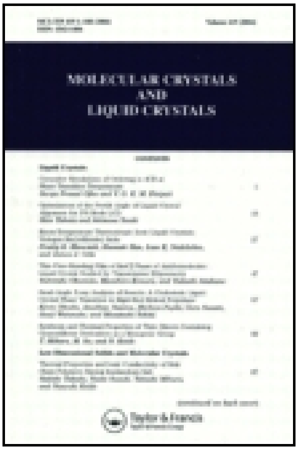

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The Crystal and Molecular Structures of Three Homologous, Mesogenic Trans, Trans-4'-Alkylbicyclohexyl-4-carbonitriles (Cyclohexylcyclohexanes, CCHs)

W. Haase [a] & H. Paulus [a]

[a] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraβe 20, D-6100, DARMSTADT, FRG

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The Crystal and Molecular Structures of Three Homologous, Mesogenic Trans,Trans-4′-Alkylbicyclohexyl-4-carbonitriles (Cyclohexylcyclohexanes, CCHs)

W. HAASE and H. PAULUS

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D–6100 DARMSTADT, FRG

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The crystal and molecular structures of three homologous *trans, trans*-4′-alkylbicyclohexyl-4-carbonitriles (Cyclohexylcyclohexanes, CCHs) with the following alkyl groups: propyl (CCH3); pentyl (CCH5); heptyl (CCH7) are described. All three compounds exhibit liquid crystalline phases at higher temperatures. Both cyclohexyl rings assume the chair conformation and the alkyl groups adopt the *trans*-conformation.

In the crystalline state two kinds of layer structure are discussed. In the first type, the long axes of the molecules are tilted to the normal of the layer. In the second kind of structure, the longest molecular axis lies within the layer. The role of the cyano dipoles is discussed. In CCH3 a dipole-dipole interaction in the crystal is indicated. The packing in the solid crystalline states of the three compounds is compared with the known models, derived from X-ray data, for the liquid crystalline state.

CCH7: $a = 33.729(10)$ Å, $b = 9.641(5)$ Å, $c = 5.812(4)$ Å; $P2_12_12_1$;
$R = 0.115$ for 1171 non-zero reflections.

CCH5: $a = 5.563(3)$ Å, $b = 12.658(5)$ Å, $c = 24.212(10)$ Å,
$\beta = 99.46(1)°$; $P2_1/c$; $R = 0.070$ for 1049 non-zero reflections.

CCH3: $a = 13.187(6)$ Å, $b = 9.579(5)$ Å, $c = 6.205(4)$ Å,
$\alpha = 106.31(2)°$, $\beta = 87.33(2)°$, $\gamma = 100.97(2)°$; $R = 0.054$ for 1396 non-zero reflections.

INTRODUCTION

In 1977, Eidenschink *et al.*,[1,2] reported on new liquid crystalline carbocyclic compounds—the *trans, trans*-4′-alkylbicyclohexyl-4-carbonitriles

(Cyclohexyclohexanes, CCHs). Data relating to the crystal and molecular structures have been briefly presented[3] previously for three members of this homologous series (alkyl = propyl (CCH3), pentyl (CCH5), heptyl (CCH7)). We are now able to give complete structural data for these substances.

Whereas, CCH3 and CCH5 exhibit three smectic phases and one smectic phase respectively, CCH7 only possesses a nematic phase. As a result of X-ray investigations, Brownsey and Leadbetter[4] recently indexed the sole smectic phase of CCH5 as well as the smectic phase of CCH3 with the highest transition point as bilayered smectic B-phases with an interdigitation of alkyl tails and cyano end groups. This peculiar structure is assumed to be due to a special combination of dipole-dipole attractions and steric factors. For the nematic phase of the compounds in question, the authors suggest a dimer formation, as a consequence of the greater molecular lengths in the nematic state as compared with the length of the monomers. Thus, with the above mentioned data in mind, information on the molecular structure, and additional knowledge of the crystal packing, would certainly help us to gain further insight into the relationship between the solid crystalline state and the liquid crystalline state.

EXPERIMENTAL

Crystal data

Crystals of all compounds for X-ray examination were obtained by means of slow evaporation of a water-acetone mixture. Suitable crystals for X-ray investigations had a needle-like habit with the plane perpendicular to the axis of the needles being 0.1 mm × 0.2 mm (CCH3), 0.05 mm × 0.05 mm (CCH5) and 0.05 mm × 0.2 mm (CCH7). Their lattice dimensions were determined by a least squares refinement of the setting angles for a number of strong reflections on an automatic STOE-4-circle-diffractometer. The X-ray source used was Mo K_α. The selected space groups are based on the reflections which are systematically absent (CCH5, CCH7). The centrosymmetric triclinic space group (CCH3) was evaluated, based on the intensity distribution test. The crystal data for the three compounds investigated are given in Table I.

The reflection intensities used for the determination were measured with the STOE-4-circle-diffractometer.

Structure determination and refinement

The structures of the three compounds were solved by direct methods. Lorentz and polarization corrections were performed.

TABLE I

Crystal data

	CCH7	CCH5	CCH3
Molecular formula	$C_{20}H_{35}N$	$C_{18}H_{31}N$	$C_{16}H_{27}N$
Molar mass [g/mol]	289.51	261.45	233.40
$F(000)$	648	584	260
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a[Å]	33.729 (10)	5.563 (3)	13.187 (6)
b[Å]	9.641 (5)	12.658 (5)	9.579 (5)
c[Å]	5.812 (4)	24.212 (10)	6.205 (4)
α[°]			106.31 (2)
β[°]		99.46 (1)	87.33 (2)
γ[°]			100.97 (2)
V_c[Å^3]	1889.95	1681.74	738.50
D_c[g · cm^{-3}]	1.017	1.033	1.050
Z	4	4	2
Independent reflections	1957	1576	1935
Reflections for calculation	1171	1049	1396
(Mo K_α)	0.29	0.29	0.30

The best E-map of CCH7 depicts the whole molecule. The isotropic refinement with 1171 non-zero reflections ($F > 2\delta(F)$) leads to $R = 0.16$. At this stage, the hydrogen atom locations were calculated using a C—H bond length of 1.08 Å in geometrically relevant positions. Their positions were shifted by the following refinement, but only in conjunction with the appropriate carbon atoms. The refinement procedure with anisotropic parameters and fixed isotropic thermal parameters for the H-atoms resulted in $R = 0.115$ ($R_W = 0.075$).

