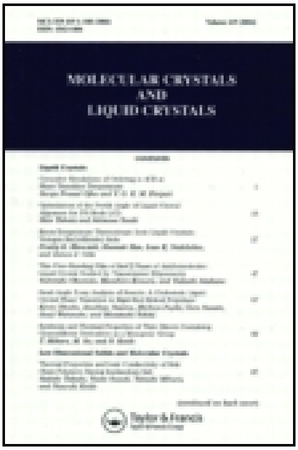

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Conformational Behaviour of the Nematogenic Compound 4-Cyanophenyl-trans-4-[(trans-4-n-butylcyclohexyl)methyl]-cyclohexanoate—Crystal Structure and Theoretical Conformational Analysis

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Conformational Behaviour of the Nematogenic Compound 4-Cyanophenyl-*trans*-4-[(*trans*-4-*n*-butylcyclohexyl)methyl]-cyclohexanoate—Crystal Structure and Theoretical Conformational Analysis

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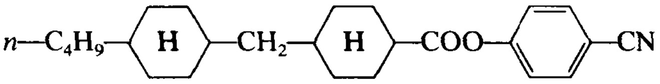
The title compound, with the formula C_4H_9—C_6H_{10}—CH_2—C_6H_{10}—COO—C_6H_4CN (CBMC), crystallizes in the monoclinic space group $P2_1/n$ with a = 6.4075(7) Å, b = 18.345(2) Å, c = 19.423(2) Å, β = 98.614(9) ° and four molecules per unit cell. The structure was solved by direct methods and refined to R = 0.052. The CBMC molecules adopt an elongated banana-shaped form enabling the formation of a monotropic nematic phase 2 degrees below the melting point.

The X-ray experiments were complemented by a conformational analysis of the phenyl-4-cyclohexylmethyl-cyclohexanoate moiety using the EPEN/2 method. The molecular structure existing in the crystal (and probably also in the mesophase) agrees very well with the most stable conformation indicated by calculation. In the conformational analysis the molecular length:width ratio was also taken into consideration.

The synthesis of CBMC, which represents a new type of mesogen, is described.

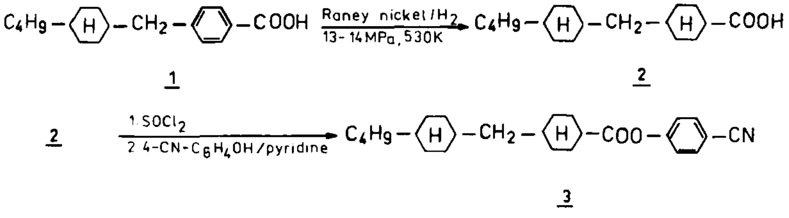
INTRODUCTION

This paper describes the continuation of our previous studies of the conformational behaviour of mesogenic compounds.[1] The most probable conformation (or conformations) of a given molecule can be calculated by a theoretical conformational analysis. In general it is straight forward to use X-ray structure analysis to determine the actual conformation of a molecule "embedded" in a crystal lattice. Quite often, however, it is difficult to obtain detailed information about the conformation of more extended molecules in liquids and in liquid crystals. Therefore, it is tempting to assume that the conformation derived for the isolated molecule or for the crystalline state occurs in the mesophase also. It has been demonstrated, however, that this assumption is questionable and is valid only if the most stable conformation (or one of the most stable conformations) calculated for the free molecule corresponds to the molecular conformation found for the solid state.[2] For this reason we have complemented the X-ray analysis of the title compound,



(abbreviated CBMC in the following) by a theoretical conformational analysis.

The hitherto unknown CBMC[3] was prepared according to the following scheme:[4]



Both *2* and *3* were obtained as mixtures of their *cis*- and *trans*-isomers, the separation of the isomers achieved by recrystallisation.

CBMC forms a monotropic nematic mesophase 2 degrees below the melting point of 383 K. Such behaviour is somewhat surprising when the chemical formula is considered, since the methylene bridge between the two cyclohexane rings should cause a bend of the molecular long axis and there is also a substantial flexibility of the molecule, and both of these factors are, to a certain degree, inconsistent with the classical model of rod-shaped molecules commonly accepted for nematogenic compounds.

The phenylcyclohexanoate moiety of the CBMC molecule is a well known component of mesogens[5] whose conformation has been already studied,[6] the dicyclohexylmethane moiety on the other hand is a novel component in the field of mesogenic compounds. A search of the literature for structures containing this fragment retrieved only one compound[7] which will be discussed below.

