.063(1)
C(12)	0.7523(1)	0.1311(1)	0.2732(2)	0.0523(9)
C(13)	0.8061(1)	0.0752(1)	0.1967(2)	0.064(1)
C(14)	0.6440(1)	0.10520(9)	0.2812(2)	0.501(8)
C(15)	0.5729(1)	0.0620(1)	0.1760(2)	0.061(1)
C(16)	0.6077(1)	0.1235(1)	0.3991(2)	0.060(1)
C(17)	0.4525(1)	0.05958(9)	0.3051(2)	0.0508(9)
C(18)	0.3485(1)	0.03229(9)	0.3196(2)	0.0498(9)
C(19)	0.2930(1)	−0.0253(1)	0.2311(2)	0.063(1)
C(20)	0.3058(1)	0.0632(1)	0.4237(2)	0.059(1)
C(21)	0.1980(1)	−0.0523(1)	0.2468(2)	0.063(1)
C(22)	0.2105(1)	0.0363(1)	0.4401(2)	0.060(1)
C(23)	0.1567(1)	−0.02153(9)	0.3522(2)	0.0522(9)
C(24)	0.0591(1)	−0.0526(1)	0.3705(2)	0.0562(9)
N(1)	0.4779(1)	0.03849(9)	0.1857(1)	0.0606(9)
N(2)	0.5133(1)	0.10179(9)	0.4130(2)	0.0606(9)
N(3)	−0.0171(1)	−0.07846(9)	0.3854(2)	0.069(1)

TABLE III

Fractional co-ordinates and isotropic thermal parameters of the hydrogen atoms.

	X	Y	Z	U
H(11)	1.541(2)	0.184(1)	−0.114(3)	0.118(8)
H(12)	1.515(2)	0.160(2)	−0.280(3)	0.139(9)
H(13)	1.474(2)	0.243(2)	−0.235(3)	0.14(1)
H(21)	1.320(2)	0.155(1)	−0.294(2)	0.115(8)
H(22)	1.390(2)	0.096(1)	−0.169(2)	0.106(7)
H(31)	1.402(2)	0.190(1)	0.023(2)	0.097(7)
H(32)	1.328(1)	0.243(1)	−0.106(2)	0.077(6)
H(41)	1.254(1)	0.100(1)	−0.035(2)	0.080(6)
H(42)	1.185(1)	0.153(1)	−0.166(2)	0.082(6)
H(51)	1.239(1)	0.198(1)	0.134(2)	0.081(6)
H(52)	1.175(1)	0.248(1)	0.006(2)	0.075(5)
H(61)	1.096(1)	0.108(1)	0.083(2)	0.077(6)
H(62)	1.035(1)	0.155(1)	−0.061(2)	0.084(6)
H(71)	1.074(1)	0.208(1)	0.233(2)	0.071(5)
H(72)	1.019(2)	0.263(1)	0.093(2)	0.088(6)
H(81)	0.867(1)	0.175(1)	0.019(2)	0.063(5)
H(91)	0.968(1)	0.106(1)	0.302(2)	0.085(6)
H(92)	0.950(1)	0.063(1)	0.145(2)	0.084(6)
H(101)	0.906(1)	0.242(1)	0.304(2)	0.079(6)
H(102)	0.856(1)	0.285(1)	0.158(2)	0.082(6)
H(111)	0.697(1)	0.203(1)	0.099(2)	0.076(6)
H(112)	0.714(1)	0.245(1)	0.253(2)	0.082(6)
H(121)	0.798(1)	0.138(1)	0.373(2)	0.063(5)
H(131)	0.816(1)	0.024(1)	0.248(2)	0.082(6)
H(132)	0.760(1)	0.071(1)	0.093(2)	0.076(5)
H(151)	0.592(1)	0.045(1)	0.087(2)	0.077(6)
H(161)	0.654(1)	0.155(1)	0.481(2)	0.077(6)
H(191)	0.323(1)	−0.046(1)	0.157(2)	0.083(6)
H(201)	0.346(1)	0.106(1)	0.485(2)	0.083(6)
H(211)	0.157(1)	−0.093(1)	0.183(2)	0.083(6)
H(221)	0.178(1)	0.058(1)	0.507(2)	0.081(6)

TABLE IV

Anisotropic thermal parameters.

