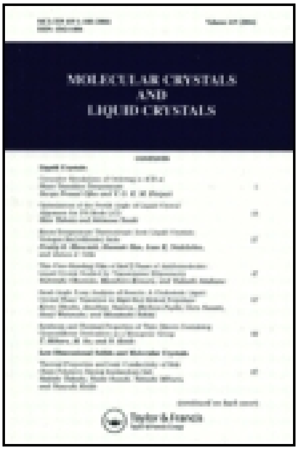

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Liquid Crystalline 4-(4-Cyanocyclohexyl)cyclohexyl Esters. Crystal and Molecular Structure of Smectogenic trans-4-(cis-4-Cyanocyclohexyl)cyclohexyl trans-4-n-Heptylcyclohexanoate

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Liquid Crystalline 4-(4-Cyanocyclohexyl)cyclohexyl Esters. Crystal and Molecular Structure of Smectogenic trans-4-(cis-4-Cyanocyclohexyl)cyclohexyl trans-4-*n*-Heptylcyclohexanoate

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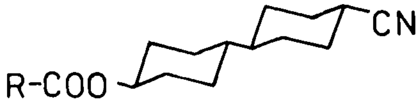
Liquid crystalline 4-(4-cyanocyclohexyl)cyclohexyl esters were synthesized and characterized by physical methods. For compounds with the cyano group in an axial position clearing temperatures about 100 K below those of their equatorially substituted isomers are expected.

The title compound, with the formula C_7H_{15}—C_6H_{10}—COO—C_6H_{10}—$C_6H_{10}CN$ (CCCHC), crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.643(1)$, $b = 47.512(6)$, $c = 5.5435(6)$ Å and four molecules per unit cell. The structure was solved by direct methods and refined to $R = 0.052$. Apart from the axially bonded terminal cyano group, the CCCHC molecules adopt a fully stretched conformation. In the crystalline state, CCCHC has a tilted layer structure with a herringbone arrangement of layers.

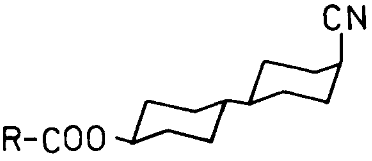
Keywords: mesogenic cyclohexyl esters, synthesis, X-ray analysis, molecular structure, crystal structure

INTRODUCTION

Liquid crystalline compounds containing cycloaliphatic structural fragments with a cyano group in terminal position possess physical properties favorable for several applications.[1-3] Recently we reported a series of cyclohexyl esters[4] representing substances of such a kind. In continuation of these investigations we present now some newly synthesized 4-(4-cyanocyclohexyl)cyclohexyl esters. The reaction products contained both isomers, with the cyano group in equatorial (a) and in axial position (b), which were successfully separated by fractional recrystallization. In addition to NMR, IR and dielectric measurements, the X-ray analysis of trans-4-(cis-4-cyanocyclohexyl)cyclohexyl trans-4-*n*-heptylcyclohexanoate (abbreviated CCCHC in the following) reported in this paper provided the final proof of the molecular configuration.



(a)



(b)