The second best E-map of CCH5 shows both cyclohexyl rings of the compound followed by the carbon atom at the end of each ring. The non-fixed carbon atoms were solved by Fourier synthesis. The nitrogen atom was obtained from the difference Fourier map. The isotropic refinement at this stage was $R = 0.23$ and the anisotropic refinement amounted to $R = 0.18$. The positions of the hydrogen atoms were calculated analogously to those of CCH7. The refinement of all atomic positions and the anisotropic thermal coefficients of all non-hydrogen atoms lead to $R = 0.070$ ($R_W = 0.050$) for 1049 nonzero reflections.

The E-map of CCH3 shows an arrangement of equal-sided triangles. As a result of this, the orientation of the molecule in the elementary cell was distinguishable. The material did not permit an exact positioning of the molecules. The central unit of molecule consisting of 14 carbon atoms (2 rings and the adjacent carbon atoms) was shifted around in the elementary cell and structure factor calculations of all positions were performed. One of these models leads to $R = 0.43$. A Fourier synthesis of this model permitted the localization of all the unknown non-hydrogen positions. The isotropic refinement resulted in $R = 0.18$ and the anisotropic one in $R = 0.14$. The refinement was performed in the same manner as for CCH5. With the calculated hydrogen positions, one obtains $R = 0.054$ ($R_W = 0.047$) for 1396 non-zero reflections.

The atomic parameters for the three compounds are given in Table II for all the non-hydrogen atoms and in Table III for the hydrogen atoms. A list of observed and calculated structure factors is available from the authors on request.

RESULTS AND DISCUSSION

Molecular Structures

The molecular structure of CCH5 is presented in Figure 1 as a projection perpendicular to the plane of the rings. One can clearly recognize that the cyclohexyl rings are substituted in the equatorial positions. Further the alkyl chain is completely extended in the *trans*-conformation. The homologous compounds CCH3 and CCH7 exhibit the same structural features as CCH5. Figure 2, for CCH3, illustrates the chair conformation of the cyclohexyl units. In Figure 3, CCH7 is depicted as a result of a projection of the molecule parallel to the plane of the rings. This figure permits one to visualize the dimensional extension of the molecule in question. Thus one finds for CCH7 a molecular length of 19.33 Å for the distance N...H(201). When the coralent radii (N = 0.55 Å, H = 0.30 Å) are considered the length amounts to approximately 20.18 Å.

The analogous data for CCH5 and CCH3 are (N...H(182)) 16.67 Å, 17.52 Å and (N...H(162) 14.28 Å, 15.13 Å, respectively. The consecutive decrease of the molecular length in the series CCH7, CCH5 and CCH3 is equivalent to a shorter distance of approx. 2.53 Å between every second carbon atom in the alkyl chain. The same molecules possess a width (within the plane of the rings) of approx. 4.5 Å and a thickness (perpendicular to the plane of the rings of approx. 3.5 Å.

In Table IV the bond lengths between all non-hydrogen atoms are given. The corresponding bond angles are to be found in Table V. It is obvious that the standard deviations of all bond lengths and bond angles of CCH7 are somewhat greater than those of CCH5 and CCH3, these being dependent upon the accuracy of the refinement.