EXPERIMENTAL

Preparation

4-(4-n-butylcyclohexyl)methyl-cyclohexane carboxylic acid (2)

4-(4-n-butylcyclohexyl)methylbenzoic acid *(1)* (27.5 g, 0.1 mol) in 10% aqueous KOH (150 cm^3) was shaken together with Raney nickel (40 g alloy) in a 1 l autoclave at a hydrogen pressure of 13–14 MPa and 530 K for about 80 hours. Then the catalyst was filtered off and the hot solution was acidified by the addition of conc. HCl. The product was extracted with diethyl ether and the solution washed with water and dried with Na_2SO_4. After evaporation of the solvent 24 g of *2* were yielded in the form of a mixture of the *cis-* and *trans*-isomers. This crude product was used, without purification, in the preparation of *3*. A sample of crude *2* was recrystallized from *n*-hexane to give the pure all-*trans* isomer *2a* exhibiting the following phase transitions: K 380 N (378) I (temperatures in K).

4-Cyanophenyl-*trans*-4-[(*trans*-4-n-butylcyclohexyl)methyl]-cyclohexanoate (CBMC, *3a*)

A solution of 4-cyanophenol (0.72 g, 6 mmol) in dry pyridine (15 cm^3) was added to the acid chloride (1.90 g, 6 mmol) formed by the action of $SOCl_2$ on *2*. After standing at room temperature for about 15 hours the reaction mixture was poured into a mixture of crushed ice (200 g) and conc. HCl (20 cm^3). Then *3* was extracted with diethyl ether and the solution was washed with 1 M HCl, 1 M KOH and water and dried with Na_2SO_4. After evaporation of the solvent and recrystallization from ethanol 0.9 g of the pure *3a* were yielded. Phase transitions: K 383 N (381) I.

Formulae and chemical constitution of the new compounds *2* and *3* were confirmed by their analytical data and IR spectra. The phase transitions were determined using a polarizing microscope in conjunction with a Boetius heating stage.

X-ray measurements

CBMC forms colourless needle-shaped crystals. Preliminary unit cell parameters and the space group were determined from oscillation and Weissenberg photographs. All other X-ray experiments were performed on a Syntex $P2_1$ four circle diffractometer using graphite-monochromatized CuKα radiation and a crystal with dimensions 0.12 x 0.24 x 0.35 mm. Precise lattice parameters were obtained by a least-squares fit of the setting angles of 15 counter reflections. Their values together with other relevant crystal data are given in Table I. A total of 2840 unique reflections ($2\theta \leq 115°$) were measured as previously described[8] and 1865 of them (65.7%) with $|F| > 3.92\ \sigma(F)$ were treated as observed and used in the structure analysis. The Lp correction was applied in the usual way but absorption and extinction effects were ignored.

TABLE I

Crystal data

4-Cyanophenyl-4-[(4-n-butylcyclohexyl)methyl]-cyclohexanoate (CBMC)	
$C_{25}H_{35}NO_2$	M.W. = 381.5
M.p. = 383 K	
Monoclinic	
Space group $P2_1/n$	
a = 6.4075(7) Å	Z = 4
b = 18.345(2) Å	D_c = 1.12 g.cm^{-3}
c = 19.423(2) Å	F(000) = 832
β = 98.614(9) °	μ(CuKα) = 4.7 cm^{-1}
V = 2257.3(4) Å^3	

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods and completed by Fourier calculations. All hydrogen atoms were located from a difference electron density map. Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms and fixed positional and isotropic thermal parameters for hydrogen atoms led to the final R = 0.052. For the last cycles of refinement 8 reflections with large $\|F_o|-|F_c\|/\sigma(F)$ were excluded. The maximum shift/sigma ratio in the final refinement was 0.06. Max. and min. heights in the final Fourier difference map were 0.174 and −0.188 e.Å^{-3}, respectively. Unit weights were used throughout the refinement.

The structure solution and refinement and the subsequent geometric calculations were performed on an ESER 1040 computer of the Halle University using programs PRARA,[9] SHELX 76,[10] GEOME[11] and PLANE[12] of the CRYPOZ library.[13]

Final atomic parameters are presented in Table II. Lists of structure factors, anisotropic thermal parameters and H atom parameters are available from the German authors on request.

