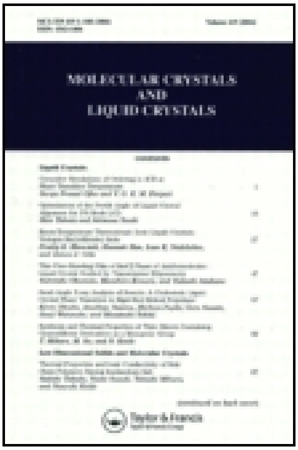

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Solid State Polymorphism of Mesogenic Cholesteryl Benzoate

A. P. Polishchuk [a] , V. I. Kulishov [a] , T. V. Tiomofeeva [b] , M. Yu. Antipin [b] & Yu. T. Struchkov [b]

[a] Institute of Physics, Academy of Sciences of Ukrainian S.S.R., 144 Prospect Nauki, Kiev, 28, U.S.S.R.

[b] A. N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the U.S.S.R., 28 Vavilov St., Moscow, B-334, U.S.S.R.

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Solid State Polymorphism of Mesogenic Cholesteryl Benzoate

A. P. POLISHCHUK and V. I. KULISHOV

*Institute of Physics, Academy of Sciences of Ukrainian S.S.R.,
144 Prospect Nauki, Kiev-28, U.S.S.R.*

and

T. V. TIMOFEEVA,† M. Yu. ANTIPIN and Yu. T. STRUCHKOV

A. N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the U.S.S.R., 28 Vavilov St., Moscow B-334, U.S.S.R.

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Crystal and molecular structures of two (of six known) solid polymorphs of mesogenic cholesteryl benzoate have been determined. Crystals of the modification 1 are monoclinic, space group C2, $z = 4$, $a = 19.51(1)$, $b = 6.0668(1)$, $c = 27.828(2)$ Å, $\beta = 116.447(4)°$. Crystals of the modification 2 are orthorhombic, space group $P2_12_12_1$, $z = 4$, $a = 5.9404(5)$, $b = 9.4728(7)$, $c = 53.772(5)$ Å. Comparison of molecular structures of 1 and 2 and the recently investigated tetragonal modification 3 reveals significantly different molecular conformations. Physically valid treatment of molecular packing mode in the polymorphs 1–3 was fulfilled on the basis of intermolecular energy calculations and allowed some speculations on the structure of liquid crystalline phase.

INTRODUCTION

For the first time the liquid crystalline state was discovered by Reinitzer[1] (in 1888) and Lehman,[2] who investigated cholesteryl benzoate (CB). Most of all subsequent investigations of this compound were concerned just with the study of liquid crystalline state. However, a very valuable information on the nature of mesophase can be obtained from a study of solid state (crystal) structure of this compound. Lately

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†To whom correspondence should be sent.

X-ray structural studies of mesogenic crystals attract much attention, because according to Bernal and Crowfoot[3] molecular packing in such crystals involves some structural features, which can be retained in corresponding mesophases. X-ray studies of single crystals allows also to obtain information on molecular structure and the nearest molecular environment, whereas structural investigations of mesophases provide information on cybotactic groups, consisting of a large number of molecules. The calculations of energy of intermolecular interactions on the basis of X-ray data on crystal structure of mesogenes also seems to be useful, as such calculations enable to draw some conclusions on degrees of freedom of molecules, arising on phase transitions solid crystal→liquid crystal.

It is well known that very often mesogenic compounds have several solid polymorphs,[4,5] but only in a few cases crystal structures of all polymorphs of the given compound are investigated. Earlier we reported the structures of two solid modifications of cholest-5-en-3-ol-m-bromobenzoate.[6,7] The series (scheme) of CB phase transitions was carefully investigated by the means of DSC and IR-spectroscopy.[5] Therefore it was interesting to establish the relations between this scheme and crystal data of polymorphs. In the present paper we have carried out an X-ray study of two of six known[5] solid polymorphs of CB, viz. monoclinic (1) and orthorhombic (2). The structure of tetragonal (3) (Table 1) was reported previously.[8] The energy of pair intermolecular interactions (EPIMI) in crystals 1–3 was also calculated (the sum of such energies over all interactions is equal to the potential energy of crystal). In the present paper the results of investigation of solid polymorphs 1–3 are discussed as a basis for the analysis of molecular organization in liquid crystalline phase of CB.

EXPERIMENTAL

Crystals of 1 and 2 for an X-ray study and differential scanning calorimetry (DSC) were obtained by slow evaporation of solution in the mixture of benzene, propanol and chloroform (1:1:1). Monoclinic crystals of 1 are elongated prisms, orthorhombic crystals of 2 are plates. The relevant crystal data are given in Table 1. Cell dimensions and reflection intensities were measured with a Hilger and Watts four-circle autodiffractometer (graphite-monochromated CuKα radiation, $\theta/2\theta$ scan, $2° \leq 2\theta \leq 114°$).

Both structures were solved by the direct method (MULTAN program) and refined by the anisotropic block-diagonal least-squares

TABLE 1

Crystal data of CB solid polymorphs

N	Crystal system and space group	a(Å)	b(Å)	c(Å)	β°	z	R	V(Å)^3	^{d}calcd, g. cm^{-3}
1	Monoclinic C2	19.516(1)	6.0668(1)	27.828(2)	116.447(4)	4	0.071	2950.0(4)	1.11
2	Orthorhombic $P2_12_12_1$	5.9409(5)	9.4728(7)	53.772(5)	90	4	0.098	3026.1(8)	1.08
3	Tetragonal $P4_12_12$	10.520(3)	10.520(3)	54.42(2)	90	8	0.106	6023(6)	1.09
4	Orthorhombic $P2_12_12_1$ or $P22_12_1$	9.7	12.6	50.0	90	8	—	6111	1.07
5	Orthorhombic $P2_12_12_1$[15]	10.14	10.06	26.00	90	4	—	2652	1.228