	U11	U22	U33	U12	U13	U23
C(1)	0.073(1)	0.130(2)	0.087(2)	−0.010(1)	0.038(1)	−0.007(1)
C(2)	0.070(1)	0.078(1)	0.087(1)	−0.003(1)	0.036(1)	−0.013(1)
C(3)	0.063(1)	0.070(1)	0.062(1)	−0.0062(9)	0.0207(8)	−0.0055(9)
C(4)	0.060(1)	0.067(1)	0.073(1)	−0.0046(9)	0.0232(9)	−0.0070(9)
C(5)	0.060(1)	0.069(1)	0.062(1)	−0.0071(9)	0.0206(8)	−0.0043(9)
C(6)	0.058(1)	0.064(1)	0.069(1)	−0.0037(8)	0.0245(9)	−0.0017(9)
C(7)	0.061(1)	0.066(1)	0.066(1)	−0.0094(8)	0.0242(8)	−0.0077(8)
C(8)	0.0550(9)	0.0517(9)	0.0516(9)	−0.0011(7)	0.0170(7)	0.0002(7)
C(9)	0.058(1)	0.057(1)	0.076(1)	0.0069(8)	0.0288(9)	0.0078(9)
C(10)	0.070(1)	0.050(1)	0.086(1)	−0.0055(8)	0.034(1)	−0.0072(9)
C(11)	0.061(1)	0.051(1)	0.082(1)	0.0038(8)	0.0287(9)	−0.0001(9)
C(12)	0.0488(8)	0.060(1)	0.0478(8)	0.0008(7)	0.0140(7)	0.0025(7)
C(13)	0.064(1)	0.0501(9)	0.084(1)	0.0030(8)	0.0333(9)	0.0051(9)
C(14)	0.0510(8)	0.0511(9)	0.0482(8)	0.0037(7)	0.0148(7)	0.0036(7)
C(15)	0.062(1)	0.076(1)	0.0504(9)	−0.0077(9)	0.0242(8)	−0.0074(8)
C(16)	0.0565(9)	0.068(1)	0.057(1)	−0.0069(8)	0.0192(8)	−0.0127(8)
C(17)	0.0538(9)	0.0523(9)	0.0478(8)	0.0013(7)	0.0172(7)	−0.0001(7)
C(18)	0.0535(9)	0.0521(9)	0.0454(8)	0.0009(7)	0.0172(7)	0.0003(7)
C(19)	0.067(1)	0.072(1)	0.055(1)	−0.0091(9)	0.0276(8)	−0.0133(8)
C(20)	0.061(1)	0.061(1)	0.061(1)	−0.0075(8)	0.0255(8)	−0.0126(8)
C(21)	0.065(1)	0.068(1)	0.059(1)	−0.0140(9)	0.0223(8)	−0.0142(9)
C(22)	0.061(1)	0.063(1)	0.064(1)	−0.0035(8)	0.0288(8)	−0.0112(8)
C(23)	0.0514(9)	0.0529(9)	0.0536(9)	0.0009(7)	0.0178(7)	0.0038(7)
C(24)	0.0568(9)	0.0533(9)	0.059(1)	0.0005(7)	0.0187(8)	−0.0016(8)
N(1)	0.0590(8)	0.077(1)	0.0504(8)	−0.0110(7)	0.0231(6)	−0.0100(7)
N(2)	0.0580(8)	0.0686(9)	0.0593(8)	−0.0086(7)	0.0239(7)	−0.0142(7)
N(3)	0.0635(9)	0.068(1)	0.081(1)	−0.0092(7)	0.0292(8)	−0.0073(8)

TABLE V

Bond distances of the non-hydrogen atoms (A) with standard deviations in parentheses.

