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I. H. Ibrahim [a], H. Paulus [b] & W. Haase [b]
[a] Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[b] Institut für Physikalische Chemie, TH Darmstadt, Petersenstr. 20, D-6100, Darmstadt, F.R. Germany
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Structural Determination and Thermal Analysis of New Solid Modification for CCH5 Compound

I. H. IBRAHIM

Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt

and

H. PAULUS and W. HAASE

Institut für Physikalische Chemie, TH Darmstadt, Petersenstr. 20, D-6100 Darmstadt, F.R. Germany

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A new solid modification of trans,trans-4′-pentylbicyclohexyl-4-carbonitrile (CCH5) is investigated by X-ray diffraction and thermoanalytical methods. It is crystallized in an orthorhombic cell: a = 31.281 (8) Å, b = 9.477 (3) Å, c = 5.707 (2) Å, $P2_12_12_1$, Z = 4. The results illustrate that the structures of this solid modification and that of the homologous compound CCH7 are quite similar.

DSC and thermomicroscopic analysis show that the CCH5 compound possesses two stable and one metastable solid phases. It also exhibits additional metastable smectic phases.

Keywords: liquid crystals, structure, thermal analysis

INTRODUCTION

The kind of crystallized solid phase of many mesogenic compounds depends on the thermal history of such samples. This solid state polymorphism is attributed to the coexistence of metastable and stable solid phases.

From the investigation of the crystal structures of such polymorphous phases at least two main informations can be obtained: The molecular conformation and geometry in the different solid phases as well as the packing of the molecules and their distinct intermolecular distances.

The synthesis of trans,trans-4′-alkylbicyclohexyl-4-carbonitriles was reported by Eidenschink *et al.*[1,2] in 1977, they have determined the phase behaviour of CCH3, CCH5 and CCH7. All of these three compounds possess a nematic phase, whereas CCH3 and CCH5 exhibit three monotropic smectic phases and one monotropic smectic phase, respectively. In 1981, Brownsey and Leadbetter[3] have identified, by X-ray investigations, the smectic phase of CCH5 as well as the smectic phase of CCH3, which has the highest transition point, as bilayered smectic-B phases.

The crystal and molecular structures of CCH3, CCH5 and CCH7 were determined by Haase and Paulus.[4] They have found out that these structures are packed in layers in which the molecules are tilted relative to the normal on the layers.

In this work, we have carried out more detailed studies of the thermal behaviour of the CCH5 compound. Moreover, the crystal and molecular structure of a new solid modification for this compound has been determined and this can provide more information on the solid-mesophase relationship.

EXPERIMENTAL

Thermal Measurements

The CCH5 compound was provided by E. Merck, Darmstadt, Germany, and recrystallized from acetone at room temperature. The phase transition temperatures and transition enthalpies of CCH5 were determined using a differential scanning calorimeter (DSC) model Du Pont 990. Optical textures of the different phases were observed by means of a polarizing microscope (Leitz Orthoplan Pol) which is connected with a Mettler FP82 hot stage.

Crystal Structure Determination

Suitable crystals of the new solid modification of CCH5(II) were obtained by slow evaporation of the dissolved sample in an acetone solution at $-18°C$. The grown crystals were in the form of colourless needles. X-ray diffraction scans were carried out at 25°C on an automatic STOE-STADI4 four-circle diffractometer with graphite monochromatized CuK_α-radiation (λ = 1.54178 Å). The lattice dimensions were determined by a least-squares refinement of forty strong reflections. The basic crystal data of CCH5(II) are compared in Table I with those of CCH5(I).[4]

A total number of 4690 reflections were measured in the range $3° < 2\theta < 70°$ (scan $\omega:\theta$ = 1:1) leading to 2111 independent reflections (merging R = 0.0201)

TABLE I

Crystal data

	CCH5(II)	CCH5(I)[4]
Molecular formula	$C_{18}H_{31}N$	$C_{18}H_{31}N$
Molar mass ($g.mol^{-1}$)	261.45	261.45
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	31.281(8)	5.563(3)
b (Å)	9.477(3)	12.658(5)
c (Å)	5.707(2)	24.212(10)
β (°)		99.46(1)
V ($Å^3$)	1691.84	1681.74
Z	4	4
D_c ($g.cm^{-3}$)	1.026	1.033
F (000)	584	584
μ (cm^{-1})	3.68 (CuK_α)	0.29 (MoK_α)