TABLE 2A

Atomic coordinates of 1 multiplied by 1000

Atom	X	Y	Z	B11	B22	B33	B12	B13	B23
03	1471(2)	−934(6)	10558(1)	6.2(1)	5.1(2)	4.2(1)	0.9(1)	2.4(1)	−0.0(1)
028	1116(3)	2404(9)	10710(1)	12.8(3)	6.8(2)	5.9(2)	3.9(2)	4.0(2)	0.1(2)
C1	1167(2)	1057	9195(2)	5.3(2)	3.9(2)	5.1(2)	−0.9(2)	2.0(2)	−0.7(2)
C2	1574(3)	716(9)	9795(2)	5.8(2)	4.7(2)	4.8(2)	−1.0(2)	2.2(2)	−0.8(2)
C3	1072(2)	−542(9)	9982(2)	5.3(2)	4.8(2)	4.6(2)	0.4(2)	2.1(2)	−0.5(2)
C4	875(3)	−2800(9)	9711(2)	6.0(2)	4.8(2)	4.5(2)	−0.7(2)	2.1(2)	0.0(2)
C5	495(2)	−2570(8)	9107(2)	4.7(2)	3.8(2)	4.7(2)	−0.2(2)	2.6(1)	−0.0(2)
C6	−167(2)	−3580(9)	8814(2)	5.1(2)	4.6(2)	5.3(2)	−0.9(2)	2.6(2)	0.0(2)
C7	−568(2)	−3542(9)	8218(2)	4.7(2)	5.5(3)	5.2(2)	−1.3(2)	2.2(2)	−0.7(2)
C8	−117(2)	−2538(8)	7951(2)	4.0(2)	3.9(2)	4.6(2)	−0.5(2)	2.0(1)	−0.7(2)
C9	350(2)	−552(7)	8278(1)	3.6(1)	3.4(2)	4.1(2)	−0.6(1)	1.3(1)	−0.5(1)
C10	901(2)	−1139(7)	8867(1)	3.6(1)	3.8(2)	3.9(2)	−0.6(1)	1.4(1)	−0.2(1)
C11	748(2)	664(8)	7987(2)	4.9(2)	4.6(2)	4.4(2)	−1.7(2)	1.7(1)	−0.1(2)
C12	214(3)	1261(9)	7402(2)	5.5(2)	4.4(2)	4.4(2)	−0.9(2)	1.7(2)	0.0(2)
C13	−213(2)	−749(8)	7078(1)	4.1(2)	4.0(2)	3.8(2)	−0.1(2)	1.4(1)	−0.4(2)
C14	−638(2)	−1776(8)	7381(2)	4.1(2)	4.1(2)	4.2(2)	−0.4(2)	1.7(1)	−0.6(2)
C15	−1198(2)	−3406(10)	6992(2)	4.5(2)	5.5(3)	5.6(2)	−1.4(2)	1.3(2)	−1.1(2)
C16	−1443(2)	−2291(10)	6436(2)	4.7(2)	6.2(3)	4.9(2)	−0.8(2)	0.7(2)	−0.5(2)
C17	−906(2)	−301(8)	6517(2)	4.4(2)	4.6(2)	4.5(2)	0.5(2)	1.5(1)	−0.8(2)
C18	340(2)	−2391(10)	7014(2)	4.7(2)	5.7(3)	5.2(2)	0.7(2)	2.1(2)	0.0(2)

TABLE 2A (*continued*)

Atomic coordinates of 1 multiplied by 1000

Atom	X	Y	Z	B11	B22	B33	B12	B13	B23
C19	1608(2)	−2431(10)	8900(2)	4.6(2)	5.6(2)	5.4(2)	1.0(2)	2.2(2)	0.8(2)
C20	−760(3)	119(9)	6029(2)	6.6(2)	5.1(2)	3.8(2)	0.1(2)	1.7(2)	−0.6(2)
C21	−215(4)	2027(13)	6102(2)	9.4(3)	7.7(4)	5.5(2)	−1.7(3)	3.3(2)	0.2(3)
C22	−1521(3)	520(12)	5533(2)	7.5(3)	7.2(3)	4.4(2)	1.8(3)	1.5(2)	−0.3(2)
C23	−1494(3)	491(12)	4984(2)	8.8(3)	7.3(4)	4.5(2)	1.9(3)	2.2(2)	0.5(2)
C24	−1347(3)	−1759(12)	4824(2)	6.6(2)	6.8(3)	5.9(2)	0.3(3)	2.7(2)	0.1(2)
C25	−1211(4)	−1879(13)	4324(2)	9.7(3)	7.4(4)	5.5(2)	0.1(3)	2.8(2)	−0.4(3)
C26	−999(5)	−4167(18)	4238(3)	14.1(5)	10.1(6)	7.2(3)	3.1(5)	5.3(4)	−0.4(4)
C27	−1826(4)	−1009(20)	3855(2)	11.0(4)	15.2(8)	5.7(3)	5.1(6)	2.1(3)	−1.8(4)
C28	1463(3)	682(10)	10880(2)	6.7(2)	5.3(2)	5.3(2)	0.7(2)	3.4(2)	−0.7(2)
C29	1896(2)	157(10)	11448(2)	5.0(2)	6.0(3)	5.2(2)	−0.0(2)	3.0(2)	−1.0(2)
C30	2281(3)	−1829(10)	11641(2)	5.1(2)	6.5(3)	5.5(2)	1.0(2)	3.0(2)	−0.4(2)
C31	2678(2)	−2203(13)	12182(2)	4.7(2)	9.1(4)	5.6(2)	0.7(3)	2.3(2)	0.5(3)
C32	2697(3)	−658(15)	12543(2)	5.6(2)	10.7(5)	4.8(2)	−0.7(3)	2.0(2)	−0.9(3)
C33	2308(3)	1287(13)	12367(2)	8.4(3)	8.0(4)	5.7(2)	−0.4(3)	3.4(2)	−2.0(3)
C34	1926(3)	1734(11)	11829(2)	7.7(3)	5.8(3)	5.9(2)	0.5(3)	2.9(2)	−1.2(2)

Anisotropic temperature factors are given in the form:
$T = \exp[-\tfrac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}\,a^*b^*hk + 2B_{13}\,a^*b^*hl + 2B_{23}\,b^*c^*kl)]$

method (isotropic approximation was used for the C(20)-C(27)atoms in 2). Positions of H atoms in the structure 1, except for those in methyl groups, were calculated. Some H atoms of methyl groups were located in the difference map, which allowed the calculations of positions of the missing H atoms. All H atoms were included in refinement with fixed positional and isotropic temperature factors (B_{iso} = 6 Å^2). In the structure 2 hydrogen atoms of methyl groups were not located in the difference map. All other H atoms were included in refinement with fixed calculated positional and isotropic temperature factors (B_{iso} = 6 Å^2). The final R-factors are 0.071 and 0.098 for 1 and 2 respectively. All structural calculations were performed with an Eclipse S/200 computer using the INEXTL programs.[9] The geometry of molecules 1 and 2 with bond lengths is shown in Figures 1 and 2. The final positional parameters of nonhydrogen atoms, bond angles and torsion angles are given in Tables 2–4.