C(1)—C(2)	1.510(3)	C(14)—C(16)	1.388(3)
C(2)—C(3)	1.510(3)	C(15)—N(1)	1.337(2)
C(3)—C(4)	1.518(3)	C(16)—N(2)	1.333(2)
C(4)—C(5)	1.513(3)	C(17)—C(18)	1.485(2)
C(5)—C(6)	1.522(3)	C(17)—N(1)	1.336(2)
C(6)—C(7)	1.521(3)	C(17)—N(2)	1.333(2)
C(7)—C(8)	1.532(3)	C(18)—C(19)	1.387(2)
C(8)—C(9)	1.522(2)	C(18)—C(20)	1.392(3)
C(8)—C(10)	1.523(3)	C(19)—C(21)	1.378(3)
C(9)—C(13)	1.525(3)	C(20)—C(22)	1.384(3)
C(10)—C(11)	1.525(3)	C(21)—C(23)	1.390(3)
C(11)—C(12)	1.528(2)	C(22)—C(23)	1.381(2)
C(12)—C(13)	1.523(3)	C(23)—C(24)	1.445(3)
C(12)—C(14)	1.509(2)	C(24)—N(3)	1.141(2)
C(14)—C(15)	1.383(2)		

TABLE VI

Bond angles of the non-hydrogen atoms with standard deviations in parentheses.

C(1)—C(2)—C(3)	115.0(2)
C(2)—C(3)—C(4)	113.3(2)
C(3)—C(4)—C(5)	114.8(2)
C(4)—C(5)—C(6)	113.6(2)
C(5)—C(6)—C(7)	113.6(2)
C(6)—C(7)—C(8)	115.3(1)
C(7)—C(8)—C(9)	112.5(1)
C(7)—C(8)—C(10)	111.5(1)
C(9)—C(8)—C(10)	109.9(2)
C(8)—C(9)—C(13)	112.7(1)
C(8)—C(10)—C(11)	113.2(1)
C(10)—C(11)—C(12)	111.4(1)
C(11)—C(12)—C(13)	109.5(2)
C(11)—C(12)—C(14)	112.2(1)
C(13)—C(12)—C(14)	113.4(1)
C(9)—C(13)—C(12)	112.0(1)
C(12)—C(14)—C(15)	124.6(2)
C(12)—C(14)—C(16)	121.3(1)
C(15)—C(14)—C(16)	114.1(2)
C(14)—C(15)—N(1)	123.9(2)
C(14)—C(16)—N(2)	124.1(2)
C(18)—C(17)—N(1)	117.0(1)
C(18)—C(17)—N(2)	117.5(2)
N(1)—C(17)—N(2)	125.6(2)
C(17)—C(18)—C(19)	120.6(2)
C(17)—C(18)—C(20)	120.6(1)
C(19)—C(18)—C(20)	118.8(2)
C(18)—C(19)—C(21)	120.9(2)
C(18)—C(20)—C(22)	120.6(2)
C(19)—C(21)—C(23)	119.8(2)
C(20)—C(22)—C(23)	119.9(2)
C(21)—C(23)—C(22)	120.0(2)
C(21)—C(23)—C(24)	118.9(1)
C(22)—C(23)—C(24)	121.1(2)
C(23)—C(24)—N(3)	178.7(2)
C(15)—N(1)—C(17)	116.2(1)
C(16)—N(2)—C(17)	116.1(2)

The molecule as a whole is not planar; the phenyl ring, the pyrimidine ring and the heptyl chain are planar within 0.01, 0.01 and 0.06 Å respectively. The cyclohexyl ring is in the chair conformation. The phenyl and pyrimidine rings make an angle of 15° (see Newman projection in Figure 2). The coupling of the pyrimidine and cyclohexane rings is illustrated in Figure 2b. The length of the molecule in the crystalline state is 23.5 Å, whereas its theoretical length is at a maximum 24 Å, indicating that the molecule is in its most extended conformation. Calculations with Sybil[9] and Insight[10] confirm this observation.