TABLE II

Atomic parameters for the non-hydrogen atoms.
(The first line for every atom stands for CCH7, the second for CCH5 and the third for CCH3; U_{ij} is to be read as $U_{ij} \cdot 10^3$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N	0.2673(3)	0.130(2)	−0.578(3)	58(10)	187(11)	146(16)	−90(13)	−13(9)	−30(9)
	1.1661(8)	−0.2725(4)	0.2462(2)	108(4)	124(4)	122(4)	18(3)	− 1(3)	43(3)
	0.3909(2)	−0.0079(2)	−0.6631(4)	86(2)	106(2)	62(2)	− 5(1)	− 7(1)	35(1)
C(1)	0.2860(4)	0.126(2)	−0.443(3)	30(10)	112(12)	160(23)	−41(16)	−17(11)	−35(9)
	0.9919(10)	−0.2313(4)	0.2277(2)	90(5)	78(4)	77(4)	5(3)	8(4)	12(4)
	0.3801(2)	0.0380(3)	−0.4760(5)	52(2)	64(2)	75(2)	8(2)	− 7(2)	19(1)
C(2)	0.3076(3)	0.098(1)	−0.216(2)	68(9)	75(8)	61(12)	− 3(9)	−16(8)	−20(8)
	0.7697(8)	−0.1740(4)	0.2029(2)	55(4)	68(4)	74(4)	8(3)	16(3)	3(3)
	0.3628(2)	0.1021(2)	−0.2330(4)	59(2)	52(2)	56(2)	11(1)	− 4(1)	15(1)
C(3)	0.3374(3)	0.215(1)	−0.182(2)	76(11)	101(10)	90(16)	−13(12)	4(9)	9(8)
	0.7623(9)	−0.1625(4)	0.1402(2)	77(4)	67(4)	68(4)	− 0(3)	11(3)	9(3)
	0.2486(2)	0.1102(3)	−0.1916(4)	57(2)	54(2)	60(2)	11(1)	− 4(1)	4(1)
C(4)	0.3645(3)	0.196(1)	0.022(2)	69(9)	62(8)	82(15)	− 9(10)	2(9)	− 9(7)
	0.5459(9)	−0.0968(4)	0.1126(2)	79(4)	67(4)	51(3)	− 5(3)	10(3)	6(3)
	0.2291(2)	0.1846(3)	0.0531(4)	50(1)	57(2)	57(2)	12(1)	− 0(1)	3(1)
C(5)	0.3847(3)	0.053(1)	0.033(3)	49(9)	52(7)	152(17)	−40(11)	23(9)	−25(8)
	0.5299(7)	0.0103(4)	0.1405(2)	44(3)	61(4)	57(3)	− 0(3)	13(2)	− 9(2)
	0.2948(1)	0.3387(2)	0.1412(3)	43(1)	48(1)	48(1)	16(1)	− 2(1)	6(1)
C(6)	0.3532(3)	−0.063(1)	0.009(2)	81(10)	84(9)	64(13)	−53(10)	26(8)	− 9(8)
	0.5328(9)	−0.0044(4)	0.2022(2)	71(4)	75(4)	59(4)	− 7(3)	14(3)	10(3)
	0.4082(2)	0.3272(3)	0.0972(4)	46(1)	57(2)	57(2)	10(1)	− 0(1)	5(1)
C(7)	0.3281(3)	−0.043(1)	−0.209(2)	73(10)	62(8)	63(12)	−10(10)	10(8)	−28(7)
	0.7519(9)	−0.0663(4)	0.2304(2)	76(4)	84(4)	60(3)	− 2(3)	1(3)	10(3)
	0.4307(2)	0.2549(3)	−0.1467(4)	50(1)	61(2)	62(2)	14(1)	5(1)	10(1)
C(8)	0.4131(3)	0.035(1)	0.235(2)	47(8)	62(7)	85(11)	− 5(10)	14(8)	− 5(6)
	0.3113(7)	0.0769(3)	0.1119(2)	49(3)	57(3)	54(3)	− 3(2)	17(2)	− 5(2)
	0.2728(2)	0.4129(2)	0.3867(3)	45(1)	49(2)	51(2)	19(1)	− 3(1)	5(1)

TABLE II (Continued)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(9)	0.4450(3)	0.140(1)	0.249(2)	42(8)	43(6)	123(16)	17(10)	5(9)	1(6)
	0.3040(9)	0.0896(4)	0.0497(2)	77(4)	67(4)	64(4)	− 9(3)	10(4)	18(3)
	0.1589(2)	0.4229(3)	0.4276(4)	45(2)	64(2)	55(2)	9(1)	− 1(1)	− 0(1)
C(10)	0.4743(3)	0.121(1)	0.443(3)	58(9)	54(7)	106(16)	−13(10)	17(9)	3(6)
	0.0922(9)	0.1567(4)	0.0219(2)	75(4)	69(4)	61(3)	−11(3)	3(3)	2(3)
	0.1354(2)	0.5023(3)	0.6670(4)	42(1)	64(2)	54(2)	10(1)	1(1)	3(1)
C(11)	0.4922(3)	−0.022(1)	0.455(2)	86(9)	53(6)	14(7)	12(7)	28(6)	− 8(6)
	0.0848(7)	0.2650(4)	0.0477(2)	46(3)	56(4)	68(4)	− 1(3)	12(3)	− 3(2)
	0.2005(2)	0.6563(2)	0.7494(4)	47(1)	53(2)	47(2)	14(1)	− 2(1)	9(1)
C(12)	0.4596(3)	−0.130(1)	0.449(2)	68(9)	66(8)	77(13)	−13(10)	− 3(9)	16(7)
	0.0894(9)	0.2526(4)	0.1103(2)	81(4)	71(4)	73(4)	−10(3)	9(3)	11(3)
	0.3138(2)	0.6449(3)	0.7159(4)	48(2)	55(2)	56(2)	8(1)	− 3(1)	2(1)
C(13)	0.4307(3)	−0.110(1)	0.251(3)	72(9)	36(7)	119(16)	6(10)	22(9)	−11(6)
	0.3032(9)	0.1853(4)	0.1383(2)	78(4)	73(4)	63(3)	− 8(3)	12(4)	21(3)
	0.3387(2)	0.5667(3)	0.4762(4)	42(1)	59(2)	62(2)	15(1)	− 1(1)	3(1)
C(14)	0.5196(3)	−0.047(1)	0.664(2)	76(10)	67(7)	89(13)	35(10)	2(8)	13(7)
	−0.1316(8)	0.3314(4)	0.0208(2)	54(3)	73(4)	68(4)	6(3)	23(3)	4(3)
	0.1779(2)	0.7345(3)	0.9911(4)	57(2)	64(2)	55(2)	10(1)	− 8(1)	7(1)
C(15)	0.5576(3)	0.036(1)	0.668(3)	73(11)	43(7)	138(16)	−37(11)	36(10)	− 7(7)
	−0.1498(9)	0.3570(4)	−0.0405(4)	61(4)	71(4)	68(4)	2(3)	19(3)	3(3)
	0.0713(2)	0.7719(3)	1.0355(4)	57(2)	89(2)	60(2)	4(2)	2(2)	15(2)
C(16)	0.5837(3)	0.006(1)	0.870(3)	56(10)	80(9)	118(14)	12(10)	−28(10)	16(7)
	−0.3721(9)	0.4211(4)	−0.0645(2)	66(4)	71(4)	75(4)	2(3)	8(3)	10(3)
	0.0537(2)	0.8542(3)	1.2753(4)	75(2)	88(2)	66(2)	− 1(2)	15(2)	9(2)
C(17)	0.6229(3)	0.082(1)	0.874(3)	63(10)	68(8)	115(15)	15(10)	33(9)	17(7)
	−0.4036(9)	0.4423(4)	−0.1260(2)	70(4)	101(5)	69(4)	12(3)	21(3)	15(4)
C(18)	0.6478(3)	0.042(1)	1.084(2)	107(13)	59(8)	76(12)	30(10)	−22(10)	11(8)
	−0.6314(9)	0.5017(4)	−0.1494(2)	89(4)	126(5)	69(4)	20(3)	17(3)	26(4)
C(19)	0.6878(4)	0.111(1)	1.088(3)	92(12)	95(9)	116(16)	−32(13)	2(11)	3(9)
C(20)	0.7137(4)	0.062(2)	1.284(3)	79(13)	169(14)	196(25)	−43(18)	−34(13)	24(10)