The EPIMI calculations were carried out in the atom-atom approximation with the potential 6-exp, using the local program with a BESM-6 computer, as was reported previously.[10] The lattice energy was evaluated by direct summation of the atom-atom interactions in the sphere of radius 20 Å. This ensured an accuracy in the lattice energy of the order of 1 per cent.

RESULTS AND DISCUSSION

Conformations of the steroid nucleus in crystals 1–3 are similar and typical for Δ^5-steroids. However, the molecules in crystals 1–3 display significant differences in the C(20)-C(22)-C(23)-C(24) torsion angles (69° in 1 and 179° in 2 and 3) and in the torsion angles around the ester C(3)-O(3) bond. The values of the C(2)-C(3)-O(3)-C(28) torsion angle (φ) are 83, 85° and 154° in 1, 2, and 3 respectively. The significant difference in the φ torsion angles is in a good agreement with our previous conformational calculations,[10] which have shown that the value of φ can vary from 80 to 160° without noticeable changes of conformational energy. Notably, such conformational variations, involving the relative reorientations of molecular parts around the long axis of the molecule, almost do not influence an anisometric molecular form, which is essential for formation of a mesophase.

The molecular packing mode is the most interesting feature of the solid polymorphs 1–3 (Figures 3–5). The molecular packing in 1 is characterized by an antiparallel imbrication. The molecules form the layers parallel to the *ab* plane, but the external parts of the C(17)-

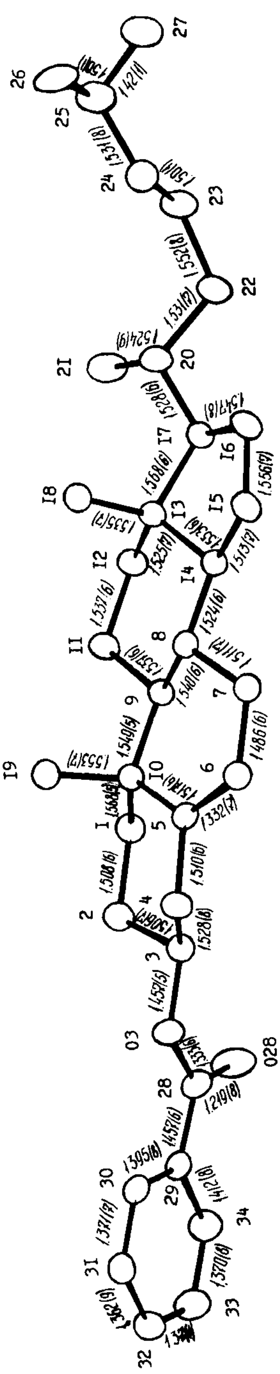

FIGURE 1 Bond lengths (Å) in molecule 1. Thermal ellipsoids are drawn to the 50% boundary level.

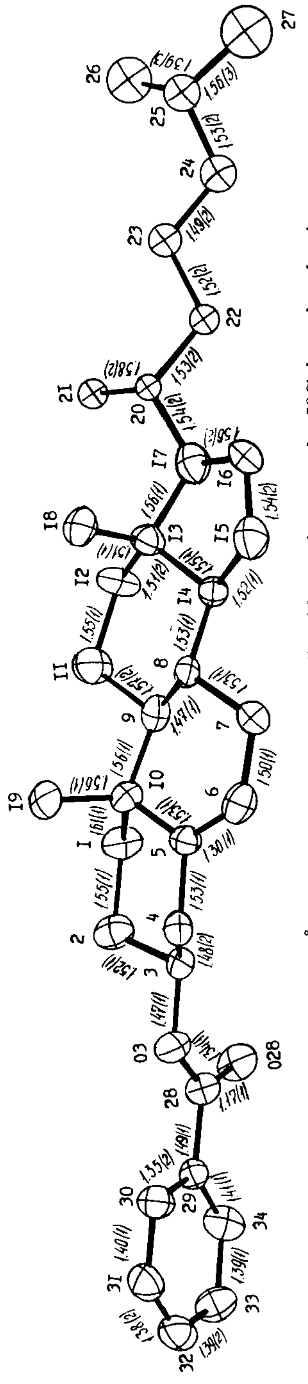

FIGURE 2 Bond lengths (Å) in molecule 2. Thermal ellipsoids are drawn to the 50% boundary level.