4.2 Molecular packing and liquid crystal phase

Figures 3 and 4 show the projections of the structure along [001] and [010] respectively. The molecules lie nearly extended in these planes, parallel to the *a* axis.

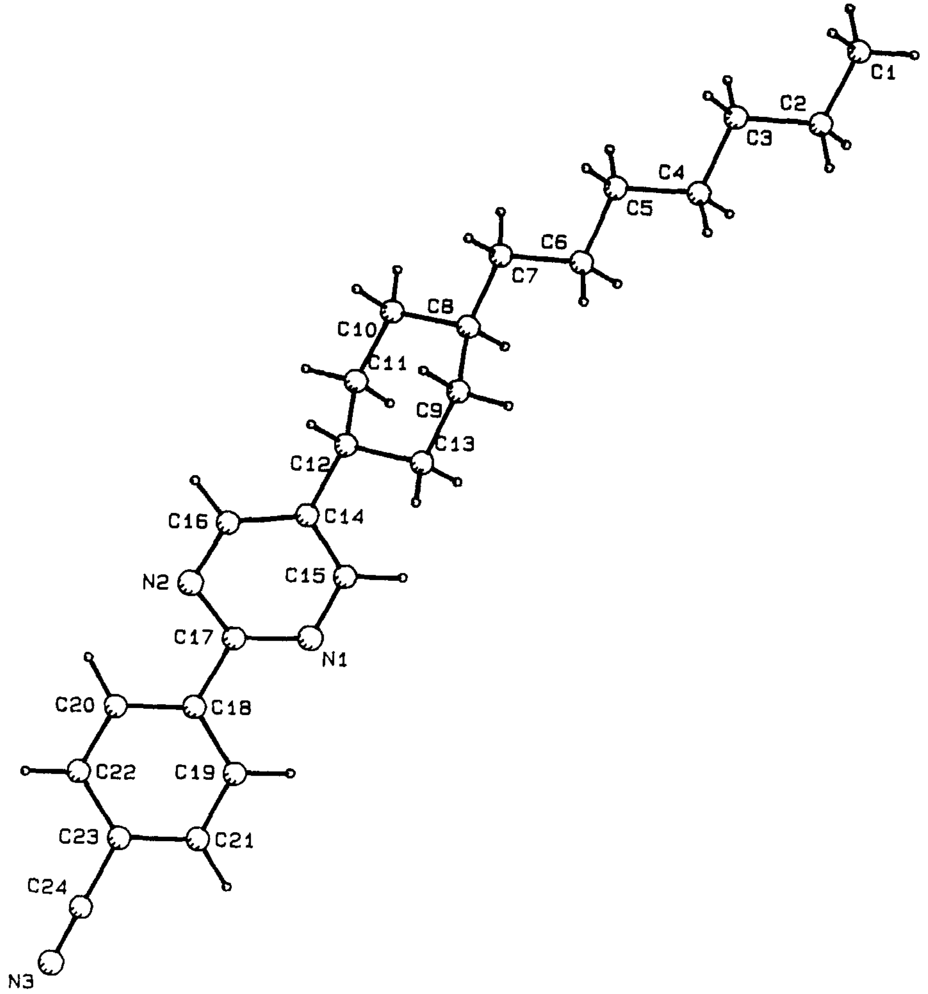

FIGURE 1 HCCPP molecule looking down the normal to the least squares plane, along with the numbering scheme.

In Figure 5, the projection of the structure along [100] has been shown; here the angle in the molecule is apparent.