TABLE II

Positional parameters with e.s.d.'s and equivalent temperature factors for the non-hydrogen atoms of CCH5(II)

Atom	x/a	y/b	z/c	U_{eq}
N	0.2618(1)	0.2869(5)	1.5594(10)	0.124
C(1)	0.2430(1)	0.2777(6)	1.3903(10)	0.096
C(2)	0.2168(1)	0.2628(4)	1.1825(8)	0.085
C(3)	0.1979(1)	0.1133(4)	1.1686(10)	0.093
C(4)	0.1684(1)	0.0994(4)	0.9558(9)	0.086
C(5)	0.1318(1)	0.2072(3)	0.9615(8)	0.065
C(6)	0.1522(1)	0.3567(4)	0.9671(9)	0.086
C(7)	0.1804(1)	0.3725(4)	1.1882(10)	0.089
C(8)	0.1003(1)	0.1885(3)	0.7562(8)	0.062
C(9)	0.0789(1)	0.0428(3)	0.7621(9)	0.074
C(10)	0.0474(1)	0.0232(3)	0.5595(9)	0.075
C(11)	0.0120(1)	0.1337(3)	0.5584(8)	0.065
C(12)	0.0333(1)	0.2802(3)	0.5524(8)	0.072
C(13)	0.0647(1)	0.3006(3)	0.7544(8)	0.073
C(14)	-0.0184(1)	0.1102(4)	0.3544(8)	0.072
C(15)	-0.0601(1)	0.1955(4)	0.3643(8)	0.073
C(16)	-0.0893(1)	0.1662(4)	0.1577(8)	0.077
C(17)	-0.1308(1)	0.2509(5)	0.1656(9)	0.086
C(18)	-0.1593(1)	0.2260(5)	-0.0465(9)	0.100

of which 2078 had $F_0 > 2\sigma(F_0)$. Lorentz, polarization, and absorption corrections were performed.

The structure of CCH5(II) was solved by direct methods using the program package SHELX590,[5] which led to the positions of all non-hydrogen atoms. The refinement of these atoms with isotropic temperature factors led to a value of R = 0.1587. The anisotropic refinement of all non-hydrogen atoms enhanced the value of R to 0.1340. By consideration of the anisotropic thermal factors and geometrically idealized H-positions related to their respective carbon atoms (C—H = 1.080 Å), as well as fixed isotropic thermal factors for the hydrogen atoms, the final refinement converged at R = 0.0602 (R_w = 0.0612, where $w = 1/\sigma^2(F_0)$).

The positional parameters and equivalent temperature factors for the non-hydrogen atoms are given in Table II. Lists of the observed and calculated structure factors, the anisotropic thermal parameters of all but the hydrogen atoms and the positioned hydrogen atoms are available from the authors on request.

RESULTS AND DISCUSSION

Thermal Behaviour

Figure 1 shows the DSC thermograms of CCH5 compound over the temperature range 25–100°C. The heating and cooling rates throughout the measurements were 2°C/min. The first heating cycle (Run 1), of the virgin sample as well as the recrystallized sample from acetone at room temperature, shows two endothermic transitions, whereas four exothermic peaks are observed during the first cooling