TABLE 2B

Atomic coordinates of 2 multiplied by 1000

Atom	X	Y	Z	B11	B22	B33	B12	B13	B23
03	2081(12)	913(7)	8007(1)	6.0(4)	3.9(3)	5.6(3)	0.5(4)	-0.4(3)	-0.4(3)
028	5446(12)	140(7)	8128(1)	4.8(4)	5.2(4)	8.1(4)	0.6(4)	-2.4(3)	-0.5(4)
C1	3665(15)	4547(11)	8241(2)	2.5(5)	4.7(5)	6.5(5)	-1.8(5)	1.8(5)	-1.0(5)
C2	3471(19)	3303(12)	8056(2)	4.5(6)	4.9(5)	7.0(6)	0.9(6)	-0.3(6)	-0.7(5)
C3	2248(20)	2096(10)	8183(2)	6.7(7)	3.5(5)	4.1(5)	-1.2(5)	0.2(5)	0.7(4)
C4	-64(19)	2522(10)	8255(2)	4.7(6)	5.1(6)	4.2(5)	0.5(6)	0.0(5)	0.9(5)
C5	-8(19)	3759(9)	8437(2)	4.9(5)	3.9(5)	3.9(4)	-0.2(5)	0.5(5)	-0.5(4)
C6	-948(19)	3693(10)	8654(2)	4.9(6)	4.9(5)	6.6(6)	-1.1(6)	0.5(5)	1.3(5)
C7	-958(20)	4825(11)	8849(2)	6.7(7)	5.2(6)	4.1(4)	0.0(6)	0.2(5)	-0.2(5)
C8	-89(18)	6241(9)	8750(1)	3.8(5)	3.6(4)	3.2(4)	1.0(5)	1.0(4)	0.6(4)
C9	1814(18)	6041(10)	8579(2)	4.5(6)	4.5(5)	4.5(5)	- -0.0(5)	-0.5(5)	1.1(4)
C10	1288(18)	5071(10)	8352(2)	6.2(6)	3.6(5)	4.9(5)	-0.4(6)	-0.3(5)	0.2(4)
C11	2929(24)	7454(12)	8491(2)	7.6(8)	6.1(6)	6.0(6)	-1.5(8)	2.0(6)	-0.7(6)
C12	3410(20)	8458(12)	8713(2)	5.1(6)	6.0(6)	5.3(5)	-0.9(6)	0.5(5)	-2.6(5)
C13	1396(19)	8689(10)	8880(2)	5.0(6)	4.8(5)	3.6(4)	1.0(6)	-0.1(5)	-0.6(4)
C14	593(19)	7212(10)	8965(1)	5.0(6)	4.1(5)	3.8(4)	1.3(5)	0.9(5)	0.2(4)
C15	-1064(21)	7529(13)	9174(2)	6.9(7)	7.2(7)	5.8(6)	0.0(7)	0.8(6)	1.2(6)
C16	-77(26)	8851(11)	9301(2)	9.6(8)	6.2(6)	3.9(5)	-0.0(8)	0.1(6)	-0.6(5)
C17	1896(19)	9389(13)	9136(2)	5.1(6)	6.8(6)	5.3(5)	1.3(6)	0.1(5)	0.7(5)
C18	-357(20)	9519(11)	8738(2)	4.6(6)	5.4(5)	6.0(6)	1.1(6)	-0.4(5)	0.6(5)
C19	-53(20)	5830(11)	8142(2)	5.0(6)	5.3(6)	5.4(5)	0.7(6)	-1.9(5)	0.7(5)
C28	3869(16)	50(10)	7998(2)	3.4(5)	4.4(5)	5.5(5)	0.0(5)	-0.0(4)	-0.4(5)
C29	3515(17)	-1133(9)	7820(1)	3.6(5)	3.9(5)	3.9(4)	1.0(5)	0.2(4)	0.0(4)
C31	4938(22)	-3247(11)	7630(2)	5.6(6)	5.0(6)	7.8(6)	1.1(6)	0.2(7)	-0.5(5)
C32	3016(24)	-3356(11)	7488(2)	8.4(8)	5.6(6)	5.0(5)	-2.5(7)	0.9(6)	-0.8(5)
C33	1347(20)	-2339(12)	7510(2)	5.8(6)	6.8(6)	4.8(5)	0.4(6)	-0.9(6)	-0.4(5)
C34	1498(19)	-1250(11)	7682(2)	5.8(6)	5.1(6)	5.3(5)	-0.2(6)	0.2(6)	-0.5(5)
C30	5155(20)	-2117(12)	7797(2)	4.2(6)	6.5(6)	5.7(6)	-0.6(6)	1.1(5)	-1.0(5)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
C20	2117(20)	11001(11)	9156(2)	5.5(3)	C21	4082(24)	11572(14)	8986(2)	7.5(3)
C22	2589(26)	11448(14)	9425(2)	7.8(3)	C23	2422(28)	13030(15)	9465(2)	8.5(4)
C24	2848(32)	13476(17)	9725(2)	10.5(4)	C25	2656(32)	15061(18)	9779(3)	10.8(4)
C26	4254(44)	15869(22)	9654(4)	15.7(7)	C27	3260(47)	15333(25)	10057(4)	18.3(8)

TABLE 3

Bond angles ω (degr.) in the structures 1 and 2

	1	2		1	2
C3-03-C28	117.3(4)	115.7(7)	C14-C13-C18	112.0(4)	114.0(8)
C2-C1-C10	113.7(3)	114.1(8)	C17-C13-C18	109.7(4)	110.9(8)
C1-C2-C3	110.4(4)	108.6(8)	C8-C14-C13	114.6(4)	113.7(8)
03-C3-C2	110.6(4)	108.5(8)	C8-C14-C15	118.7(4)	120.2(8)
03-C3-C4	106.9(4)	108.3(8)	C13-C14-C15	105.3(4)	103.9(8)
C2-C3-C4	110.1(4)	110.9(9)	C14-C15-C16	103.4(4)	103.9(9)
C3-C4-C5	110.9(4)	110.9(8)	C15-C16-C17	107.7(4)	107.4(9)
C4-C5-C6	120.0(4)	122.1(9)	C13-C17-C16	103.8(4)	102.8(9)
C4-C5-C10	116.7(4)	116.2(8)	C13-C17-C20	119.5(4)	120.2(9)
C6-C5-C10	123.3(4)	121.6(9)	C16-C17-C20	112.4(4)	110.4(9)
C5-C6-C7	124.2(4)	126.6(9)	C17-C20-C21	113.9(5)	111.2(9)
C6-C7-C8	115.0(4)	112.7(9)	C17-C20-C22	109.8(4)	111.0(9)
C7-C8-C9	110.2(4)	111.2(8)	C21-C20-C22	109.7(5)	108.5(9)
C7-C8-C14	111.7(4)	110.8(8)	C20-C22-C23	116.3(5)	113(1)
C9-C8-C14	108.8(3)	110.2(8)	C22-C23-C24	113.3(5)	114(1)
C8-C9-C10	113.3(3)	114.3(8)	C23-C24-C25	116.5(5)	116(1)
C8-C9-C11	111.6(3)	113.9(8)	C24-C25-C26	111.1(6)	113(2)
C10-C9-C11	113.0(3)	110.4(8)	C24-C25-C27	113.5(6)	109(2)
C1-C10-C5	109.4(3)	107.5(8)	C26-C25-C27	112.2(7)	102(2)
C1-C10-C9	108.3(3)	107.2(8)	03-C28-028	122.7(5)	124.7(9)
C1-C10-C19	109.9(3)	108.8(8)	03-C28-C29	113.1(4)	111.6(8)
C5-C10-C9	110.1(3)	110.2(8)	028-C28-C29	124.2(5)	123.4(9)
C5-C10-C19	108.1(4)	109.5(8)	C28-C29-C30	124.1(5)	118.4(9)
C9-C10-C19	111.0(4)	113.5(8)	C28-C29-C34	118.5(5)	121.0(8)
C9-C11-C12	114.1(4)	111.5(9)	C30-C29-C34	117.5(5)	120.6(9)
C11-C12-C13	111.9(4)	113.6(9)	C29-C30-C31	120.7(5)	121.2(9)
C12-C13-C14	106.4(4)	106.8(8)	C30-C31-C32	120.8(6)	119(1)
C12-C13-C17	116.8(4)	115.9(9)	C31-C32-C33	120.1(6)	120(1)
C12-C13-C18	111.1(4)	108.7(8)	C32-C33-C34	120.4(6)	122(1)
C14-C13-C17	100.2(3)	100.5(8)	C29-C34-C33	120.5(6)	117.5(9)