TABLE II

Final fractional coordinates (× 10^4) and isotropic equivalents (× 10^3) of the anisotropic thermal parameters for the nonhydrogen atoms
$U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C(1)	−8153(8)	64(3)	−2325(2)	101(2)
C(2)	−5940(7)	28(2)	−1925(2)	75(2)
C(3)	−5544(6)	612(2)	−1365(2)	62(1)
C(4)	−3301(6)	588(2)	−970(2)	67(2)
C(5)	−2727(5)	1223(2)	−471(2)	57(1)
C(6)	−410(6)	1181(3)	−146(2)	81(2)
C(7)	231(6)	1785(2)	377(2)	76(2)
C(8)	−1121(5)	1810(2)	952(2)	56(1)
C(9)	−3411(6)	1884(3)	611(2)	73(2)
C(10)	−4080(5)	1272(2)	101(2)	68(2)
C(11)	−486(6)	2413(2)	1481(2)	61(1)
C(12)	1717(5)	2347(2)	1911(2)	56(1)
C(13)	1969(6)	1643(2)	2328(2)	67(2)
C(14)	4109(6)	1579(2)	2790(2)	66(2)
C(15)	4536(5)	2239(2)	3270(2)	56(1)
C(16)	4370(6)	2940(2)	2840(2)	65(2)
C(17)	2202(6)	2997(2)	2396(2)	65(2)
C(18)	6668(7)	2153(2)	3704(2)	64(2)
C(19)	8419(6)	1374(2)	4606(2)	60(2)
C(20)	8340(6)	1306(2)	5299(2)	66(2)
C(21)	10046(6)	1008(2)	5726(2)	70(2)
C(22)	11804(6)	788(2)	5445(2)	61(1)
C(23)	11863(6)	861(2)	4740(2)	73(2)
C(24)	10145(7)	1150(2)	4315(2)	71(2)
C(25)	13610(7)	474(2)	5889(2)	73(2)
N	15054(6)	232(2)	6229(2)	92(2)
O(1)	8265(5)	2464(2)	3640(2)	89(1)
O(2)	6573(4)	1622(1)	4196(1)	70(1)

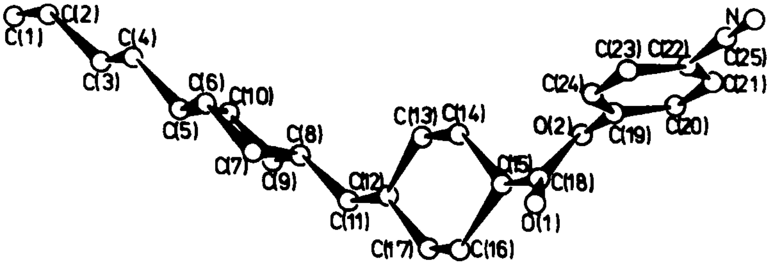


FIGURE 1 Molecular structure of CBMC projected along [010] with atom numbering scheme

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Molecular structure

The essential structural and conformational features of the CBMC molecule are given in Figure 1 and in Tables III and IV. The observed bond lengths and angles for the non-hydrogen atoms are quite normal and agree very well with standard values. The C—H distances range from 0.92 to 1.16 Å (mean 1.02(7)Å) with the exception of 0.77 Å for C(1)—H(13) in the terminal methyl group.

For a more detailed discussion of the molecular geometry it is useful to begin with separate considerations of the cyanophenylcyclohexanoate moiety and the butyl-substituted dicyclohexylmethane moiety which are two overlapping fragments of the CBMC molecule (common cyclohexane ring II). A comparison of the former moiety with the related compound 4-cyanophenyl-4-n-pentylcyclohexanoate (CPPCH)[6] reveals an excellent agreement (within 3σ) of all corresponding bond lengths and angles. Moreover, the conformations are rather similar, too. This is obvious from a comparison of the torsion angles for the carboxylic group in CBMC and CPPCH. Listed in the same order as for CBMC in Table IV, the values for CPPCH are 96.2, −24.6, −80.1, 159.1, 168.2, −8.3, 120.1, and −64.5°. As stated in the introduction, until now no structural data for the dicyclohexylmethane group have been reported apart from the structure of 1,1,2,2-tetracyclohexylethane.[7] This compound, however, is hardly comparable with CBMC. The Cy—C—Cy bond angle in it is 115.2° which is virtually the same value as that observed for C(8)—C(11)—C(12) in CBMC, but its conformational behaviour is strongly influenced by internal strain and is fixed by steric demands and is therefore quite different from that of CBMC. For the above-mentioned reason the torsion angles which describe the conformation