TABLE III

Atomic parameters for the hydrogen atoms. (The first line for every atom stands for CCH7, the second for CCH5 and the third for CCH3)

	x	y	z	$U \cdot 10^2$
H(2)	0.2862	0.097	−0.077	7
	0.644(6)	−0.216(3)	0.209(2)	7
	0.383(1)	0.036(2)	−0.162(3)	6
H(31)	0.3213	0.311	−0.160	9
	0.762(6)	−0.236(3)	0.121(1)	7
	0.204(1)	0.006(2)	−0.240(3)	6
H(32)	0.3555	0.222	−0.335	7
	0.892(7)	−0.126(3)	0.137(2)	7
	0.230(1)	0.170(2)	−0.280(3)	6
H(41)	0.3873	0.274	0.016	7
	0.407(7)	−0.140(3)	0.118(2)	7
	0.244(1)	0.122(2)	0.144(3)	5
H(42)	0.3471	0.209	0.177	7
	0.541(7)	−0.089(3)	0.072(1)	7
	0.152(1)	0.188(2)	0.071(3)	5
H(5)	0.4045	0.045	−0.113	7
	0.674(6)	0.048(3)	0.134(1)	6
	0.275(1)	0.402(2)	0.050(3)	5
H(61)	0.3341	−0.061	0.158	8
	0.391(6)	−0.045(3)	0.208(2)	7
	0.453(1)	0.427(2)	0.148(3)	6
H(62)	0.3681	−0.162	−0.000	8
	0.527(6)	0.063(3)	0.223(1)	7
	0.427(2)	0.268(2)	0.184(3)	6
H(71)	0.3057	−0.123	−0.214	7
	0.751(7)	−0.078(3)	0.269(1)	7
	0.504(2)	0.245(2)	−0.175(3)	6
H(72)	0.3470	−0.053	−0.359	7
	0.897(6)	−0.031(3)	0.228(2)	7
	0.419(2)	0.317(2)	−0.235(3)	6
H(8)	0.3941	0.051	0.383	7
	0.169(6)	0.042(3)	0.119(1)	6
	0.290(1)	0.354(2)	0.468(3)	5
H(91)	0.4614	0.138	0.089	7
	0.308(7)	0.026(3)	0.029(1)	7
	0.115(1)	0.327(2)	0.382(3)	6
H(92)	0.4313	0.241	0.269	7
	0.447(7)	0.121(3)	0.046(2)	7
	0.141(2)	0.479(2)	0.326(3)	6
H(101)	0.4591	0.140	0.604	7
	−0.049(7)	0.123(3)	0.023(2)	7
	0.149(1)	0.443(2)	0.770(3)	6
H(102)	0.4979	0.195	0.423	7
	0.093(7)	0.163(3)	−0.017(1)	7
	0.060(2)	0.509(2)	0.683(3)	6

Table III (Continued)

	x	y	z	$U \cdot 10^2$
H(11)	0.5177	−0.031	0.306	7
	0.229(6)	0.306(3)	0.042(1)	7
	0.182(2)	0.715(2)	0.655(3)	6
H(121)	0.4432	−0.124	0.609	7
	0.114(7)	0.319(3)	0.124(2)	7
	0.357(1)	0.745(2)	0.764(3)	6
H(122)	0.4730	−0.231	0.434	7
	−0.059(7)	0.221(3)	0.113(2)	7
	0.330(2)	0.587(2)	0.813(3)	6
H(131)	0.4463	−0.132	0.093	7
	0.286(7)	0.178(3)	0.178(1)	7
	0.326(2)	0.623(2)	0.382(3)	6
H(132)	0.4067	−0.184	0.271	7
	0.438(7)	0.217(3)	0.137(2)	7
	0.411(2)	0.560(2)	0.462(3)	6
H(141)	0.5274	−0.155	0.667	8
	−0.150(6)	0.401(3)	0.040(1)	7
	0.229(2)	0.825(2)	1.042(3)	6
H(142)	0.5031	−0.022	0.818	8
	−0.268(7)	0.295(3)	0.025(2)	7
	0.190(2)	0.675(2)	1.084(3)	6
H(151)	0.5500	0.145	0.673	8
	−0.139(6)	0.298(3)	−0.066(1)	7
	0.020(2)	0.686(2)	0.988(4)	8
H(152)	0.5739	0.014	0.573	8
	−0.014(7)	0.398(3)	−0.045(2)	7
	0.059(2)	0.829(2)	0.938(4)	8
H(161)	0.5676	0.032	1.024	8
	−0.504(7)	0.378(3)	−0.060(2)	7
	0.0660(2)	0.787(2)	1.382(4)	9
H(162)	0.5899	−0.104	0.869	8
	−0.373(7)	0.489(3)	−0.045(1)	7
	−0.0240(2)	0.878(2)	1.301(4)	9
H(163)[+]	0.109(2)	0.957(2)	1.317(4)	9
H(171)	0.6392	0.057	0.719	8
	−0.391(7)	0.371(3)	−0.146(2)	8
H(172)	0.6171	0.192	0.879	8
	−0.261(7)	0.480(3)	−0.134(2)	8
H(181)	0.6519	−0.069	1.083	8
	−0.783(7)	0.456(3)	−0.140(3)	9
H(182)	0.6319	0.072	1.237	8
	−0.646(7)	0.510(3)	−0.194(3)	9
H(183)[†]	0.634(7)	0.579(3)	−0.131(3)	9
H(191)	0.7027	0.088	0.928	10
H(192)	0.6837	0.222	1.104	10
H(201)	0.7435	0.103	1.273	12
H(202)	0.7148	−0.050	1.284	12
H(203)	0.7000	0.097	1.441	12