SYNTHESIS AND CHARACTERIZATION

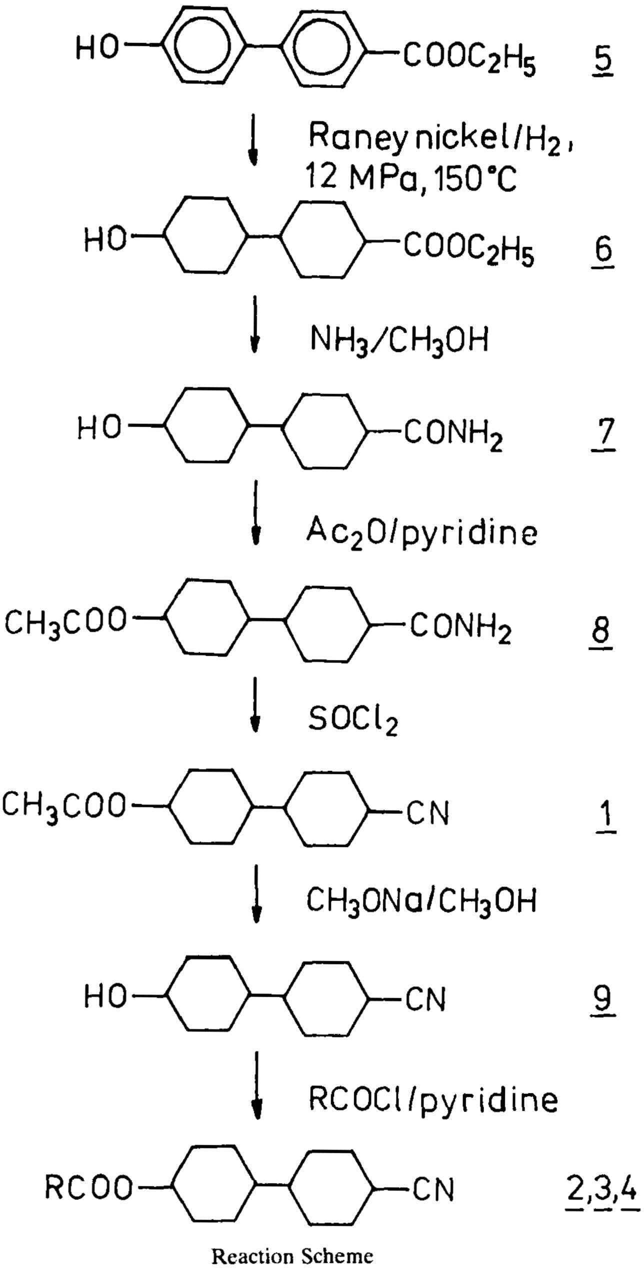
The 4-(4-cyanocyclohexyl)cyclohexyl esters (Table I) were synthesized according to the following reaction scheme by the use of known methods.

The main problem consisted in the separation of the isomers a and b. Repeated recrystallization of the intermediate products owing to lower solubility of the trans-compounds proved to be an effective method.

The equatorial position of the carboxyl group in the cyclohexanoates 2a,3a and 2b,3b is indicated by intense C—O single bond stretching vibrations around 1010 and 1130 cm^{-1}.[5] In the benzoates 4a and 4b they can be observed at 1000 and 1090 cm^{-1} (Figure 1).

A complete and unequivocal determination of molecular stereochemistry by means of comparing ^{1}H-NMR studies of the trans-4-butylcyclohexanoates 2a and 2b was impossible due to the considerable complexity of the spectra (Figure 2). The relatively large line width of ca. 30 Hz for H_{a_1} at 4.58 ppm and ca. 28 Hz for H_{a_2} at 2.31 ppm observed for 2a is due to axial couplings. For 2b an axial coupling for H_a at 4.60 ppm with a line width of ca. 30 Hz has been found. The band at 2.89 ppm with a relatively small line width of 3 Hz indicates an equatorial coupling.

Further evidence for the configuration of the cyanocyclohexyl fragment is provided by dielectric measurements.[6] By adding of compound 3a to a liquid crystalline basic mixture an increase of dielectric anisotropy $\Delta\epsilon$ was found whereas addition of 3b resulted in a decrease of $\Delta\epsilon$. These observations are clear hints at the dipole



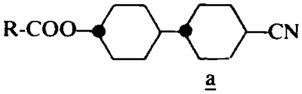
Reaction Scheme

moment of the cyano group acting approximately parallel to the molecular long axis in the case of 3a and perpendicular in the case of 3b.

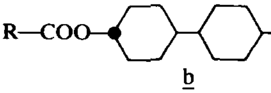
Finally, the all-trans configuration of the esters of series *a* is supported by their higher mesomorphic transition temperatures. Even the intermediate compound trans-4-(4-acetyloxycyclohexyl)cyclohexane carbonitrile (1a) exhibits a monotropic

TABLE I

n temperatures (°C) of 4-(4-cyanocyclohexyl)cyclohexyl esters (values given in parentheses represent monotropic transitions, i.e. tr
temperatures obtained only temperature downwards).



a



b

	a							b		
	C		S$_B$		N		I	C		S$_B$
	·	97	–		(·	49.5)	·			
	·	91	·	114	·	206	·	·	118	(· 77)
	·	115	·	117	·	190.5	·	·	128	(· 91)
	·	98	–		·	204	·	·	130	–[a]

b can be supercooled by up to 70°C without forming a mesophase.