TABLE III

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

Atoms	Distance (Å)	Atoms	Angle (°)
	Alkyl group		
C(1)—C(2)	1.513(6)	C(1)—C(2)—C(3)	112.3(4)
C(2)—C(3)	1.521(5)	C(2)—C(3)—C(4)	112.5(3)
C(3)—C(4)	1.525(5)	C(3)—C(4)—C(5)	114.6(3)
C(4)—C(5)	1.525(5)		
	Cyclohexane ring I		
C(5)—C(6)	1.526(5)	C(4)—C(5)—C(6)	110.6(3)
C(6)—C(7)	1.518(6)	C(4)—C(5)—C(10)	113.8(3)
C(7)—C(8)	1.513(5)	C(5)—C(6)—C(7)	112.9(3)
C(8)—C(9)	1.522(5)	C(6)—C(7)—C(8)	112.9(3)
C(9)—C(10)	1.515(5)	C(7)—C(8)—C(9)	107.6(3)
C(10)—C(5)	1.512(5)	C(7)—C(8)—C(11)	113.3(3)
		C(11)—C(8)—C(9)	111.9(3)
		C(8)—C(9)—C(10)	112.3(3)
		C(9)—C(10)—C(5)	112.8(3)
		C(10)—C(5)—C(6)	109.2(3)
	Methylene group		
C(8)—C(11)	1.522(5)	C(8)—C(11)—C(12)	116.2(3)
C(11)—C(12)	1.533(5)		
	Cyclohexane ring II		
C(12)—C(13)	1.520(5)	C(11)—C(12)—C(13)	111.8(3)
C(13)—C(14)	1.527(5)	C(11)—C(12)—C(17)	111.2(3)
C(14)—C(15)	1.527(5)	C(12)—C(13)—C(14)	113.2(3)
C(15)—C(16)	1.528(5)	C(13)—C(14)—C(15)	111.1(3)
C(16)—C(17)	1.526(5)	C(14)—C(15)—C(16)	110.0(3)
C(17)—C(12)	1.522(5)	C(14)—C(15)—C(18)	108.9(3)
		C(18)—C(15)—C(16)	112.2(3)
		C(15)—C(16)—C(17)	110.4(3)
		C(16)—C(17)—C(12)	112.4(3)
		C(17)—C(12)—C(13)	109.8(3)
	Carboxylic group		
C(15)—C(18)	1.503(5)	C(15)—C(18)—O(1)	127.9(4)
C(18)—O(1)	1.194(4)	C(15)—C(18)—O(2)	109.5(4)
C(18)—O(2)	1.374(4)	O(1)—C(18)—O(2)	122.6(4)
O(2)—C(19)	1.399(4)	C(18)—O(2)—C(19)	120.3(3)
	Phenyl ring		
C(19)—C(20)	1.360(5)	O(2)—C(19)—C(20)	116.1(4)
C(20)—C(21)	1.382(5)	O(2)—C(19)—C(24)	121.7(3)
C(21)—C(22)	1.383(6)	C(19)—C(20)—C(21)	119.1(4)
C(22)—C(23)	1.382(5)	C(20)—C(21)—C(22)	119.8(4)
C(23)—C(24)	1.380(5)	C(21)—C(22)—C(23)	120.5(3)
C(24)—C(19)	1.378(5)	C(21)—C(22)—C(25)	120.3(4)
		C(25)—C(22)—C(23)	119.2(4)
		C(22)—C(23)—C(24)	119.5(4)
		C(23)—C(24)—C(19)	119.1(4)
		C(24)—C(19)—C(20)	122.0(4)
	Cyano group		
C(22)—C(25)	1.455(6)	C(22)—C(25)—N	178.6(5)
C(25)—N	1.143(5)		

TABLE IV

Selected torsion angles (angles measured in a clockwise sense)

Atoms	Angle (°)	Atoms	Angle (°)
Methylene group		Carboxylic group	
C(7)—C(8)—C(11)—C(12)	−64.2(4)	C(14)—C(15)—C(18)—O(1)	105.2(4)
C(9)—C(8)—C(11)—C(12)	173.9(3)	C(16)—C(15)—C(18)—O(1)	−16.8(4)
C(8)—C(11)—C(12)—C(13)	−59.4(4)	C(14)—C(15)—C(18)—O(2)	−72.5(4)
C(8)—C(11)—C(12)—C(17)	177.4(4)	C(16)—C(15)—C(18)—O(2)	165.5(4)
		C(15)—C(18)—O(2)—C(19)	171.7(4)
		O(1)—C(18)—O(2)—C(19)	−6.1(4)
		C(20)—C(19)—O(2)—C(18)	134.6(4)
		C(24)—C(19)—O(2)—C(18)	−51.0(4)

of the dicyclohexylmethane moiety (see Table IV) are of special interest. A detailed discussion of the conformational behaviour of both structural components of CBMC is given in the last section of this paper.