[+] only CCH3

[†] only CCH5

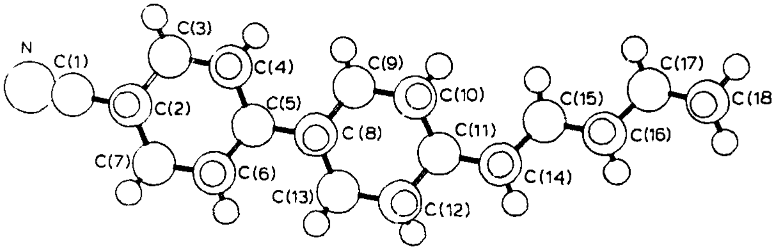

FIGURE 1 CCH5-molecule projected perpendicular to the plane through the atoms C(2), C(4) and C(6).

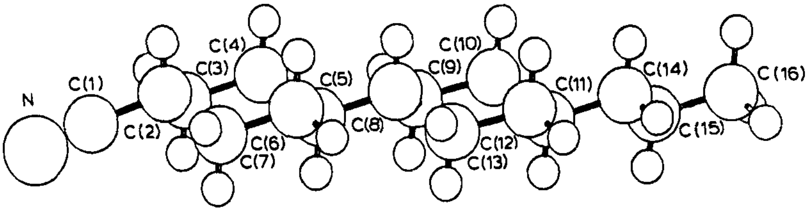

FIGURE 2 CCH3-molecule projected along the crystallographic *x*-axis.

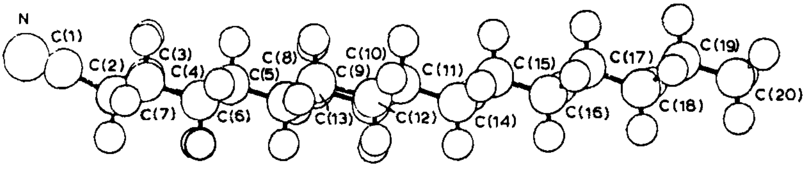

FIGURE 3 CCH7-molecule projected along the line C(4) to C(6).

Nonetheless, all the bond lengths and bond angles of the three compounds referred to here are equivalent, when one considers the appropriate standard deviations, as well as excluding the N—C(1) and C(1)—C(2) bond lengths of CCH7. Likewise the N—C(1)—C(2) bond angle of this compound has to be neglected.

We believe that the relatively high thermal parameters of the atoms and C(7) in CCH7 as well as their strong anisotropic components are to be considered as the reasons for the un-normal calculated values.

The reliable N—C(1) distances and the bond angles N—C(1)—C(2) of CCH5 and CCH3 are normal and compare well with other recent results (e.g., *p*-[*p*′-ethoxybenzylideneamino]benzonitrile[5]: N—C = 1.148(3) Å, N—C—C = 179.4(10)°; *p*-cyanobenzoic acid[6]: N—C = 1.149(8) Å, N—C—C = 176.4(5)°; 4-cyanophenyl-4-n-pentylbenzoate[7]: N—C = 1.140(9) and 1.138(10) Å, N—C—C = 177.9(7) and 178.7(8)°,

TABLE IV

Bond lengths (Å) and their standard deviations.

	CCH7	CCH5	CCH3
N—C(1)	1.009(22)	1.127(7)	1.133(3)
C(1)—C(2)	1.532(22)	1.474(7)	1.485(3)
C(2)—C(3)	1.523(16)	1.519(7)	1.529(3)
C(3)—C(4)	1.513(18)	1.524(7)	1.519(3)
C(4)—C(5)	1.539(14)	1.523(7)	1.527(3)
C(5)—C(6)	1.544(14)	1.504(6)	1.527(3)
C(6)—C(7)	1.538(16)	1.514(7)	1.518(3)
C(7)—C(2)	1.529(15)	1.527(7)	1.528(3)
C(5)—C(8)	1.526(18)	1.546(6)	1.530(3)
C(8)—C(9)	1.482(13)	1.508(7)	1.528(3)
C(9)—C(10)	1.513(17)	1.518(7)	1.514(3)
C(10)—C(11)	1.501(13)	1.510(7)	1.520(3)
C(11)—C(12)	1.516(13)	1.519(7)	1.519(3)
C(12)—C(13)	1.520(8)	1.529(7)	1.518(3)
C(13)—C(8)	1.524(13)	1.517(7)	1.527(3)
C(11)—C(14)	1.544(16)	1.525(6)	1.521(3)
C(14)—C(15)	1.509(14)	1.505(7)	1.510(4)
C(15)—C(16)	1.494(19)	1.514(7)	1.506(3)
C(16)—C(17)	1.515(15)	1.494(8)	
C(17)—C(18)	1.533(19)	1.502(7)	
C(18)—C(19)	1.503(16)		
C(19)—C(20)	1.510(21)		

BCH5CH[8] (a disubstituted biphenyl cyclohexane with R = C_5H_{11} and R′ = CN): N—C = 1.139(5) Å, N—C—C = 178.7(4)°), especially with respect to the virtual linearity of the N—C(1)—C(2) angle.

