

substituents about the C(1)–C(2) and C(2)–C(3) bonds of the ring are illustrated in Fig. 2. The acetoxy and *p*-nitrobenzoyloxy groups at C(1) and C(2) are axial; the acetyl group at C(2) is equatorial. The torsion angle involving the acetoxy and acetyl groups, O(1)–C(1)–C(2)–C(9), is $-56.3(3)^\circ$, which minimizes the *gauche* interaction between these two substituents. Both acetoxy and acetyl groups are planar, maximum deviations $0.009(7)$ and $-0.029(7)$ Å for O(1) and C(9), respectively. The dihedral angles between the mean planes through the acetoxy and acetyl groups with respect to the cyclohexene ring are $77.2(7)$ and $129.6(7)^\circ$, respectively.

The Newman projection along the C(2)–C(3) bond (Fig. 2) shows that the projected angle between the acetyl and *p*-nitrobenzoyloxy groups at C(2) is 125° which helps to reduce the *gauche* interactions between these two groups.

The phenyl ring of the *p*-nitrobenzoyloxy substituent shows normal geometry, $1.381(6)$ Å and $120(4)^\circ$ for the mean C–C bond distance and the mean internal angle, respectively. The *p*-nitrobenzoyloxy substituent forms a dihedral angle of $80.0(7)^\circ$ with the mean plane of the cyclohexene ring. The nitro group is bent out of the plane of the phenyl ring by $10.0(7)^\circ$.

There are two intermolecular approaches < 3.4 Å involving non-H atoms: C(16)···O(3)($1-x, y, 0.5-z$)

$3.27(1)$ and C(8)···O(7)($x, 1-y, -0.5+z$) $3.37(1)$ Å. The molecules are held in the crystal by van der Waals forces.

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Structure of the Smectogenic Compound 4-(2-Cyanoethyl)cyclohexyl 4-*n*-Pentylcyclohexanecarboxylate

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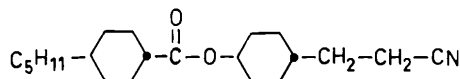
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Abstract. $C_{21}H_{35}NO_2$, $M_r = 333.5$, triclinic, $P\bar{1}$, $a = 5.611(1)$, $b = 12.827(1)$, $c = 14.348(2)$ Å, $\alpha = 93.07(1)$, $\beta = 89.15(1)$, $\gamma = 95.762(8)^\circ$, $V = 1025.9(2)$ Å³, $Z = 2$, $D_x = 1.079$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 5.0$ cm⁻¹, $F(000) = 368$, $T = 293$ K, final $R = 0.062$ ($wR = 0.064$) for 2266 observed reflections. The linearity of the almost fully stretched molecule is only distorted by the *gauche* conformation of the cyanoethyl group [torsion angle $-57.7(4)^\circ$]. The crystal packing is characterized by an antiparallel arrangement of neighboring molecules.

Introduction. In a series of previous publications (Hartung, Baumeister, Jaskólski, Mädicke & Wiegeleben, 1986, and references therein) we have described the results of our structural investigations on mesogenic cyano-substituted phenyl benzoates and phenyl cyclohexanecarboxylates in their crystalline state. This type of compound is of potential importance for practical use in liquid-crystal displays. The title compound, here abbreviated as CECPC, is one such material. It was studied to examine the influence of the dimethylene spacer between the polar cyano group and

the cyclohexane ring on the mesomorphic behavior and to allow a comparison to be made between the analogous phenyl and cyclohexyl cyclohexanecarboxylates (Deutscher, Krieg, Frach, Zaszke & Kresse, 1988). CECPC melts at 336 K to an isotropic liquid and forms a monotropic smectic *B* phase by strong undercooling of the melt at 311 K. To our knowledge the present X-ray analysis of CECPC is the first example of a cyclohexyl cyclohexanecarboxylate structure.