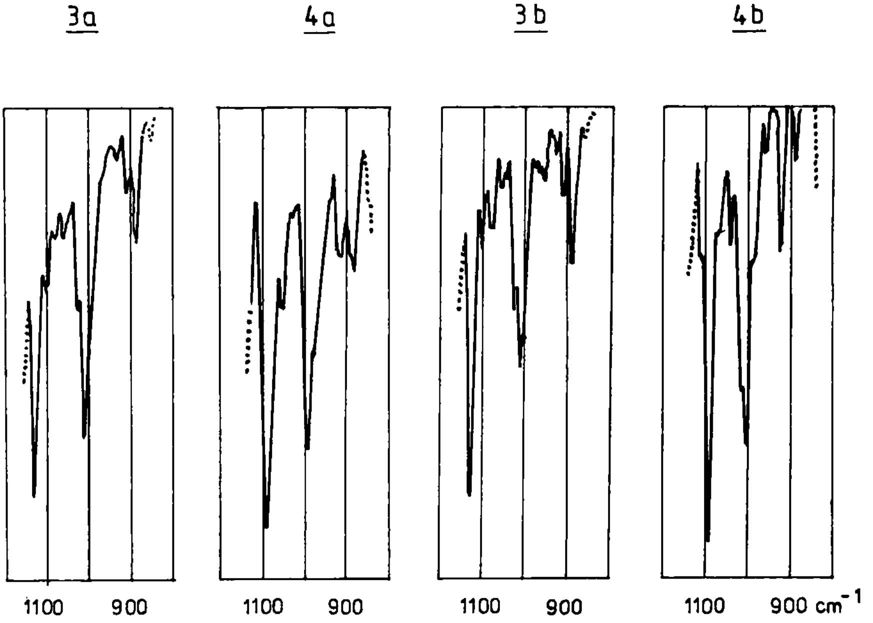


FIGURE 1 IR spectra of compounds 3 and 4 (in KBr pellets).

nematic phase (v. Table I). Compared with the analogous 4-cyanobiphenyl esters, the clearing points of the esters a are about 40°C lower. The clearing temperatures of the axially substituted derivatives of series b are, as expected, about 100°C lower than those of their equatorially substituted isomers. This effect is chiefly caused by the different length: width ratios.

Experimental

Phase transitions were determined using a Boetius heating stage microscope equipped with a polarization filter. The elemental analyses were performed using Carlo Erba Elemental Analyzer 1102. IR spectra were recorded with the instruments Specord M80, 75 IR and UR 20 (VEB Carl Zeiss Jena). ^{1}H-NMR spectra were obtained using a Bruker WP 200 spectrometer with TMS as an internal standard. Hydrogenations were carried out in high pressure shaking autoclaves with capacity of 0.5 and 1 l (VEB Apparatebau Rheindorf).

Ethyl-4-(4-hydroxyphenyl)benzoate 5 was prepared according to procedures described in literature.[7,8] All following synthesis steps have been described for the analogous cyanocyclohexyl esters in the preceding publication.[4]

Hydrogenation of 5 at 12 MPa and 150°C yielded a cis-trans mixture of ethyl-4-(4-hydroxycyclohexyl)-cyclohexanoate 6 with a boiling temperature 160–190°C (0.13 kPa). Compound 6 after standing for some days in an ammonia atmosphere was converted into the amide 7 (m.p. 257°C for 7a after recrystallization from ethanol). By concentrating the mother liquor, an amorphous product with high percentage of the cis-isomer 7b (m.p. 180–198°C) could be obtained. It underwent a treatment