As can be seen in Figure 1, the CBMC molecule has a marked banana shape. The bend of the molecular long axis can be described by an arbitrarily defined bend angle C(1)—centre—N between the lines connecting the centre of the cyclohexane ring II C(12). . .C(17) with the two ends of the molecule. This bend angle has a value of 137° for CBMC. The analogously defined angle in CPPCH (C(1) is here the terminal atom of the pentyl group) amounts 149°. (More correctly this value should be compared with the angle C(5)—centre—N = 138° instead of C(1)—centre—N in CBMC because C(5) corresponds in its distance from the centre to C(1) in CPPCH, but this distinction is trivial, bearing in mind the similarity of the values for the two angles.) The comparison just drawn suggests that the bend of the CBMC molecule is mainly caused by the cyanophenylcyclohexanoate moiety with only minor influence of the butylcyclohexylcyclohexylmethane moiety. This experimental finding confirms the result obtained from model considerations, that an insertion of a 1,4-equatorial cyclohexane moiety into an alkyl chain between its α, β atoms doesn't cause a substantial additional bend of the molecular long axis.

Crystal structure

Figure 2 illustrates the molecular packing of CBMC in a perspective stereoscopic drawing. The packing mode closely resembles that of CPPCH.[6] In both cases the crystals contain corrugated sheets of molecules. The sheets (built up of molecules related by *a* and *c* trans-

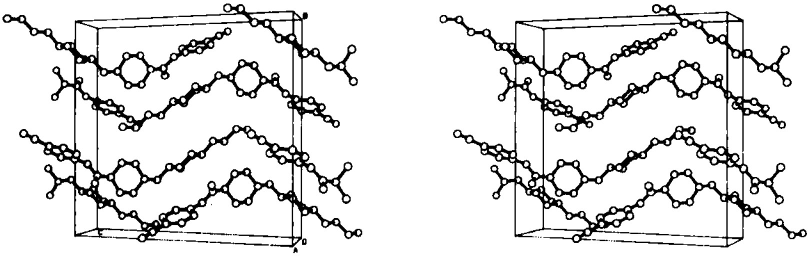


FIGURE 2 Perspective stereoscopic PLUTO plot of molecular packing in CBMC

lations) are stacked on top of one another in the *b* direction by the action of the corresponding space group symmetry elements, i.e. the inversion centre and n-glide plane in the case for CBMC and only the inversion centre in the case of CPPCH.

In the structure of CPPCH two different regions can be clearly discerned[6]: one comprises the benzene rings with the adjacent polar cyano and carboxylic groups while the other contains the non-polar hydrocarbon groups. In CBMC this local separation does not exist due to the action of the additional n-glide planes.

In Figure 3 (crystal structure viewed along [010]) the bent shape of the CBMC molecules is much less evident and the parallel arrangement of the molecular long axes (characteristic of most nematogens) is obvious.

All intermolecular contacts between non-hydrogen atoms are greater than the sums of the corresponding van der Waals radii.

CONFORMATIONAL ANALYSIS

As pointed out in the introduction, conformational studies of the CBMC molecule were performed in order to determine whether the confirmation found in the solid state represents a stable state of the free molecule too. They were aimed also at the determination of the barriers to rotate around selected bonds to give an indication of the molecular flexibility. Additionally the length:width ratio for the most stable conformers was calculated in order to estimate the relevance of this parameter.