aliphatic chains of one layer penetrate into the adjacent layer. In crystal 2 the molecules are also arranged in the layers parallel to the *ab* plane; but the long axes C(25)→C(32) of the molecules in the neighbouring layers form the angle of 73° with each other and this results in a herring-bone type of the molecular packing (Figure 4). The tetragonal CB polymorph 3 is characterized by a layer-helical molecular packing, wherein the molecules form helicas around 4_1 screw axes, normal to the layers.[8,11] For the physically valid treatment of molecular packing we use a concept of a "structural subclass,"[12] i.e. the set of symmetry operations involved in combining of molecules into stable associates (dimers, chains or stacks, layers) and packing of the latter in crystal.

TABLE 4

Torsion angles τ (degr.) in the structures 1 and 2

Cycle A	1	2	Cycle D	1	2
C1-C2-C3-C4	60	62	C13-C14-C15-C16	-34	-34
C2-C3-C4-C5	-57	-61	C14-C15-C16-C17	10	9
C3-C4-C5-C10	51	55	C15-C16-C17-C13	17	20
C4-C5-C10-C1	-46	-47	C16-C17-C13-C14	-37	-40
C5-C10-C1-C2	48	48	C17-C13-C14-C15	45	47
C10-C1-C2-C3	-57	-56			
Cycle B			Aliphatic chain		
C9-C10-C5-C6	15	15	C13-C17-C20-C21	-56	-60
C7-C6-C5-C10	4	1	C13-C17-C20-C22	-180	180
C5-C6-C7-C8	9	11	C16-C17-C20-C21	-178	-179
C6-C7-C8-C9	-38	-39	C16-C17-C20-C22	58	60
C7-C8-C9-C10	57	57	C17-C20-C22-C23	-168	-170
C8-C9-C10-C5	-45	-45	C20-C22-C23-C24	69	179
Cycle C			C22-C23-C24-C25	-172	-179
			C23-C24-C25-C26	175	-64
C14-C8-C9-C11	-51	-51	C23-C24-C25-C27	-58	-177
C8-C9-C11-C12	51	48	Benzoate group		
C9-C11-C12-C13	-54	-51			
C11-C12-C13-C14	56	55	C2-C3-03-C28	83	85
C12-C13-C14-C8	-61	-60	C4-C3-03-C28	-157	-155
C13-C14-C8-C9	59	59	C3-03-C28-C29	-178	179
			C3-03-C28-028	3	4
			C30-C29-C28-03	0	-178
			C30-C29-C28-028	179	-3
			C34-C29-C28-03	-179	0
			C34-C29-C28-028	0	175

According to EPIMI calculations (Table 5) in monoclinic crystal 1 (Figure 3) the strongest interactions are between the I(000) and I(010) and also between the I(000) and I($0\bar{1}0$) molecules.† The molecular stacks, parallel to the *b* axis, are formed as a result of these strongest interactions. The symmetry of the stacks is $P_{c(y)}111$, $z' = 1$, where z' is the number of molecules in a period along the stack (chain). The next strongest interactions join molecular stacks into the layers, parallel to the *ab* plane (the layer symmetry is $P_{1(z)}12_11$, $z'' = 2$). Thus the structural subclass of 1 should be written as follows:

$$P_{c(y)}111,\ z' = 1—P_{1(z)}12_11,\ z'' = 2—C2,\ z = 4.$$

The potential energy of crystal 1 is −49.8 kcal/mole with the inter-

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†The molecules are designated according to P. M. Zorkii *et al.*[13]

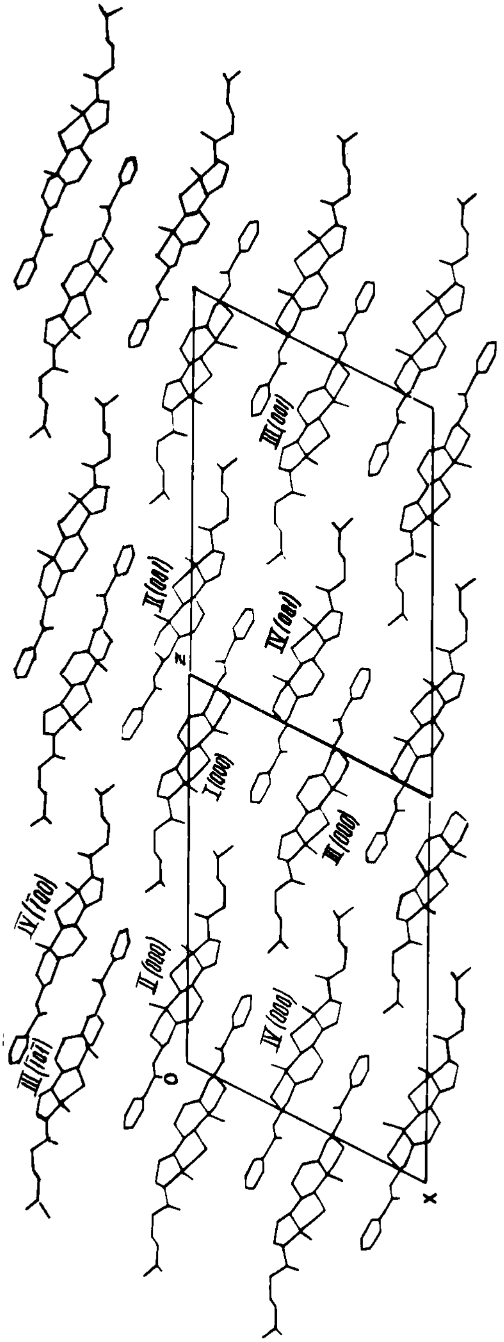


FIGURE 3 Monoclinic crystal structure 1 projected along *b*.