It should be noted here that normal carbon-carbon distances were found for all alkyl chains. Furthermore no unusual bond angles occur in the investigated compounds.

Molecular packing

The packing in the crystalline state is quite different in all three compounds. The numbers of molecules per elementary cell are 2 in CCH3 and 4 in CCH5 and CCH7. CCH3 crystallized in the centrosymmetric triclinic, CCH5 in a centrosymmetric monoclinic and CCH7 in a non-centrosymmetric orthorhombic cell.

The packing of CCH7 is demonstrated in Figures 4 and 5. The molecules are packed parallel to the long crystallographic *a*-axis with a tilt angle of ~33°. This is shown clearly in Figure 5. No overlapping of any molecules or atoms occurs along the short crystallographic *c*-axis. Further to this, the packing is characterized in such a manner that one-half of the molecule with

TABLE V

Bond angles(°) and their standard deviations.

	CCH7	CCH5	CCH3
N—C(1)—C(2)	167.7(1.7)	177.8(.6)	177.5(.3)
C(1)—C(2)—C(3)	107.3(1.1)	109.7(.4)	109.9(.2)
C(1)—C(2)—C(7)	112.8(1.1)	111.8(.4)	110.8(.2)
C(3)—C(2)—C(7)	111.1(.9)	111.0(.4)	110.9(.2)
C(2)—C(3)—C(4)	113.9(1.0)	112.3(.4)	111.4(.2)
C(3)—C(4)—C(5)	114.4(1.0)	113.1(.4)	113.6(.2)
C(4)—C(5)—C(6)	109.6(.8)	109.7(.4)	108.5(.2)
C(4)—C(5)—C(8)	114.1(1.0)	112.8(.3)	112.8(.2)
C(6)—C(5)—C(8)	114.9(.9)	113.0(.4)	113.3(.2)
C(5)—C(6)—C(7)	111.4(.9)	112.9(.4)	113.6(.2)
C(6)—C(7)—C(2)	112.2(1.0)	111.8(.4)	111.6(.2)
C(5)—C(8)—C(9)	114.9(1.0)	113.2(.4)	112.6(.2)
C(5)—C(8)—C(13)	113.1(.9)	112.4(.3)	113.1(.2)
C(9)—C(8)—C(13)	110.1(.8)	109.0(.4)	109.2(.2)
C(8)—C(9)—C(10)	115.2(1.0)	113.3(.4)	113.9(.2)
C(9)—C(10)—C(11)	114.4(.9)	113.3(.4)	113.2(.2)
C(10)—C(11)—C(12)	109.6(.8)	108.9(.4)	108.8(.2)
C(10)—C(11)—C(14)	114.8(.9)	113.4(.4)	113.0(.2)
C(12)—C(11)—C(14)	110.2(.8)	111.5(.4)	111.9(.2)
C(11)—C(12)—C(13)	113.4(.9)	112.6(.4)	113.1(.2)
C(12)—C(13)—C(8)	114.2(.9)	113.1(.4)	113.7(.2)
C(11)—C(14)—C(15)	116.0(1.0)	117.4(.4)	116.1(.2)
C(14)—C(15)—C(16)	114.0(1.0)	114.4(.4)	114.2(.2)
C(15)—C(16)—C(17)	115.4(1.1)	115.7(.5)	
C(16)—C(17)—C(18)	111.6(1.0)	114.8(.5)	
C(17)—C(18)—C(19)	113.3(1.0)		
C(18)—C(19)—C(20)	113.3(1.1)		

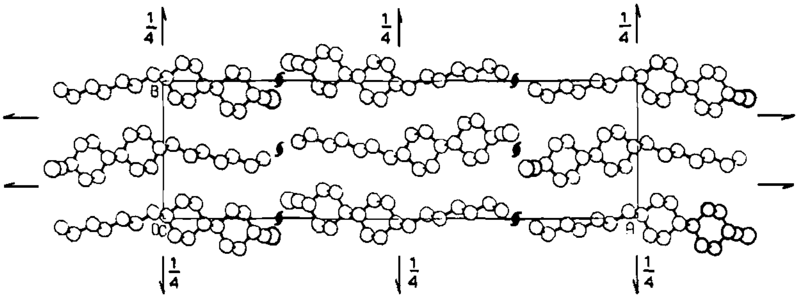

FIGURE 4 CCH7 projection along [001].

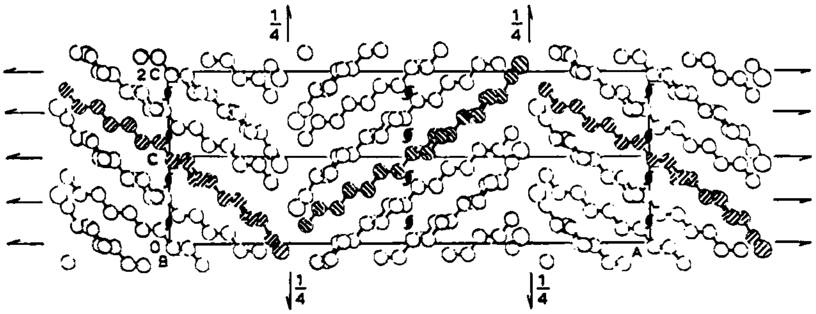

FIGURE 5 CCH7 projection along [010]. For clarity, complete molecules are represented with shading.

its bulky cyclohexylcyclohexyl and polar cyano group overlaps the opposite half of four neighboring molecules, i.e., their alkyl groups, and *vice versa*, in a head-to-tail alternation. This is shown in Figures 4 and 5. It can also be seen from this figure that the central part of the molecule, i.e., C(11)—C(14) bond is either situated in the $x = 0$ or $x = \frac{1}{2}$ position.