The intermolecular distances smaller than 3.8 Å are given in Table VII. Most of these distances occur between the polar parts of the molecules, in particular between the molecules related through a center of symmetry (see Figures 3 and 4). These short contacts suggest associated pairs of molecules bound together by weak interactions between benzene rings, pyrimidine rings and cyano-groups, with the respective chains stretching out at both sides of the pair. The length of such a pair is approximately 28 Å from the position of C1 to and including C1′. Taking into account a Van der Waals radius for C1 of 2 Å, the total length of an associated

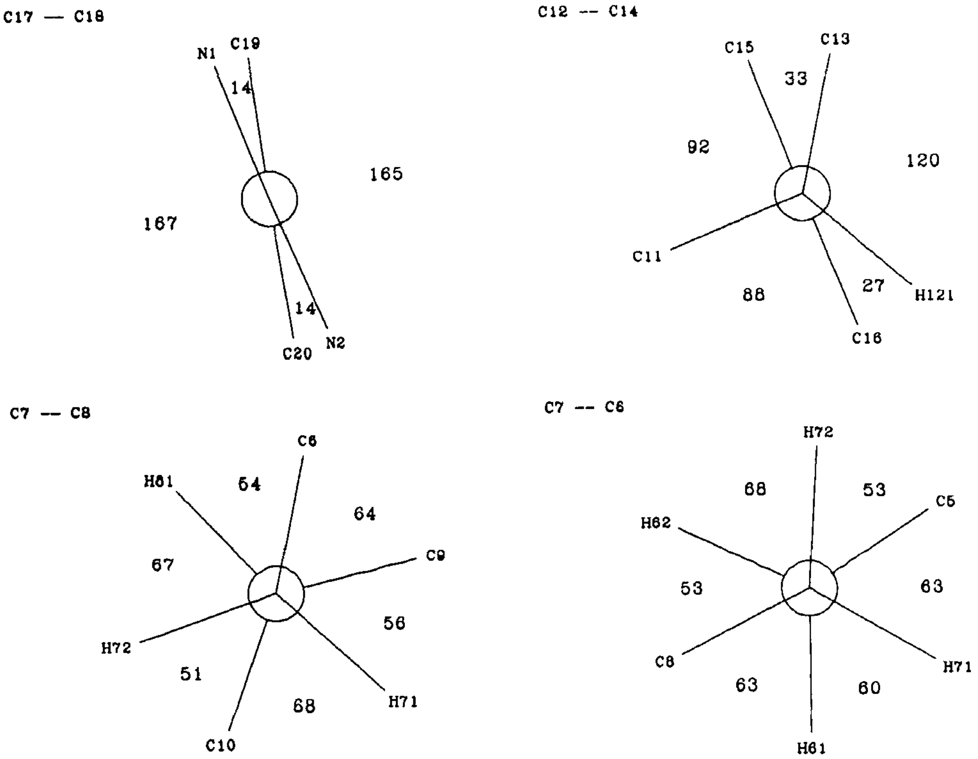

FIGURE 2 Newman projections along bonds (*a*) C17—C18, (*b*) C12—C14, (*c*) C7—C8 and (*d*) C7—C6.