Method

Similarly to the case of phenylbenzoate,[1] the calculations were made using the EPEN/2 (Empirical Potential Based on the Interaction of

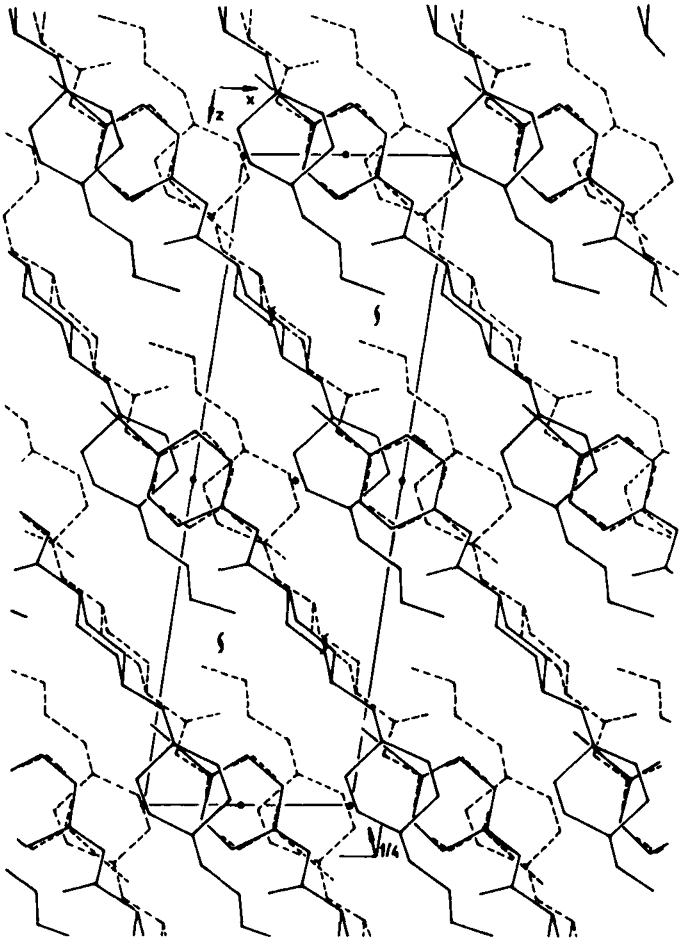


FIGURE 3 Crystal structure of CBMC projected along [010] (dashed lines: molecules within the region y = 0 to 1/2, full lines: molecules within the region y = 1/2 to 1)

Electrons and Nuclei) method. In this method, developed by Scheraga *et al.*[14], electrons and nuclei are treated as potential centers contributing to an empirical potential function. The EPEN/2 method has been found to give conformational data with good accuracy for larger molecules also.

As the basis for the conformational analysis, standard bond lengths and angles were used. The calculations were performed with full consideration of the 1—4 interactions.[15]

Assuming that the cyclohexane rings are in the chair form with equatorial substituents, the conformation of the dicyclohexyl-methane moiety can be characterized by two torsion angles: τ_1 = C(7)—C(8)—C(11)—C(12) and τ_2 = C(8)—C(11)—C(12)—C(13) (atom labelling refers to Figure 1). Simultaneous variation of these angles yielded a conformational map (isoenergy contour map) from which the most stable conformations were gathered. The minima approximately determined by this way were then refined up to 0.5° for both angles.

For the conformational characterization of the phenylcyclohexanoate moiety the three torsion angles α = C(14)—C(15)—C(18)—O(1), β = C(19)—O(2)—C(18)—O(1) and γ = C(18)—O(2)—C(19)—C(24) were used. In order to reduce the number of variables, the torsion angle β was held at constant values of 10, 0 and $-10°$, and for these discrete values and selected τ_1, τ_2-pairs the α, γ-conformational maps of the phenyl-4-cyclohexylmethyl-cyclohexanoate moiety were computed. Finally, the τ_1, τ_2, α and γ coordinates of the energy minima were refined to 0.5°.

The length:width ratios for both the experimentally determined molecular conformation and for the calculated conformers were investigated using a local computer program.[16] (In these calculations the molecular length was defined as the axis of minimum moment of inertia).

Results and discussion

The τ_1, τ_2-conformational map for the isolated dicyclohexyl-methane moiety is depicted in Figure 4. It exhibits two mirror lines: one of these (running from the left bottom to the right top corner) results from the equivalence of the two cyclohexyl groups, the other is due to the symmetry of the cyclohexyl ring. Because of this symmetry only two of the four local minima marked by crosses in Figure 4 are unique. The refined values for these two most stable conformations (denoted by 1 and 2) and their symmetry equivalents (1′ and 2′) together with the corresponding values for the CBMC molecule are listed in Table V, and conformation 1 is illustrated in Figure 5. It is clearly apparent that the dicyclohexylmethane conformation in the crystal is nearly identical with the low energy conformation 1. For transitions between conformation 1 and conformation 2 an energy of about 35 kJ.mol^{-1} is required.