Thus, two types of layers can be discussed in the following respect. One type of layer is perpendicular to the crystallographic 2_1-axis along a. The molecules, of which this layer is composed of, are arranged in the head-to-tail alternation. These layers would have a thickness of half of the crystallographic a-axis (=16.86 Å), corresponding to the length of the entire molecule (~20.18 Å) multiplied by the cosine of the tilt angle (~33°). When one considers the crystallographic 2_1-axis parallel to a, the sign of the tilt angle changes from +33° to −33°.

A second type of layer can be discussed by considering Figure 4. This layer is perpendicular to the crystallographic 2_1-axis, which in turn is parallel to b, with a thickness of $b/2$ = 4.82 Å. In these layers, the long axes of the molecules describe an angle of ~66° with one another, thus resulting in a herringbone-like packing (see Figure 5).

From Figures 4 and 5, it can clearly be seen that around the 2_1-axis parallel to the crystallographic c-axis the cyano groups form an infinite stacking parallel to this axis. The calculated distances are $N \ldots N' =$ 4.01 Å, $C(1) \ldots C(1)' =$ 4.50 Å and $N \ldots C(1)' =$ 3.72 Å with $x' = \frac{1}{2} - x$, $y' = -y$ and $z' = \frac{1}{2} + z$ respectively. But when discussing the molecular geometry as a whole, the atomic coordinates of the atoms N and C(1) are less accurate. A dipole-dipole contact, which might be assumed to prevail, is not quite justified by the intermolecular distances mentioned above. The stacking of the cyano dipoles in these compounds is similar to the stacking of the cyano dipoles around the 2_1-axis in BCH5CN.[8]

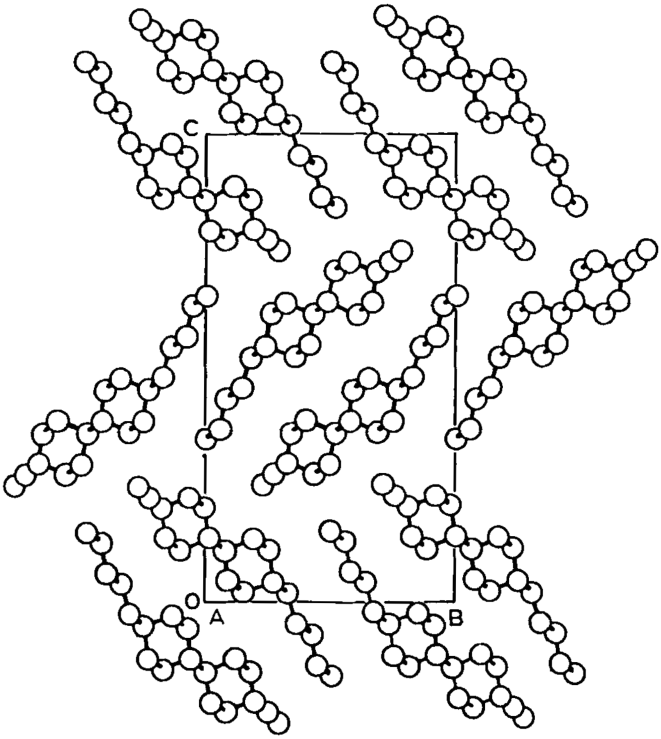

FIGURE 6 CCH5 projection along [100].

The packing for CCH5 is shown in Figure 6 as a projection along the short crystallographic *a*-axis. No overlapping occurs in this projection. The molecules related by the inversion center of symmetry lie collinear to each other. Here, the central part of the molecule is the middle of the cyclohexyl ring which is adjacent to the alkyl group. This results in an overlapping of two equivalent rings. The remaining molecular units overlap in a head-to-tail manner with respect to the neighboring centrosymmetric molecule. In addition to this, the pentyl group with its adjacent cyclohexyl ring overlaps the same unit of the alternating centrosymmetric molecule. Through implementation of the 2_1-axis to *b*, the molecules change sign from layer to layer (perpendicular to the plane-(001)). Here, one has the non-classical crossed structure of a nematic.[9] In these layers, the projection of the long axes of the molecules along [100] describe an angle of approx. 48° with the normal to the (001)-plane.

In Figure 7, the projection along the crystallographic *b*-axis is presented. Here one can see a further type of layer structure comparable with the layer perpendicular to [010] in CCH7 (Figure 4).

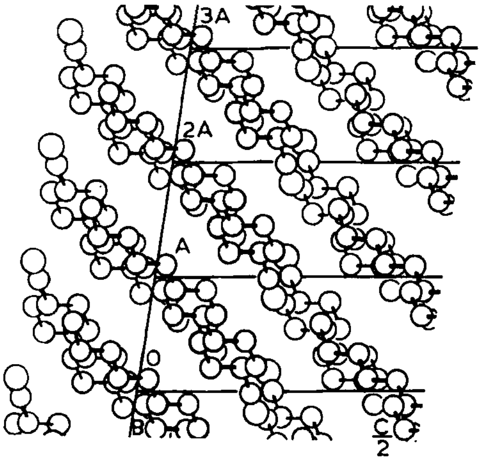

FIGURE 7 CCH5 projection along [010].

In these layers the molecules are fully stretched so that the thickness of this layer (~4.2 Å) is nearly equivalent to the thickness of the molecule as such. These layers extend along the crystallographic (104)-plane. The distance between the cyano dipoles does not compare in the same manner as that in CCH7 (and CCH3).