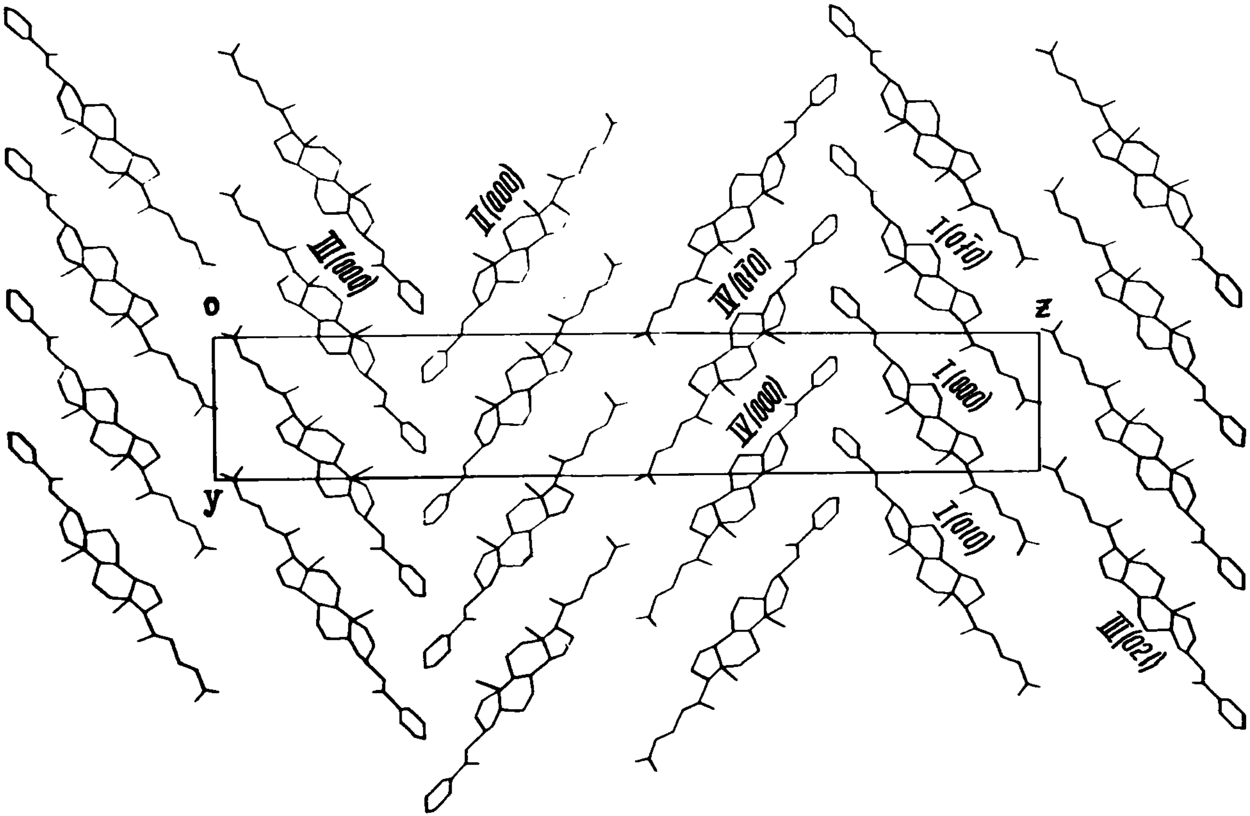


FIGURE 4 Orthorhombic crystal structure 2 projected along *a*.

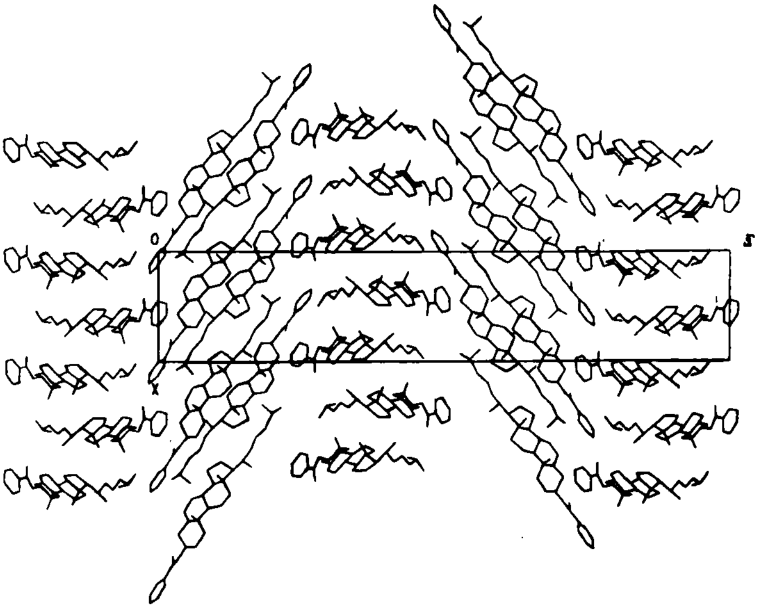


FIGURE 5 Layer molecular packing in the tetragonal modification 3 projected along *b*.

actions within the layers 2.8 times greater than between the layers (Table 5).