Starting from conformation 1 and its symmetry equivalent 1′ conformational maps for the phenyl-4-cyclohexylmethyl-cyclohexanoate moiety were computed by variation of α and γ and restriction of β to 10, 0 and $-10°$. Because the conformational energy was proved

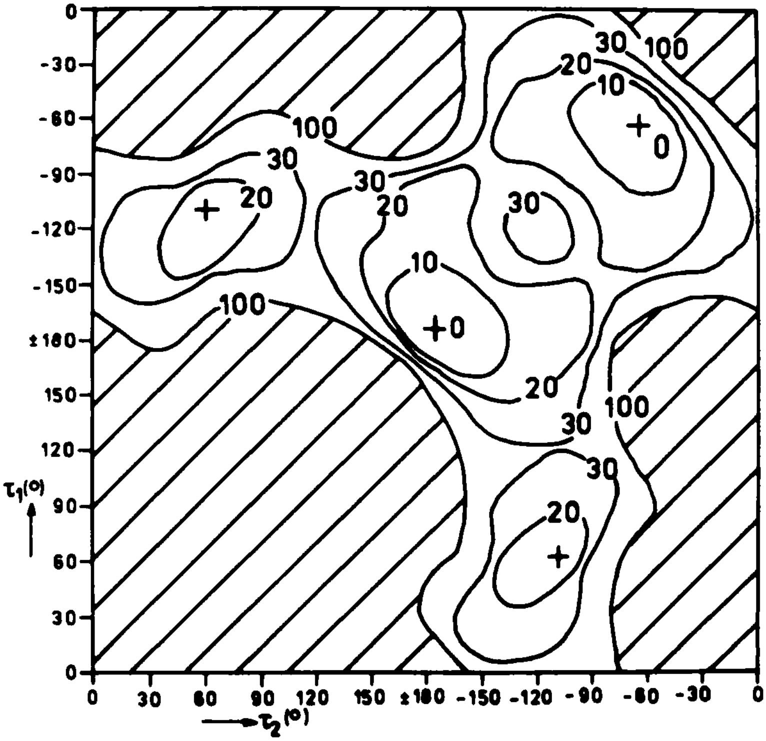


FIGURE 4 Conformational map of the dicyclohexylmethane moiety. Isoenergy contours in kJ.mol^{-1} with respect to the minimum energy as the zero level, hatching covers energies greater than 50 kJ.mol^{-1}, crosses denote local minima

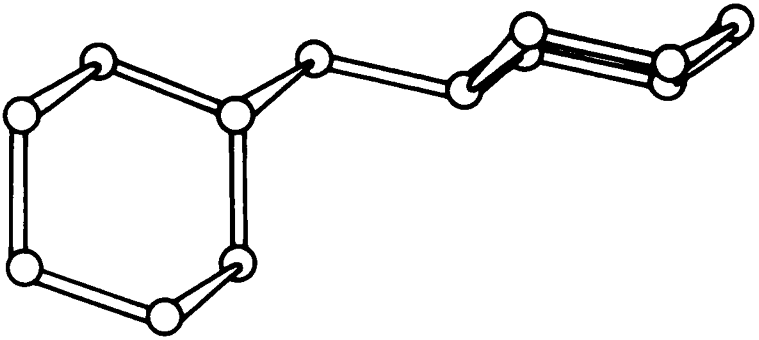


FIGURE 5 The most stable conformation of the dicyclohexyl-methane moiety ($\tau_1 = \tau_2 = -62.1°$)

TABLE V

Most stable conformations of the dicyclohexylmethane moiety

Conformation	Torsion angle (°) τ_1	Torsion angle (°) τ_2	Energy (kJ.mol^{-1})
1	−62.1	−62.1	0
1′	−174.1	−174.1	0
2	−108.5	62.5	17.4
2′	62.5	−108.5	17.4
CBMC	−64.2	−59.4	1.2

to be largely independent of β with only a slightly marked minimun for β = −10°, in the following discussion only the conformations with this value will be considered. Although the exact symmetry-equivalence of the two cyclohexyl rings within the phenyl-4-cyclohexylmethyl-cyclohexanoate moiety is broken, the conformational maps for conformations 1 and 1′ are practically identical. Therefore, in Figure 6 only the map for conformation 1 is shown. This exhibits two kinds of symmetry.