Experimental. CECPC was first synthesized and characterized by Deutscher *et al.* (1988). A clear colorless crystal, grown from methanol, with dimensions 0.23 × 0.43 × 0.49 mm was investigated on a Syntex P2₁ diffractometer using graphite-monochromated Cu K α radiation. Lattice parameters were derived from a least-squares refinement of the setting angles of 15 reflections. Intensities were measured for reflections with $2\theta \leq 115^\circ$ in an *h, k, l* range $\bar{6}, \bar{13}, 0$ to 6, 13, 15 ($\theta/2\theta$ variable scan, bisecting mode). The check reflection intensities varied from 5.37 (4) to $5.56(4) \times 10^4$ for 100 and from $11.34(6)$ to $11.76(6) \times 10^4$ for 031. 2723 unique reflections were measured and 2266 (=83.2%) with $I \geq 1.96\sigma(I)$ were considered observed. Lp correction was applied but absorption effects were ignored. The structure was solved by the direct-methods routine *EEES* in the *SHELX76* program system (Sheldrick, 1976). Full-matrix least-squares refinement on *F* with anisotropic thermal parameters for the non-H atoms and isotropic ones for H atoms (all found in a difference electron density map) led to a final *R* of 0.062 ($wR = 0.064$). The weighting scheme was $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ based on counting statistics. An empirical secondary-extinction correction was performed with $F_{\text{corr}} = F_c(1 - 10^{-6} \times \chi F_c^2 / \sin\theta)$, where χ refined to 4.72 (4). Further details of refinement: 6.3 reflections/parameter; in final cycle $\Delta/\sigma \leq 0.15$; max. and min. heights in final $\Delta\rho$ map 0.174 and $-0.200 \text{ e \AA}^{-3}$, respectively; atomic scattering factors those of *SHELX76*.

All calculations were performed on an ESER 1040 computer of the Halle University using programs *SHELX76*, *PRARA* (Jaskólski, 1980) and *EDIT* (Jaskólski, 1982).

Discussion. Final positional parameters and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1, bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44852 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) and *equivalent isotropic temperature factors* ($\text{\AA}^2 \times 10^3$) for the non-H atoms

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(1)	-1061 (7)	-2271 (3)	5068 (3)	94 (2)
C(2)	1131 (6)	-1520 (3)	4845 (2)	77 (1)
C(3)	1198 (5)	-1183 (3)	3852 (2)	64 (1)
C(4)	3374 (5)	-435 (2)	3598 (2)	60 (1)
C(5)	3383 (5)	-147 (2)	2586 (2)	61 (1)
C(6)	5648 (5)	485 (2)	2226 (2)	53 (1)
C(7)	5926 (5)	1621 (2)	2622 (2)	56 (1)
C(8)	8155 (5)	2246 (2)	2225 (2)	52 (1)
C(9)	8145 (5)	2226 (2)	1161 (2)	49 (1)
C(10)	7895 (6)	1085 (2)	761 (2)	61 (1)
C(11)	5680 (6)	471 (2)	1169 (2)	63 (1)
C(12)	10375 (5)	2782 (2)	750 (2)	53 (1)
C(13)	12253 (5)	3269 (3)	-715 (2)	65 (1)
C(14)	12225 (6)	4403 (3)	-934 (2)	65 (1)
C(15)	14287 (6)	4740 (3)	-1594 (2)	66 (1)
C(16)	14349 (5)	4047 (2)	-2480 (2)	53 (1)
C(17)	14272 (7)	2899 (3)	-2250 (3)	79 (2)
C(18)	12178 (7)	2570 (3)	-1593 (3)	82 (2)
C(19)	16479 (6)	4337 (3)	-3134 (2)	68 (1)
C(20)	16703 (6)	5459 (3)	-3457 (2)	73 (1)
C(21)	14548 (7)	5683 (3)	-3934 (2)	69 (1)
N	12854 (6)	5840 (3)	-4293 (2)	99 (2)
O(1)	12188 (4)	3044 (2)	1150 (2)	81 (1)
O(2)	10138 (3)	2928 (2)	-155 (1)	74 (1)

Table 2. *Bond lengths* (\AA) and *angles* ($^\circ$)