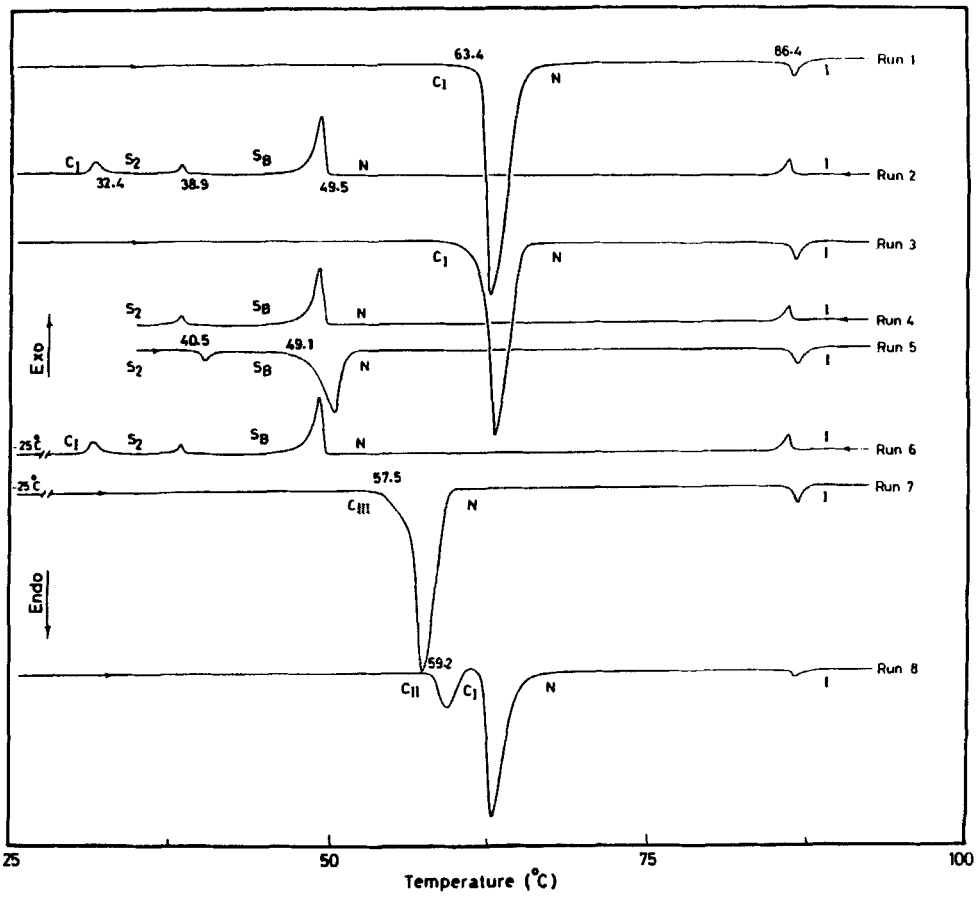

FIGURE 1 DSC thermograms of CCH5 compound. The transition temperatures are indicated on the peaks.

TABLE III

Transition enthalpies of CCH5 compound

Transition	C_{II}-C_I	C_I-N	N-I	C_{III}-N	S_2-S_1	S_1-N
Temperature(°C)	59.2±0.5	63.4±0.5	86.4±0.5	57.5±0.5	40.5±0.5	49.1±0.5
ΔH (kJ.mol^{-1})	6.1±0.3	25.6±0.9	0.5±0.1	21.8±0.7	2.6±0.3	4.2±0.2

[C] Crystalline.
[S] Smectic.
[N] Nematic.
[I] Isotropic.