In crystals of the orthorhombic modification 2 (Figure 4) the most strong and essentially equal interactions are I(000)-I(010), I(000)-I(0$\bar{1}$0), I(000)-I(100) and I(000)-I($\bar{1}$00) (Table 6), which lead to the formation of the layers $P_{1(Z)}111$, $z'' = 1$. The structure 2 is formed by superposition of these layers:

$$P_{1(z)}111,\ z'' = 1\text{—}P2_12_12_1,\ z = 4.$$

The structural subclass of the previously investigated[11] modification 3 is written as follows:

$$\begin{tikzcd}
 & P_{1(z)}12_11,\ z'' = 2 \arrow[dr, no head] & \\
\text{molecule} \arrow[ur, no head] \arrow[dr, no head] & & P4_12_11,\ z = 8. \\
 & P_{1(z)}2_111,\ z'' = 2 \arrow[ur, no head] &
\end{tikzcd}$$

The potential energy of crystal 2 (-47.2 kcal/mole) is smaller by 2.6 kcal/mole than that of crystal 1, but in crystal 2 the interactions within

TABLE 5

Energy of intermolecular interactions U (kcal/mole) in the monoclinic modification of CB (1)

Interacting molecules	−U	Interacting molecules	−U
I(000)-I(010)	7.2	I(000)-II(000)	4.2
I(000)-I(0$\bar{1}$0)	7.2	I(000)-IY($\bar{1}\bar{1}$0)	2.7
I(000)-II(001)	7.2	I(000)-IY($\bar{1}$00)	2.7
I(000)-IY(0$\bar{1}$1)	4.7	I(000)-III($\bar{1}\bar{1}\bar{1}$)	0.6
I(000)-IY(001)	4.7	I(000)-III(001)	0.6
I(000)-II(0$\bar{1}$1)	1.4	I(000)-II(0$\bar{1}$0)	0.6
I(000)-II(011)	1.4	I(000)-II(010)	0.6
−U in layer	=33.8	−U between layers	=12.0

the layers are 3.5 times greater than between the layers (Table 7). The potential energy of crystal 3 is −47.3 kcal/mole.

Thus, the monoclinic modification 1 has a stack-layer structure, whereas the orthorhombic and tetragonal modifications 2 and 3 both have a layer molecular packing. The different molecular packing in polymorphs 1–3 is interrelated with the different molecular conformations in their crystals.

For the first time the existence of several solid polymorphs of CB was reported by Lehman in 1889.[2] Now six modifications of this compound are known.[5] In addition to the above mentioned modfications 1–3 we succeeded in determination of crystal data for one more, orthorhombic modification 4. Crystals of 4 were obtained by zone melting[14] from a mesophase in glass capillaries and crystal data

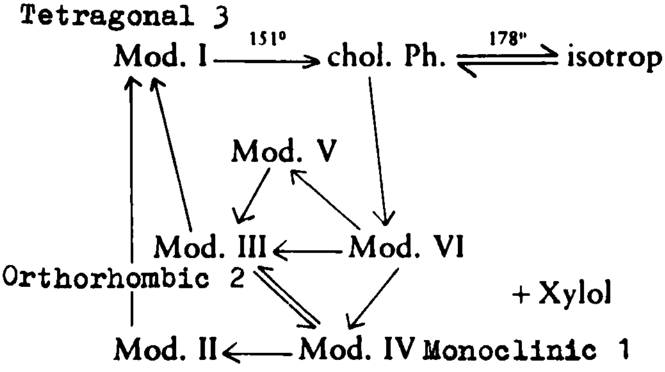
TABLE 6

Energy of intermolecular interactions U (kcal/mole) in orthorhombic modification of CB (2)

Interacting molecules	−U	Interacting molecules	−U
I(000)-I(010)	7.2	I(000)-IY(1$\bar{1}$0)	2.0
I(000)-I(0$\bar{1}$0)	7.2	I(000)-IY(100)	2.0
I(000)-I($\bar{1}$00)	7.0	I(000)-III($\bar{1}$21)	1.8
I(000)-I(100)	7.0	I(000)-III(021)	1.8
I(000)-I($\bar{1}\bar{1}$0)	1.6	I(000)-IY(0$\bar{1}$0)	1.2
I(000)-I(110)	1.6	I(000)-IY(000)	1.2
I(000)-I($\bar{1}$10)	1.3		
I(000)-I(1$\bar{1}$0)	1.3		
−U in layer	=34.2	−U between layers	=10.0

were determined by a photomethod. Yet another orthorhombic modification 5 of CB was reported by Shivaprakash *et al.*[15] Crystal data of 4 and 5 are given in Table 1. Thus for three (1–3) of six known solid polymorphs of CB the crystal and molecular structures were determined and for two polymorphs (4, 5) only space groups and unit cell parameters were obtained.

The scheme of CB phase transitions was given by Kuhnert-Brandstatter and Seidel,[5] but without assignment of crystal data to polymorphs. In order to establish relations between the known structures of CB polymorphs and the scheme of phase transitions we carried out calorimetric measurements for modfication 3 (DSC). Unfortunately, quantities of crystals 1 and 2 were not sufficient for such measurements. Temperatures of phase transitions in the modifications 1 and 2 were measured on a heating stage of a Reichert polarization microscope. Orthorhombic single crystals 2 melt at 143 ± 1°C and thus correspond to the modification III in the scheme (Figure 6). A very interesting behaviour of monoclinic single crystals 1 was observed. On slow heating of these crystals another polymorphic modfiication began to grow at ca. 110°C. This new modification melts at 148 ± 1°C and thus corresponds to the modification II (Figure 6). According to the scheme of phase transitions it may be also supposed that the monoclinic modification 1 corresponds to the modification IY. DSC-thermogram of the tetragonal modification 3 (Figure 7)



Fp. Mod. I 151°; Fp. Mod. II 147°; Fp. Mod. III 144°;
Fp. Mod. IV 139°; Fp. Mod. V; Fp. Mod. VI 137°

FIGURE 6 Scheme 5 of CB phase transitions with the proposed assignment of the structurally characterized polymorphs 1, 2 and 3 to the solid modifications IY, III and I respectively.

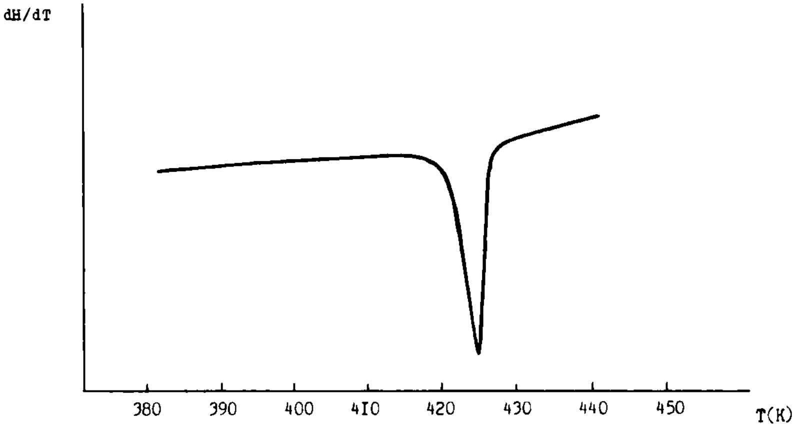


FIGURE 7 DSC-thermogram of CB (heating rate 2°C/min).

shows that it melts at 151.8°C and therefore corresponds to the modification I in the scheme. Thus the modification, which is the most stable at room temperature, is at the same time the most symmetrical (tetragonal, 3) of the known polymorphs.