C(1)–C(2)	1.526 (5)	C(12)–O(2)	1.333 (4)
C(2)–C(3)	1.509 (5)	O(2)–C(13)	1.467 (4)
C(3)–C(4)	1.527 (4)	C(13)–C(14)	1.506 (5)
C(4)–C(5)	1.517 (4)	C(14)–C(15)	1.528 (5)
C(5)–C(6)	1.536 (4)	C(15)–C(16)	1.514 (4)
C(6)–C(7)	1.529 (4)	C(16)–C(17)	1.522 (5)
C(7)–C(8)	1.535 (4)	C(17)–C(18)	1.536 (5)
C(8)–C(9)	1.525 (4)	C(18)–C(13)	1.505 (5)
C(9)–C(10)	1.537 (4)	C(16)–C(19)	1.537 (4)
C(10)–C(11)	1.529 (4)	C(19)–C(20)	1.523 (5)
C(11)–C(6)	1.515 (4)	C(20)–C(21)	1.460 (5)
C(9)–C(12)	1.505 (4)	C(21)–N	1.128 (5)
C(12)–O(1)	1.185 (4)		
C(1)–C(2)–C(3)	113.5 (3)	O(1)–C(12)–O(2)	121.9 (2)
C(2)–C(3)–C(4)	115.1 (2)	C(12)–O(2)–C(13)	119.7 (2)
C(3)–C(4)–C(5)	112.8 (2)	O(2)–C(13)–C(14)	110.2 (2)
C(4)–C(5)–C(6)	116.9 (2)	O(2)–C(13)–C(18)	107.0 (2)
C(5)–C(6)–C(7)	112.9 (2)	C(13)–C(14)–C(15)	110.8 (3)
C(5)–C(6)–C(11)	110.9 (2)	C(14)–C(15)–C(16)	113.5 (2)
C(6)–C(7)–C(8)	111.8 (2)	C(15)–C(16)–C(17)	110.5 (3)
C(7)–C(8)–C(9)	112.2 (2)	C(16)–C(17)–C(18)	112.2 (3)
C(8)–C(9)–C(10)	109.9 (2)	C(17)–C(18)–C(13)	111.0 (3)
C(9)–C(10)–C(11)	110.6 (2)	C(18)–C(13)–C(14)	111.2 (3)
C(10)–C(11)–C(6)	113.8 (2)	C(15)–C(16)–C(19)	114.6 (2)
C(11)–C(6)–C(7)	109.4 (2)	C(17)–C(16)–C(19)	110.1 (2)
C(8)–C(9)–C(12)	113.3 (2)	C(16)–C(19)–C(20)	115.6 (3)
C(10)–C(9)–C(12)	108.2 (2)	C(19)–C(20)–C(21)	111.5 (3)
C(9)–C(12)–O(1)	126.1 (2)	C(20)–C(21)–N	178.5 (3)
C(9)–C(12)–O(2)	112.0 (2)		

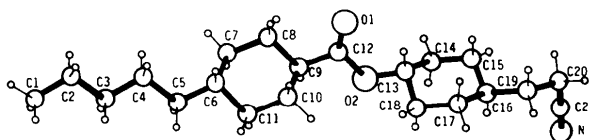


Fig. 1. Molecular structure of CECPC.

The molecular structure, with atom numbering, is shown in Fig. 1.

This study is the first crystal structure determination of a cyclohexyl cyclohexanecarboxylate. For a comparison of the observed molecular structure of CECPC with suitable examples from the literature, only structures containing only one of the two structural fragments – cyclohexanecarboxylate ($C_6H_{11}COO-$) and cyclohexyl ester moieties ($-COOC_6H_{11}$) – are available. The phenyl cyclohexanecarboxylate moiety is a well known component of mesogens whose structures have already been studied in detail [e.g. 4-cyanophenyl 4-*n*-pentylcyclohexanecarboxylate = CPPCH (Baumeister, Hartung & Jaskólski, 1982)] whereas as an example of cyclohexyl esters only 4-*tert*-butylcyclohexyl 4-bromobenzoate [= BCHBB (Ohrt & Parthasarathy, 1972)] has been investigated until now.