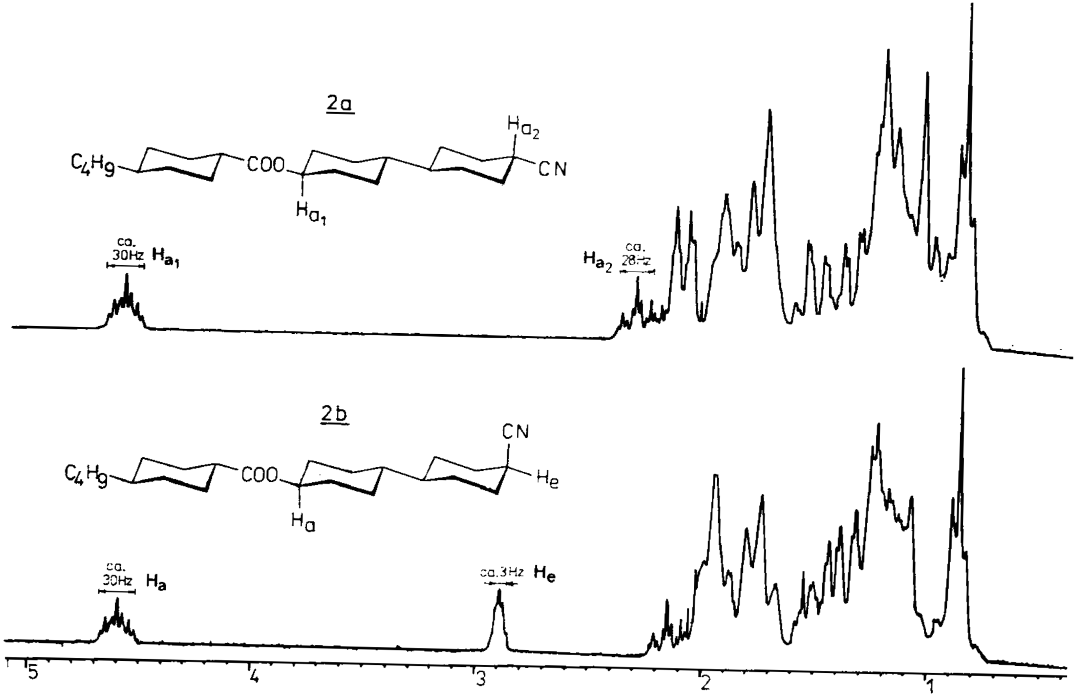


FIGURE 2 ^{1}H-NMR spectra of compounds 2a and 2b (200.13 MHz, $CDCl_3$).

analogous to that described below for the trans-isomer. Reaction with acetic anhydride converted 7 into the 4-(4-acetyl-oxyphenyl)-cyclohexane carbonamide 8 (m.p. of 8a after recrystallization from ethanol: 215–220°C). Dehydration by thionyl chloride gave the nitrile 1 (1a: b.p. = 182–185°C at 0.13 kPa, plate-like crystals after recrystallization from hexane). Saponification led to 4-(4-hydroxycyclohexyl)-cyclohexane carbonitrile 9 (9a: m.p. = 112–113.5°C after recrystallization from hexane/methanol). Esterification of 9 was performed in portions of 5 mmol by reaction with appropriate acid chlorides in pyridine). The esters 2–4 were recrystallized iteratively from ethanol until their transition temperatures became constant.

X-RAY STRUCTURE DETERMINATION

Data collection

Needle-shaped colorless crystals of CCCHC (compound 3b) were investigated by X-ray film methods yielding space group $P2_12_12_1$ in the orthorhombic crystal system as well as preliminary lattice parameters. Precise unit-cell constants (Table II) were determined by a least-squares treatment of the setting angles for 15 counter reflections measured on a Syntex $P2_1$ diffractometer from a crystal of approximate size 0.1 × 0.2 × 0.3 mm which was also used for intensity data collection. 1976 Unique intensity data with $2\theta \leqslant 115°$ were measured using graphite monochromatized CuKα radiation (2θ/θ scan, bisecting mode). The intensity of the check reflections varied by less than 4.5% $(\bar{2}\bar{4}1)$ and 2.5% $(\bar{1}51)$. 1601 (= 81.0%) of the reflections had intensities $I \geqslant 1.96\ \sigma(I)$ and were considered observed. Data reduction was carried out in the usual way neglecting absorption and extinction effects.

Structure solution and refinement

The structure was solved by an automatic run of the direct-methods program MULTAN 80.[9] 220 Reflections were involved in 4103 phase relationships. The correct phase set automatically chosen by MULTAN from 30 possible sets gave the following figures of merit: ABS FOM = 1.0762, $\chi_o = 1.25$, $R = 16.39$, COMB FOM = 3.00. An E-map calculated with these phases revealed 25 of the 30 nonhydrogen atoms ($R = 0.43$). The structure model was completed by a Fourier

TABLE II

Crystal data

4-(4-cyanocyclohexyl)cyclohexyl 4-*n*-heptylcyclohexanoate (CCCHC)
$C_{27}H_{45}NO_2$
Orthorhombic
a = 9.643(1) Å
b = 47.512(6) Å
c = 5.5435(6) Å
V = 2539.7(6) Å^3