The special energetically favourable directions in cholesterogenic crystals are supposed to correspond to nuclei of cholesterogenic microhelices.[11,16] On the basis of EPIMI calculations of cholesterogenic crystals a geometrical model of the packing rearrangement on a phase transition mesogenic crystal→cholesterogenic liquid crystal (CLC) was proposed.[11] According to this model the energetically favourable directions, parallel to 2_1 and 4_1 (in 3) axes, can predetermine the directions of microhelices, whose assembly forms a CLC macrohelix. In fact this proposal is confirmed by the observation of selected light reflection (Figure 8) in the direction of the optical (4-fold) axis of the tetragonal single crystal 3 on its transformation to the mesophase with formation of a planar texture. Notably, this experiment was performed without the orienting slip of cover and slide glasses, though the surface of the slide glass was oriented by a weak directed rubbing.[17] As a result a sufficiently perfect planar texture was obtained on heating of a single crystal 3 (ca. 100 μm thick), whose optical axis was oriented parallel to an incident light beam (perpendicular to the slide and cover glasses). In our opinion the formation of a good planar texture is due to both an orienting action of the slide glass and a quite definite orientation of a single crystal 3. However, it is difficult to separate contributions of both factors. Unfortunately, similar exper-

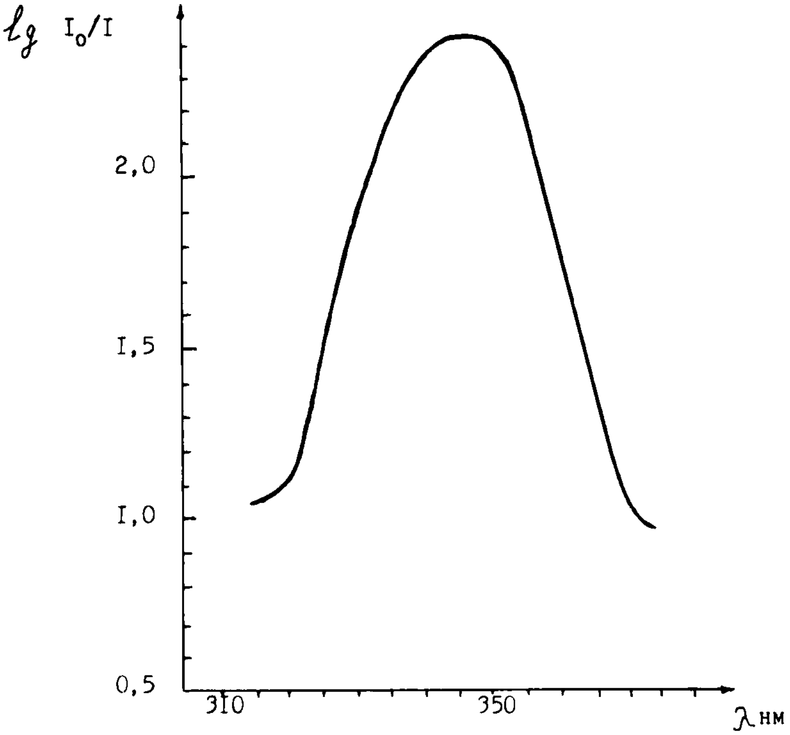


FIGURE 8 Transmission spectrum of a planar texture of the CB mesophase.

iments with the modifications 1 and 2 were not carried out because of insufficient quantities and small dimensions of single crystals.

The physical validity of distinguishing of the most stable molecular associates on the basis of EPIMI calculations is, as a rule, confirmed by crystal habitus.[11] Most of cholesterogenic crystals belong to the space groups $P2_1$ or $P2_12_12_1$,[10,16] and the directions of energetically favourable molecular stacks (giving rise to formation of microhelices of CLC) coincide with screw axes. Most of these crystals are needles or plates elongated along 2_1 axes, while crystals with a layer (not stack-layer) structure are isometric plates. It is to be noted that a slip of a cover glass is necessary to obtain a planar texture, because a great number of small needle-shaped crystals are chaotically arranged in powder, but should be oriented perpendicular to the slide glass with their long axes (parallel to 2_1). In other words, as mentioned by Prasad *et al.*[16] a slip is necessary for the orientation of microhelices in one direction. At the same time such slip was not necessary to obtain a planar texture in the case of the correct orientation of a single crystal 3.

CONCLUSION

Structural investigations of CB solid modifications have shown significant distinctions between the molecules in different modifications in respect to torsion angles around the ester bond and C-C bonds in aliphatic chains. Conformational calculations of the benzoate-group orientation[10] have demonstrated only small variations of conformational energy on changing of the mentioned torsion angles ($\Delta U_{conf} \approx$ 0.5 kcal/mole). The order of magnitude of ΔU_{conf} is the same at RT $\approx$ 0.6 kcal/mole at room temperature (300°K). Obviously in a mesophase intermolecular interactions are weakened in comparison with crystal and CB molecules can adopt different conformations, viz. those found in solid modifications 1–3.

If, as we suppose, some features of the molecular arrangement in mesogenic solids are retained in the liquid crystalline state, then the existence of several polymorphs of mesogenic compounds enables to assume that all types of structural organization found in solid polymorphs might be present in the mesophase with possible changes of molecular conformations. Therefore it may be supposed that several local types of molecular organization coexist in the CB mesophase. On changing of temperature these types are interconverted continuously with retaining of macroscopic homogeneity of the mesophase. This suggestion is equivalent to the cluster mechanism of orientational ordering in liquid crystals,[18] according to which clusters, i.e. associates of most strongly interacting molecules, can partially inherit the molecular packing of some crystal modification.

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