The observed bond lengths and angles in CECPC agree well with corresponding values in CPPCH and BCHBB. This is also true for the somewhat short C(12)–O(2) and the rather long C(13)–O(2) bonds which in BCHBB were observed to be 1.341 and 1.472 Å, respectively. The C–H distances range from 0.89 (3) to 1.11 (3) Å with a mean of 1.01 (6) Å. Both cyclohexane rings in CECPC adopt chair conformations with mean values for the endocyclic torsion angles of 55.3 (9)° [ring I C(6)⋯C(11)] and 54.5 (2.0)° [ring II C(13)⋯C(18)] and are substituted equatorially in the 1,4-positions.

The orientation of the cyclohexane rings with respect to the carboxylic bridge can be expressed by the angles between the plane of the carboxylic group and the least-squares planes through atoms C(5), C(6), C(9), C(12) and O(2), C(13), C(16), C(19) bisecting the cyclohexane rings I and II, respectively. These interplanar angles are 49.1 and 21.2°. The angle between the two bisecting planes is 35.9° and bisecting plane I

makes an angle of 50.1° with the least-squares plane through the C atoms of the pentyl group. The conformation of the cyclohexyl cyclohexanecarboxylate skeleton may also be described by the three torsion angles C(10)–C(9)–C(12)–O(1) –107.9 (3), C(9)–C(12)–O(2)–C(13) –168.2 (3) and C(12)–O(2)–C(13)–C(14) –106.5 (3)°.

It can be seen from Fig. 1 that the CECPC molecule is nearly fully stretched as expected for a classical rod-like mesogen. The pentyl chain is in an all-*trans* conformation. A significant deviation from an optimum stretching arises from the conformation of the cyanoethylene group. The torsion angle C(16)–C(19)–C(20)–C(21) lies with –57.7 (4)° in the *gauche* region and is in contrast to the ideal value of 180.0 (7)° observed in the analogous phenyl compound 4-(2-cyanoethyl)phenyl 4-*n*-pentoxybenzoate (Baumeister, Brandt, Hartung & Jaskólski, 1983).

The striking feature of the molecular packing illustrated in Fig. 2 is the perfectly parallel alignment of the molecular long axes with an antiparallel orientation of neighboring molecules generated by the space-group symmetry. In addition, a discrete layered arrangement (in the sense of smectic layers) can be recognized. The layer planes are parallel to (001) and the long axes of the molecules are strongly inclined to the layer normals.

From non-bonded contacts between the cyano groups of molecules related by an inversion center [C(21)⋯N 3.514 (5), C(21)⋯C(21) 3.499 (5), N⋯N 3.872 (5) Å] it would seem that there is no remarkable interaction between opposed cyano dipoles in the crystal structure. Furthermore, all other intermolecular non-H atomic distances are greater than the sums of the appropriate van der Waals radii and the shortest N⋯H, O⋯H, C⋯H and H⋯H distances are consistent with the normal van der Waals type of contact.

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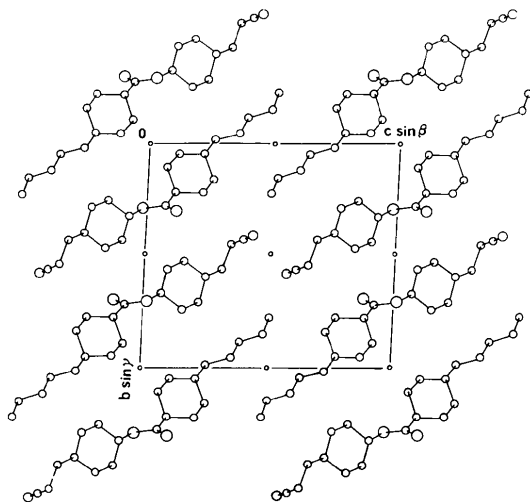


Fig. 2. Molecular packing of CECPC projected along [100].