M.W. = 415.6
Space group $P2_12_12_1$
Z = 4
D_c = 1.09 g cm^{-3}
D_m = 1.07 g cm^{-3}
μ(CuKα) = 4.44 cm^{-1}
F(000) = 920

synthesis showing all non-hydrogen atoms ($R = 0.25$). A least-squares refinement of these positions, first with isotropic and then with anisotropic thermal parameters, reduced R to 0.13. Hydrogen atoms found in a difference Fourier map were introduced and kept fixed during refinement. For the last 6 cycles of refinement the weighting scheme was changed from unit weights to counter weights ($w = K/\sigma^2(F)$) and an empirical extinction factor χ was applied to F_c giving $F_{\text{corr}} = F_c(1 - \chi 10^{-4} F_c^2/\sin\theta)$, K and χ refining to 3.577 and 7.7(4) × 10^{-3}, respectively. The final R value amounts to 0.052 ($R_w = 0.052$) for 1601 observed reflections (5.9 reflections/parameter). The maximum shift/σ during the last refinement cycle was 0.011. The final difference Fourier map had minimum and maximum peaks of -0.190 and 0.146 e.Å^{-3}, respectively.

All calculations were done on an ESER 1040 computer using the programs PRARA,[10] MULTAN 80,[8] SHELX 76,[11] and EDIT.[12]

Table III contains the positional and equivalent isotropic thermal parameters for the non-hydrogen atoms.

TABLE III

Final fractional coordinates and isotropic equivalents (× 10^3) of the anisotropic thermal parameters for the non-hydrogen atoms (esd's in parentheses)

$U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{/1/3}$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C(1)	0.6599(6)	0.02109(9)	−0.6763(10)	95(2)
C(2)	0.6130(6)	0.04025(9)	−0.4791(11)	87(2)
C(3)	0.6765(5)	0.06903(8)	−0.4970(10)	75(2)
C(4)	0.6383(5)	0.08978(9)	−0.2975(9)	72(2)
C(5)	0.7033(5)	0.11790(8)	−0.3237(9)	71(2)
C(6)	0.6706(5)	0.13942(8)	−0.1259(8)	60(2)
C(7)	0.7428(4)	0.16716(8)	−0.1622(8)	60(2)
C(8)	0.7283(4)	0.18916(8)	0.0361(8)	51(2)
C(9)	0.5817(4)	0.20114(8)	0.0573(9)	55(2)
C(10)	0.5714(4)	0.22338(9)	0.2518(8)	56(2)
C(11)	0.6724(5)	0.24762(8)	0.2143(7)	48(2)
C(12)	0.8206(4)	0.23571(8)	0.1940(8)	58(2)
C(13)	0.8304(4)	0.21325(8)	−0.0032(8)	58(2)
C(14)	0.6692(5)	0.26805(9)	0.4190(8)	51(2)
C(15)	0.7153(4)	0.31539(7)	0.5391(8)	51(2)
C(16)	0.5730(5)	0.32859(8)	0.5553(9)	65(2)
C(17)	0.5719(5)	0.35262(8)	0.7403(9)	62(2)
C(18)	0.6782(4)	0.37516(8)	0.6858(8)	53(2)
C(19)	0.8235(4)	0.36148(8)	0.6558(9)	59(2)
C(20)	0.8224(4)	0.33706(8)	0.4753(9)	63(2)
C(21)	0.6783(5)	0.39886(7)	0.8730(8)	55(2)
C(22)	0.5383(5)	0.41374(9)	0.8818(10)	70(2)
C(23)	0.5336(6)	0.43860(9)	1.0594(10)	75(2)
C(24)	0.6472(6)	0.45972(9)	1.0058(9)	70(2)
C(25)	0.7899(5)	0.44539(8)	1.0032(10)	77(2)
C(26)	0.7927(5)	0.42084(8)	0.8272(10)	69(2)
C(27)	0.6231(7)	0.47426(10)	0.7756(11)	73(2)
N	0.6047(7)	0.48434(9)	0.5938(9)	105(2)
O(1)	0.6376(4)	0.26266(6)	0.6226(6)	66(1)
O(2)	0.7144(3)	0.29380(5)	0.3518(5)	57(1)