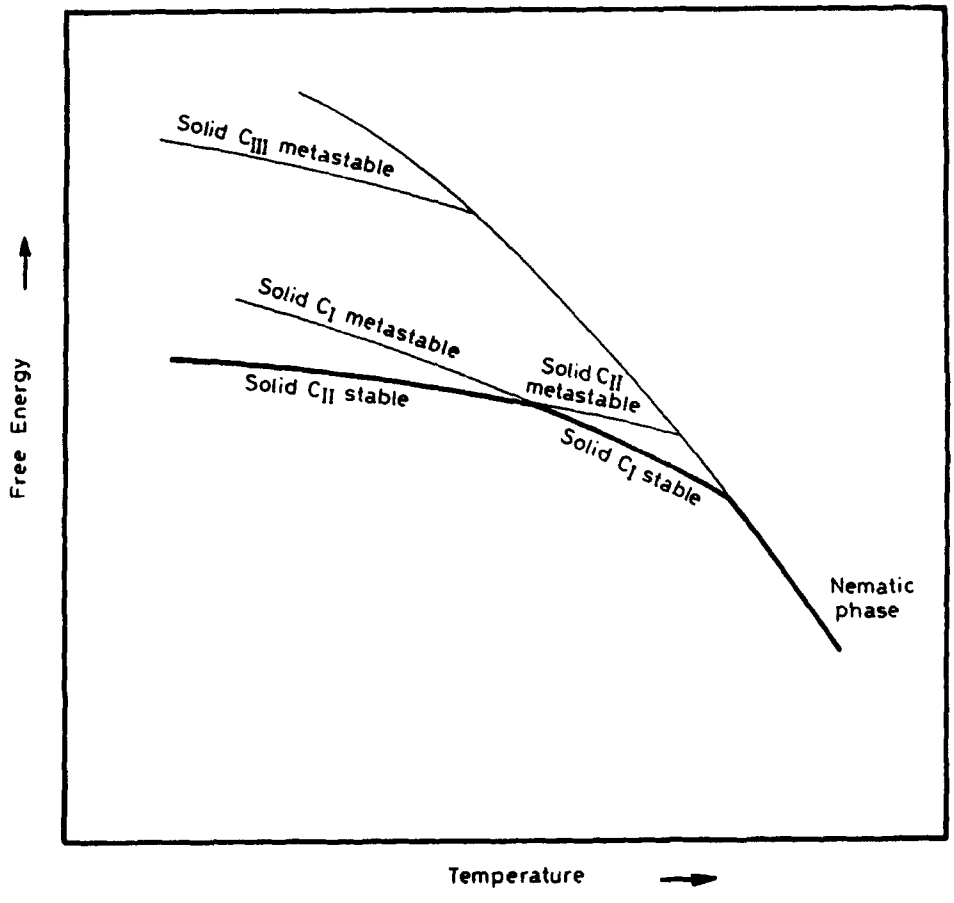

FIGURE 2 Free energy versus temperature for CCH5 compound (schematic).

cycle (Run 2). The transition temperatures are indicated on the thermograms. These values are reproducible within ±0.5°C. Run 3 shows the second heating cycle, which is quite similar to that of Run 1. The third heating cycle (Run 5) was obtained by cooling the sample from the isotropic liquid phase to 35°C (Run 4)

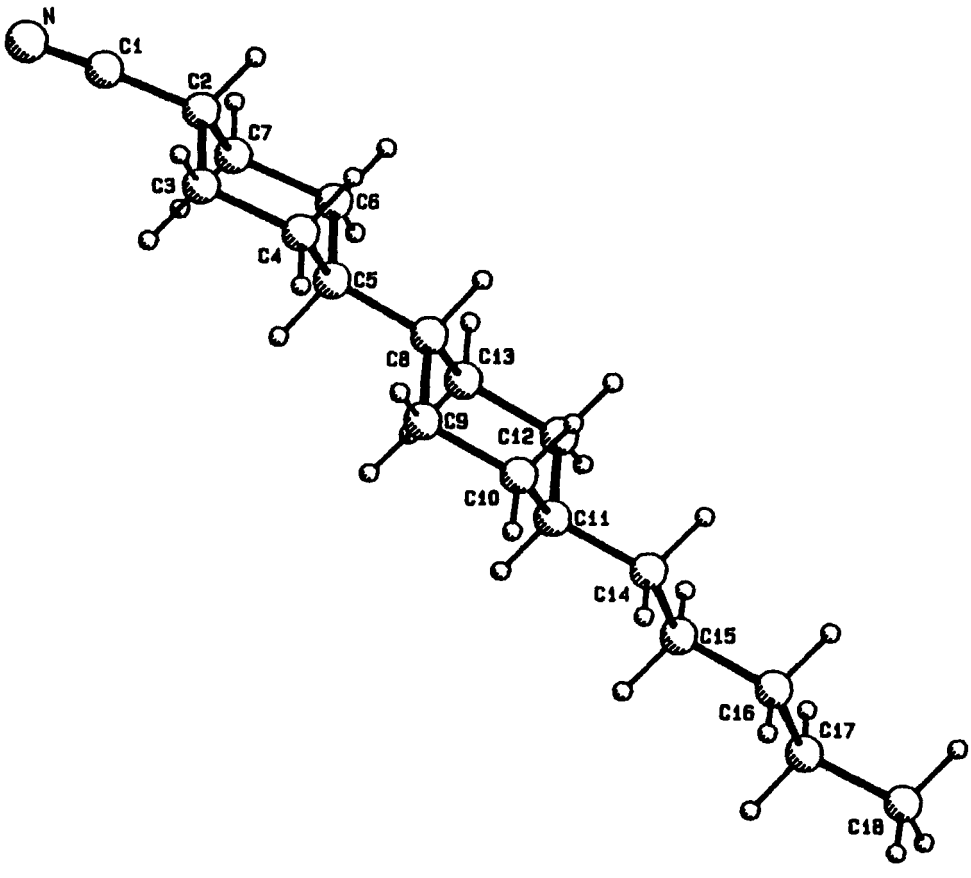

FIGURE 3 CCH5(II) molecule.

and reheating it immediately. It is concluded that the phase S_2 is a metastable phase. Run 7 (the fourth heating cycle) was obtained by rapid cooling of the sample from the isotropic liquid phase to $-25°C$ (Run 6) and reheating it immediately. This was also obtained by cooling the sample from the isotropic liquid phase to 25°C and then shocked in liquid nitrogen and heated again from 25°C. The first endothermic peak shown in Run 7 is interpreted as a metastable solid phase C_{III}-nematic transition. Run 8 shows the heating thermogram of crystals (C_{II}) obtained by slow evaporation of the acetone solution at $-18°C$. Table III summarizes the transition enthalpies of CCH5, which are found to be of normal order of magnitudes. The free energy-temperature relationship of transitions among solid phases having different thermal histories is illustrated in Figure 2.