In Figure 8, CCH3 is depicted by means of a projection along the *c*-axis. While only a crystallographic symmetry center is present, the molecules are arranged in a collinear manner, having a common direction. Here, the centrosymmetrically related molecules overlap more or less entirely with respect to their cyclohexylcyclohexyl unit.

One can also distinguish two types of layers. The first kind is perpendicular to (010) with a thickness equivalent to that of the *b*-axis (=9.58 Å). The second type of layer is parallel to the plane (021). In the former layer type, the molecules are stretched with a tilt angle to the (001)-plane of ~45°. In the latter, the normal to the layer is oriented perpendicular to the long axes of the molecules (line C(2) to C(13)) with a thickness of ~4.3 Å comparable with CCH5.

A noteworthy difference to the packing of CCH7 and CCH5 exists in as much as the inversion center of symmetry is responsible for a relatively small spacing between the cyano dipoles. The related distances are: N...N′ = 3.55 Å; C(1)...C(1)′ = 3.36 Å and N...C(1)′ = 3.27 Å with $x' = 1 - x$, $y' = -y$ and $z' = 1 - z$ respectively. This rather confined spacing can be interpreted as a weak dipole-dipole interaction between dimers of molecules in the crystals. The entire molecular length of this 'dimer' molecule is H(162) − H(162)′ = 28.32 Å, and as much as

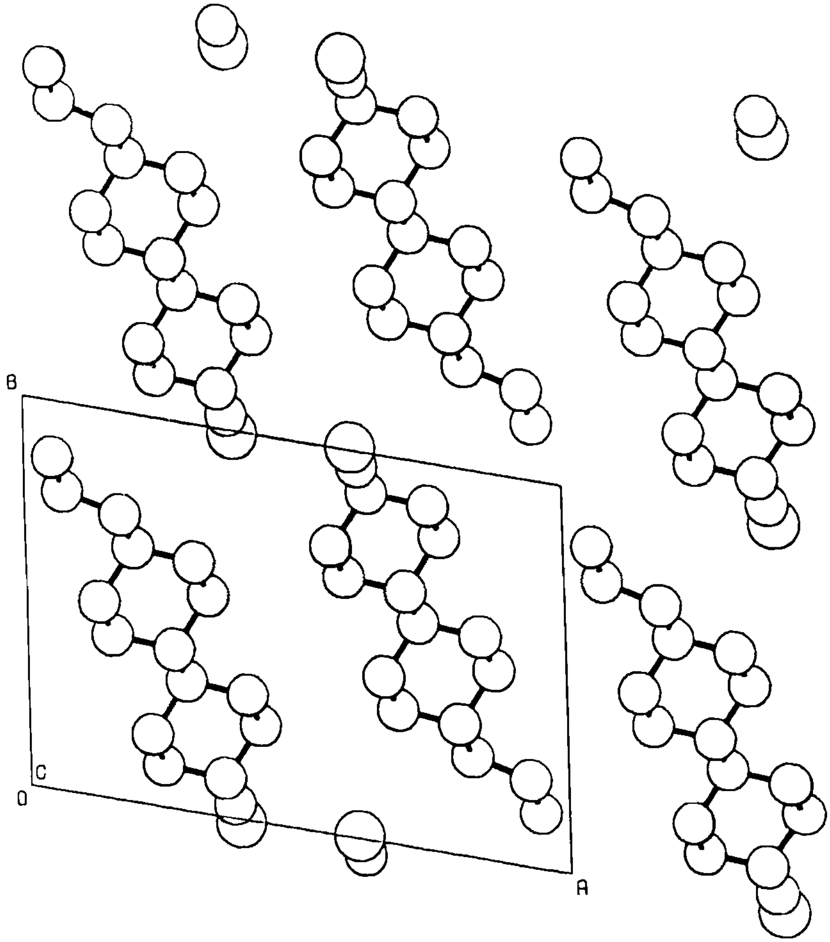

FIGURE 8 CCH3 projection along [001].

~28.92 Å when one takes the hydrogen radii into account.

In view of the various types of molecular overlapping in the three homologous compounds, one can discuss the successive changes in overlapping as being an inherent feature of a series. Thus one finds for CCH7 that practically no overlapping occurs between the bulky cyclohexyl-cyclohexyl groups. This series continues with CCH5, where only the central cyclohexyl rings of neighboring molecules now overlap in a head-to-tail manner. The series concludes with CCH3 where the bulky cyclohexyl-cyclohexyl groups overlap more or less in their entirety.

TABLE VI

Comparison of the molecular length l in the solid crystalline state with the equivalent extensions[4] in the smectic B and nematic phases.

compound	l [Å] (crystalline)	c [Å] (smectic B)	$d_{\parallel}$ [Å] (nematic)
CCH3^{+}	15.13	27.3	
CCH5	17.52	31.2	27.2
CCH7	20.18	—	31

$^{+}$If one assumes "dimerization", the length of the "dimeric unit" in the crystalline state is 28.92 Å.

Comparison with X-ray results for the mesogenic states

A comparative tabulation of the above-mentioned molecular lengths in the solid crystalline state and the data of Brownsey and Leadbetter[4] for the liquid crystalline states is given in Table VI. For the purpose of comparison, we have assumed that a 'dimerization' is more or less prevalent in the crystal structure of CCH3. With this in mind, the other two compounds, namely CCH5 and CCH7, can be also thought to exhibit this 'association', provided that this is modified by some minor molecular rearrangements. The existence of the orthogonal smectic B-type structure in CCH3 and CCH5 and its absence in CCH7 cannot, on the other hand, be deduced from the crystal structure. In the solid crystalline state, all the discussed layers consist of molecules which are tilted. Whereas, this is not the case in their liquid crystalline state, i.e. in the smectic B-phase.

Acknowledgments

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