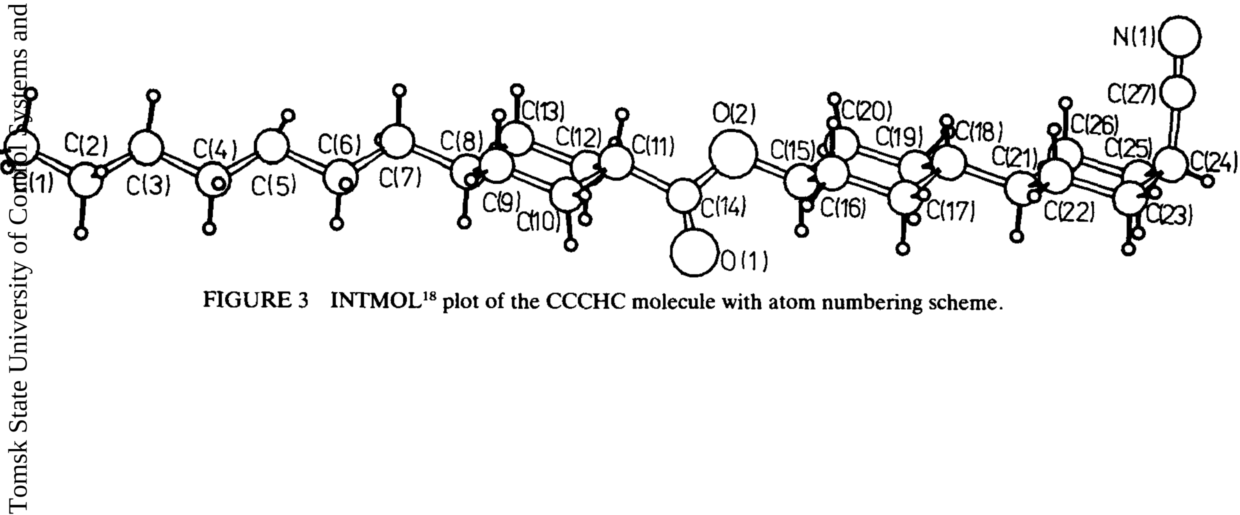


FIGURE 3 INTMOL[18] plot of the CCCHC molecule with atom numbering scheme.

Results and discussion

Figure 3 illustrates the molecular structure of CCCHC including atom numbering scheme. The bond lengths and angles summarized in Table IV agree well with expected values. The C—H distances range from 0.73 to 1.14 Å (mean 0.99(9) Å). All three cyclohexane rings form almost ideal chairs with mean endocyclic torsion angles of 55.6(9) (ring I C(8)...C(13)), 55.0(2.2) (ring II C(15)...C(20)) and 54.3(1.2)° (ring III C(21)...C(26)). The heptyl chain has an all-trans conformation.

Apart from the cyano group, the CCCHC molecule adopts a fully stretched conformation. In contrast to all other substituents which are equatorially bonded in 1,4-positions to the cyclohexane rings, the cyano group is axially attached as can be seen from both Figure 3 and the torsion angles C(22)-C(23)-C(24)-C(27) 68.1(5)° and C(26)-C(25)-C(24)-C(27) −68.8(5)°. In consequence, the angle between the direction of the CN group and the molecular long axis (defined as the line connecting atoms C(21) and C(24)) amounts to 87° and leads to the negative dielectric anisotropy found for CCCHC as mentioned above. For the equatorially substituted trans-isomer, under the assumption that the molecular geometry is the same as

TABLE IV

Bond distances and angles for the non-hydrogen atoms in CCCHC (esd's in parentheses).

Atoms	Distance (Å)	Atoms	Angle (°)
Heptyl chain			
C-C (mean)	1.507(18)*	C-C-C (mean)	115.0(18)*
Cyclohexane ring I (C(8) . . . C(13))			
C-C (mean)	1.527(10)*	C-C-C (mean endocyclic)	111.2(15)*
C(7)-C(8)	1.523(6)		
		C(7)-C(8)-C(9)	113.3(3)
		C(7)-C(8)-C(13)	110.7(3)
		C(10)-C(11)-C(14)	112.0(3)
		C(12)-C(11)-C(14)	108.2(3)
Cyclohexane ring II (C(15) . . . C(20))			
C-C (mean)	1.524(18)*	C-C-C (mean endocyclic)	111.3(11)*
C(18)-C(21)	1.531(6)		
		O(2)-C(15)-C(16)	109.2(3)
		O(2)-C(15)-C(20)	108.6(3)
		C(17)-C(18)-C(21)	112.7(3)
		C(19)-C(18)-C(21)	112.3(3)
Cyclohexane ring III (C(21) . . . C(26))			
C-C (mean)	1.529(9)*	C-C-C (mean endocyclic)	111.6(16)*
C(24)-C(27)	1.470(8)		
		C(18)-C(21)-C(22)	111.2(3)
		C(18)-C(21)-C(26)	112.8(3)
		C(23)-C(24)-C(27)	111.6(4)
		C(25)-C(24)-C(27)	110.0(4)
Carboxylic group			
C(11)-C(14)	1.494(6)	C(11)-C(14)-O(1)	125.6(3)
C(14)-O(1)	1.197(6)	C(11)-C(14)-O(2)	111.9(3)
C(14)-O(2)	1.351(5)	O(1)-C(14)-O(2)	122.4(3)
O(2)-C(15)	1.460(5)	C(14)-O(2)-C(15)	116.3(3)
Cyano group			
C(27)-N	1.130(8)	C(24)-C(27)-N	177.0(4)