The first concerns to the torsion angle γ and is an exact mirror symmetry arising from the symmetry of the phenyl ring. The second, referring to the torsion angle α is in consequence of the influence of both the phenyl ring and the cyclohexane ring I upon the interaction between cyclohexane ring II and the carboxylic group and is only approximate. In both α, γ-maps three significant local minima a, b and c may be recognized. The refined values for all six energy minima

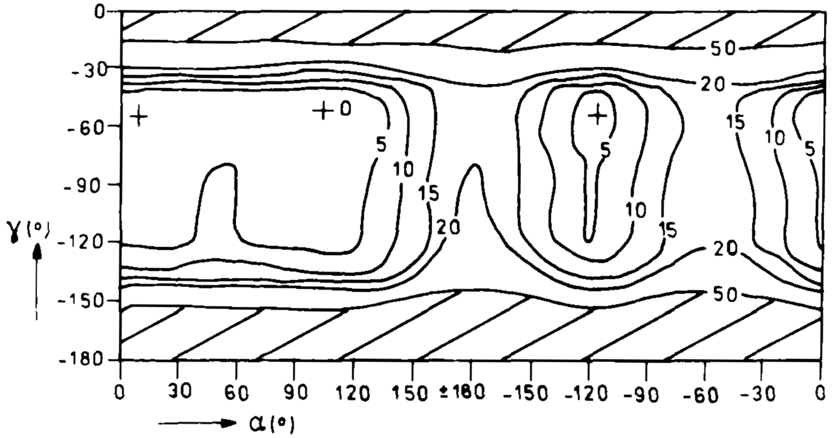


FIGURE 6 Conformational map of the phenylcyclohexanoate moiety (representation of conformational energies as in Figure 4)

TABLE VI

Most stable conformations of the phenyl-trans-4-cyclohexylmethyl-cyclohexanoate moiety (the molecular dimensions refer to the molecular skeleton including the cyano and butyl substituent)

Conformation	Torsion angles (°)					Energy	Molecular dimensions		
	τ_1	τ_2	α	β	γ	(kJ.mol^{-1})	Length l (Å)	Width w (Å)	l/w
1'a	−173.4	−174.6	101.8	−10.0†	−53.4	0	23.75	10.30	2.31
1a	−61.4	−63.2	102.7	−10.0†	−53.0	1.3	23.94	9.64	2.48
1b	−63.1	−63.7	11.3	−10.0†	−53.5	1.7	25.17	8.14	3.09
1'b	−169.8	170.0	9.1	−10.0†	−55.4	1.7	23.30	10.67	2.18
1'c	−173.6	−174.5	−116.8	−10.0†	−55.7	3.3	21.11	12.26	1.72
1c	−64.0	−62.3	−119.3	−10.0†	−55.3	4.4	23.57	9.29	2.54
CBMC	−64.2	−59.4	105.2	−6.1	−51.0	2.1	23.82	9.80	2.43

† not refined

1a. . .1′c are listed in Table VI. The results obtained can be interpreted as follows. The mutual influence of the dicyclohexylmethane and phenylcyclohexanoate moieties upon each other's conformation can be neglected. The six most stable conformations have nearly the same energy (the differences are less than 4.5 kJ.mol^{-1}) but they are separated by rather different energy barriers. The transition requiring minimum energy (3 kJ.mol^{-1}) is that between conformations a and b whereas for transitions a—c and b—c 18 and 16 kJ.mol^{-1}, respectively, are necessary. Generally, transitions between the most stable conformations within the carboxylic bridge require significantly less energy than those within the methylene bridge. Therefore, the flexibility of the CBMC molecules in the mesophase should be largely due to conformational transitions at the carboxylic bridge.

Table VI shows that the conformer of CBMC existing in the crystalline state corresponds almost exactly to the low-energy conformation 1a of the isolated molecule. Apparently the addition of the butyl chain and the cyano group does not influence the conformational behaviour in a noticeable way. This remarkable result justifies the assumption that this conformation is also present in the intermediate phases between the solid and gaseous states, namely in the liquid and liquid crystalline phases. The interpretation of the calculated length:width ratios (l/w), listed in Table VI, is not obvious. The use of the l/w values as a measure of the probability that a given conformation exists in the mesophase rests on the assumption that its magnitude is proportional to the number of intermolecular contacts. From this point of view the most stable conformation in the mesophase should be 1b whereas 1a and the conformation found to exist in the crystal would be placed in the middle of the series. It should be emphasized that such conclusions can only be drawn with caution until enough data have been collected to verify the underlying assumption.

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