Confirmation of some transition points was obtained by optical microscop. The mosaic texture of the metastable S_2 phase with zig-zag lines formed on cooling the mosaic texture of the monotropic smectic-B phase leads us to presume that S_2 phase is a smectic phase, probably a S_E one. Unfortunately, X-ray photographs of this phase were unachievable because the sample always crystallized.

TABLE IV

Bond lengths (Å) and angles (°) with e.s.d.'s for CCH5(II)

N - C(1)	1.133(6)	N - C(1) - C(2)	176.4(5)
C(1) - C(2)	1.448(6)	C(1) - C(2) - C(3)	110.5(4)
C(2) - C(3)	1.537(5)	C(1) - C(2) - C(7)	109.6(4)
C(3) - C(4)	1.530(6)	C(3) - C(2) - C(7)	109.7(3)
C(4) - C(5)	1.535(4)	C(2) - C(3) - C(4)	110.6(4)
C(5) - C(6)	1.554(4)	C(3) - C(4) - C(5)	112.0(3)
C(6) - C(7)	1.546(6)	C(4) - C(5) - C(6)	107.5(3)
C(7) - C(2)	1.543(5)	C(4) - C(5) - C(8)	112.6(3)
C(5) - C(8)	1.542(5)	C(6) - C(5) - C(8)	112.5(3)
C(8) - C(9)	1.535(4)	C(5) - C(6) - C(7)	109.8(3)
C(9) - C(10)	1.531(6)	C(6) - C(7) - C(2)	109.8(4)
C(10) - C(11)	1.524(4)	C(5) - C(8) - C(9)	111.5(3)
C(11) - C(12)	1.540(4)	C(5) - C(8) - C(13)	112.8(3)
C(12) - C(13)	1.528(5)	C(9) - C(8) - C(13)	107.8(2)
C(13) - C(8)	1.539(4)	C(8) - C(9) - C(10)	111.9(3)
C(11) - C(14)	1.520(6)	C(9) - C(10) - C(11)	112.8(3)
C(14) - C(15)	1.537(4)	C(10) - C(11) - C(12)	107.8(3)
C(15) - C(16)	1.516(5)	C(10) - C(11) - C(14)	110.9(3)
C(16) - C(17)	1.528(5)	C(12) - C(11) - C(14)	112.7(3)
C(17) - C(18)	1.521(6)	C(11) - C(12) - C(13)	112.0(3)
		C(12) - C(13) - C(8)	112.5(3)
		C(11) - C(14) - C(15)	115.2(3)
		C(14) - C(15) - C(16)	112.7(3)
		C(15) - C(16) - C(17)	113.1(3)
		C(16) - C(17) - C(18)	113.1(4)

Molecular Structure

The molecular structure of CCH5(II) is shown in Figure 3. CCH5 in the solid II modification having a chair conformation of the cyclohexyl rings which are substituted in the equatorial positions. It also shows that the alkyl chain is completely extended in the trans-conformation. Thus, CCH5(II) molecules present the same structural features as those of CCH5(I), CCH3 and CCH7.[4] The molecular length of CCH5(II) is 17.60 Å, for the distance N . . . H(181) including the covalent radii of N and H atoms (the crystallographic H(181)-position is: x/a = −0.1872, y/b = 0.2928, and z/c = −0.0384). The corresponding value for CCH5(I)[4] is 17.52 Å.