*Standard deviations of the mean values

that of the cis-isomer except for the position of the CN substituent, this angle would be only 25.1° leading to a positive dielectric anisotropy. Also the molecular length:width ratio is noticeably influenced by the change of the CN position. For the cis-isomer a value of 4.80 is found whereas for the trans-isomer it would be about 10% larger, namely 5.32. The significant differences in the mesomorphic behavior of the two isomers discussed in the Introduction and summarized in Table I are due to the above differences in their molecular geometries.

To facilitate further discussion of the molecular conformation it is convenient to consider separately the cyclohexyl-4-*n*-pentylcyclohexanoate moiety and the cyano-substituted bicyclohexyl moiety which are two overlapping fragments of the CCCHC molecule (common cyclohexane ring II).

Recently, we have reported on the X-ray analysis of 4-(2-cyanoethyl)-cyclohexyl 4-*n*-pentylcyclohexanoate (CECPC)[13] as the first structure determination of a cyclohexyl cyclohexanoate. A comparison of the conformational behavior of CCCHC and CECPC indicates only a rough agreement. It can be illustrated by the angles between the normals to the planes (= interplanar angles) defined by the carboxylic group (plane 1), atoms C(7),C(8),C(11),C(14) (plane 2 bisecting cyclohexane ring

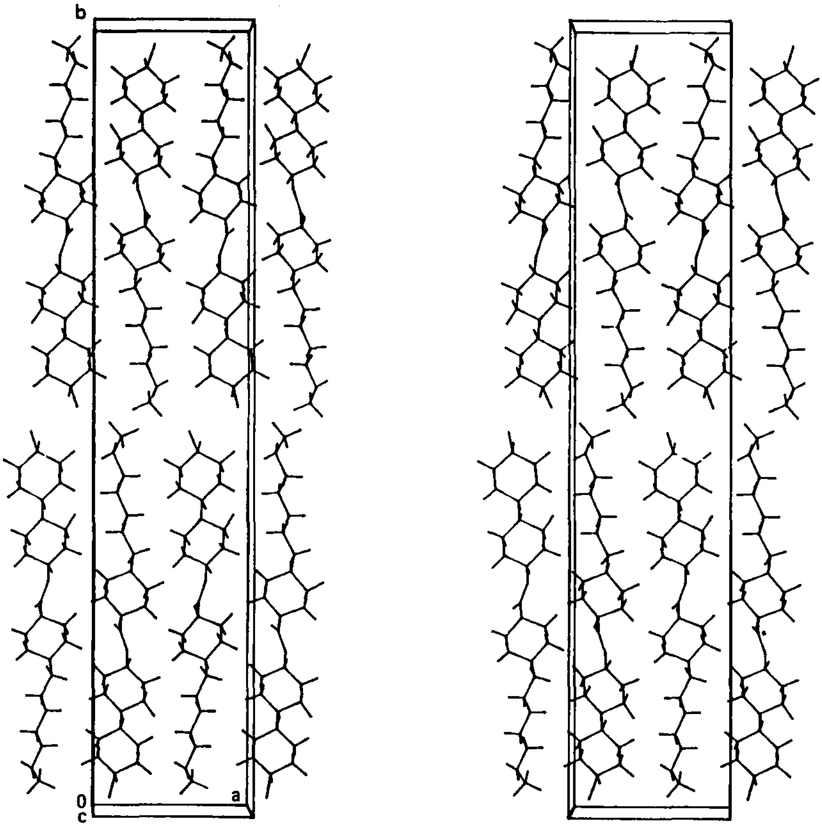


FIGURE 4 Stereo plot of the crystal structure of CCCHC.