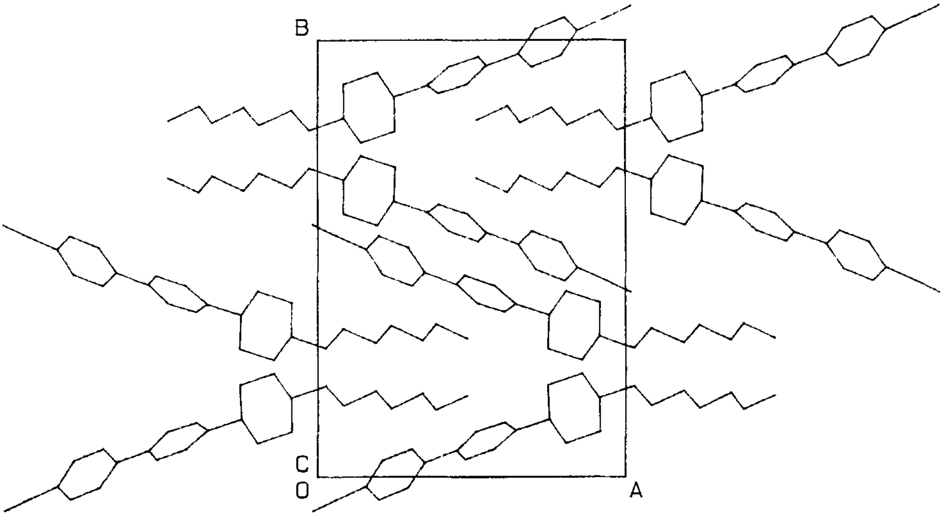

FIGURE 3 Crystal structure of HCCPP projected along [001].

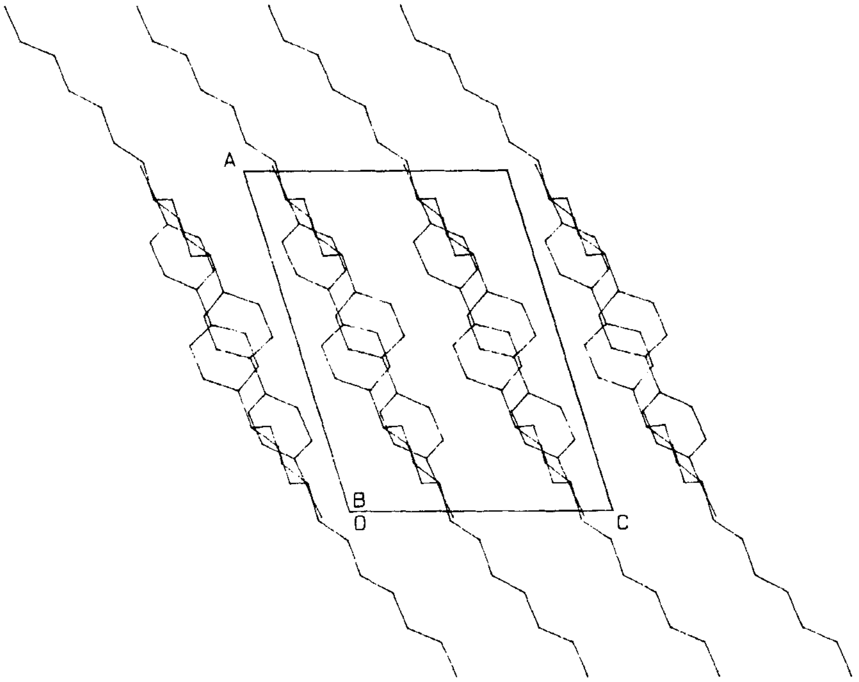

FIGURE 4 Crystal structure of HCCPP projected along [010].

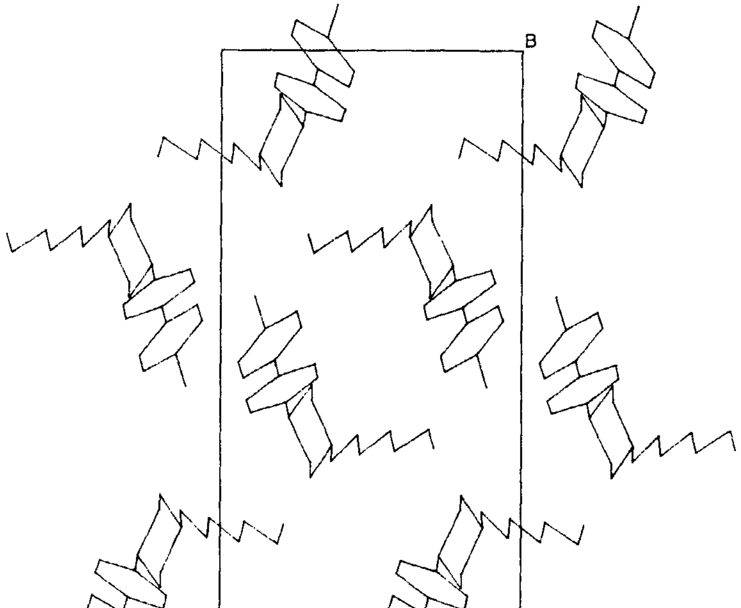

FIGURE 5 Crystal structure of HCCPP projected along [100].