The bond lengths and angles for CCH5(II) are given in Table IV. All these values are found to be of normal order of magnitudes as compared with their corresponding values for CCH's[4] and CCN's,[6] excluding those of N–C(1), C(1)–C(2) and N–C(1)–C(2) for CCH7.[4] The dihedral angle between the planes (C_3,

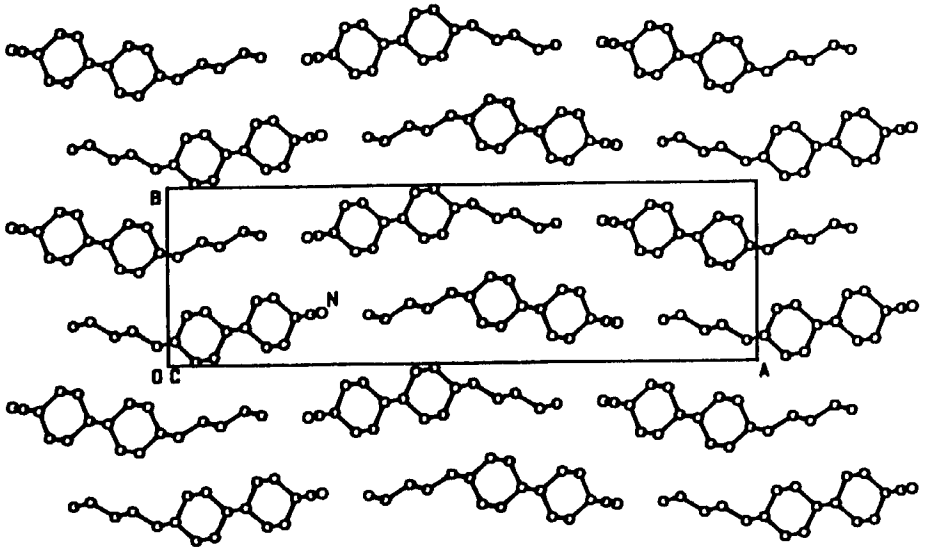

FIGURE 4 CCH5(II), viewed along the c-axis.

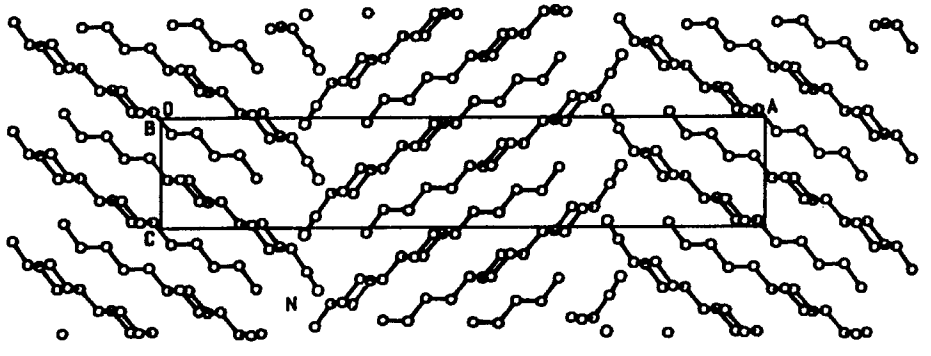

FIGURE 5 CCH5(II), viewed along the b-axis.

C_4, C_6, C_7) and (C_9, C_{10}, C_{12}, C_{13}) is 5.67° (see Figure 3). This indicates that the two cyclohexyl rings are nearly coplanar, as that in cases of CCH's[4] and CCN46.[6]

Molecular Packing

The packing of CCH5(II) molecules in the solid crystalline state is shown in Figures 4 and 5. The molecules are packed parallel to the long crystallographic a-axis, where the molecular long axes are tilted to that axis with an angle of ~27°. No overlapping of any molecules or atoms occurs along the short crystallographic c-axis as that in the case of CCH5(I)[4] (along the a-axis).

Figures 4 and 5 reveal the similarity of the arrangements of CCH5(II) and CCH7[4] molecules. Two types of layers are discussed, the first is perpendicular to the crystallographic 2_1-axis along the a-axis. The molecules in this type of layers are

arranged in the head-to-tail alternation. These layers have a thickness of a/2 (=15.64 Å) which is equal to the length of the molecule (17.60 Å) multiplied by the cosine of the tilt angle (~27°) with the a-axis. The second type of layers are perpendicular to the crystallographic 2_1-axis, which in turn is parallel to the b-axis having a thickness of b/2. In this type of layers, the long axes of the molecules describe a herringbone-like packing.

Moreover, the cyano groups form an infinite stacking around the 2_1-axis parallel to the crystallographic c-axis. Cyano-cyano contacts are not found. The calculated intermolecular distance N . . . N′ is 5.01 Å, where $x' = 1/2 - x$, $y' = -y$ and $z' = 1/2 + z$. It is interested to note that the distance between the cyano dipoles in CCH5(II) would not be compared in the same manner as that in CCH5(I).[4]

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