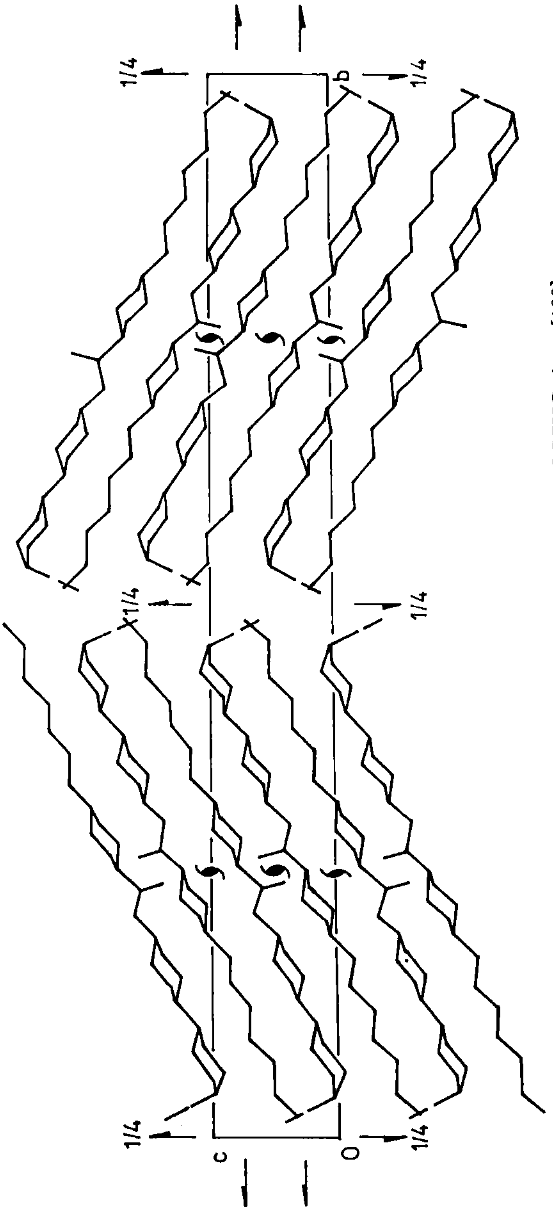


FIGURE 5 Projection of the crystal structure of CCCHC along [100].

I), and atoms C(15),C(18),C(21),O(2) (plane 3 bisecting ring II). CCCHC is characterized by the following interplanar angles (corresponding values for CECPC in parentheses): planes 1/2 36.0° (49.1°), planes 1/3 34.2° (21.2°), planes 2/3 4.4° (35.9°). The most striking difference is that the above-defined bisecting planes through the cyclohexane rings are nearly coplanar in CCCHC but considerably tilted in CECPC. The conformation of the cyclohexyl cyclohexanoate skeleton may be also described by the three torsion angles C(10)-C(11)-C(14)-O(1) 26.9(5) (14.1(3)), C(11)-C(14)-O(2)-C(15) 180.0(4) (−168.2(3)), and C(14)-O(2)-C(15)-C(16) −84.7(4)° (−106.3(3)°).

The two rings of the bicyclohexyl moiety in CCCHC have almost the same orientation, the interplanar angle between the bisecting planes defined by atoms C(15),C(18),C(21),O(2) and C(18),C(21), C(27),C(24) being 4.5°. The values of the corresponding torsion angle C(17)-C(18)-C(21)-C(26) of 176.3(4)° agrees well with those found in other related mesogenic compounds: −179.7, −177.4 and 175.8° for the propyl, pentyl and heptyl homologues, respectively, of the series of 4-alkylbicyclohexyl 4'-carbonitriles[14] and −177.5 and −166.3° for the two independent molecules in 4-butylbicyclohexyl 4'-carboxylic acid.[15]

The molecular packing of CCCHC in the crystal is shown in Figure 4. The crystal structure is built up by smectic-like layers parallel (010) with antiparallel orientation of neighboring molecules. The arrangement of the molecules within the layers is further illustrated in a projection along [100] (Figure 5). The tilt angle (the angle between the layer normal and molecular long axis) amounts to 24.1°. Adjacent layers are related by a 2-fold screw axis resulting in a herringbone pattern. The crystal structure is very similar to that of the high temperature polymorph (solid II) of ethyl *p*-azoxybenzoate (Krigbaum & Taga[16]) which also transforms to a smectic mesophase. There are no unusual intermolecular interactions within the crystal, all intermolecular distances between non-hydrogen atoms being greater than the sums of the corresponding van der Waals radii.

The packing coefficient according to Kitaigorodski[17] has been estimated to 0.66.

Acknowledgment

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