TABLE VII

Intermolecular contact distances less than 3.8 Å (involving non-hydrogen atoms)

N1—C3^a	3.766	N1—C15^b	3.782
N2—C18^c	3.573	N2—C20^c	3.796
N3—N3^d	3.494	N3—C4^b	3.798
N3—C9^a	3.657	N3—C13^a	3.683
N3—C22^d	3.494	N3—C24^d	3.457
C16—C1^e	3.769	C18—C16^c	3.787
C20—C16^c	3.743	C22—C14^c	3.750
C22—C16^c	3.726	C23—C9^a	3.749
C23—C16^c	3.753	C24—C9^a	3.454
C24—C24^d	3.782		

None: x,y,z a: $x-1,y,z$ b: $1-x,\bar{y},\bar{z}$
c: $1-x,\bar{y},1-z$ d: $\bar{x},\bar{y},1-z$ e: $-1+x,1/2-y,1/2+z$

pair is 32 Å. From the X-ray diffraction photograph in the smectic phase (Figure 6), a layer thickness of 31 Å was found. This fact makes it plausible that layers in the smectic phase are built up from pairs similar to those found in the present investigation.

In liquid crystals in general the order is not complete and is described by the orientational order parameter

$$\langle P_2 \rangle = 1/2(3\langle \cos^2\theta \rangle - 1)$$

which gives the average deviation of the long molecular axes from the so called director axis, which represents the mean direction of the molecules. The order parameter in the smectic phase calculated for a magnetically aligned sample at about 84°C is found to be 0.65, giving an average value of θ to be 29°. Of course,

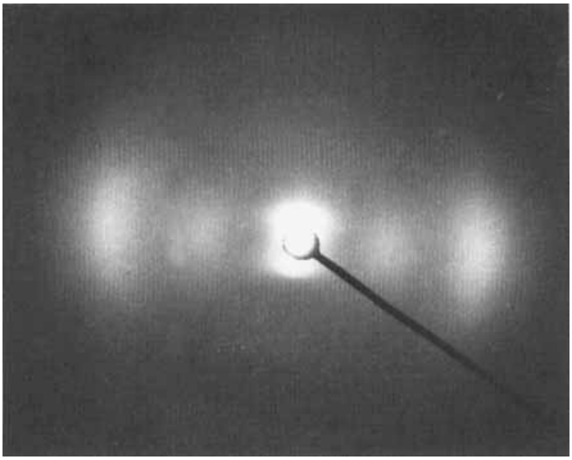

FIGURE 6 X-ray diffraction photograph of an aligned sample in the supercooled smectic phase at 75°C.

only when the order parameter is 1, will the actual layer thickness be equal to the length of the pairs. With small values of $\langle P_2 \rangle$ the layers will be thinner, although the probability character of the order of the molecules within the layer will cause the layer thickness to change in a not completely regular manner. The lack of complete order will therefore be responsible for the difference in thickness of the layers (31 Å) with respect to the length of the associated pair (32 Å).

Molecules related by centres of inversion are arranged in layers in (101) and the layers are stacked along [010]. The molecular packing therefore fulfils the geometric prerequisite for smectic phase formation on melting. Moreover, since the molecules in neighbouring layers are arranged in a herring-bone like pattern, the transformation from the crystalline to the smectic phase will be of a reconstitutive rather than a displacive type.[11]

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