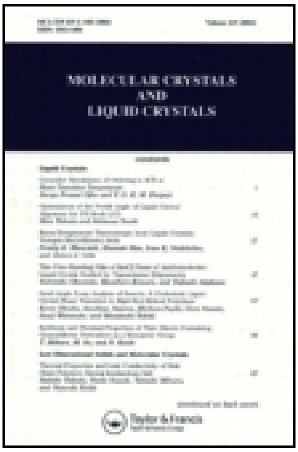

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Crystal and Molecular Structure of the Laterally Branched Nematogenic Compound 2-n-Nonyl-1,4-phenylene Bis (4-n-octyloxybenzoate)

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Crystal and Molecular Structure of the Laterally Branched Nematogenic Compound 2-*n*-Nonyl-1,4-phenylene Bis(4-*n*-octyloxybenzoate)

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The crystal and molecular structure of the nematogenic compound 2-*n*-nonyl-1,4-phenylene bis(4-*n*-octyloxybenzoate) (NPOB) has been determined at −100 °C and at room temperature by X-ray analysis. NPOB crystallizes in space group $P\bar{1}$ with two molecules in a unit cell of dimensions (values of the room temperature investigation are given in brackets) $a = 9.878(2)$ [10.165(4)], $b = 12.700(3)$ [12.863(5)], $c = 17.830(4)$ [17.940(6)] Å, $\alpha = 71.83(2)$ [69.65(2)], $\beta = 84.58(2)$ [85.23(2)], $\gamma = 76.11(2)$ [75.43(2)]°. The structure was solved by direct methods and refined to an R value of 0.056 [0.108]. The most striking features of the molecular structure are the *all-trans*-conformation of the laterally branched nonyl group and the nearly parallel alignment of all three alkyl substituents. The crystal structure is characterized by a parallel arrangement and an interlocked packing of the molecules.

Keywords: Crystalline mesogens, X-ray analysis, molecular structure, crystal structure, laterally branched mesogens, phenylene bis(benzoates).

INTRODUCTION

Three-ring compounds bearing laterally attached long-chain substituents can exhibit liquid-crystalline properties.[1-3] This fact, known since 1983,[4] seems to be inconsistent with the model of rod-shaped mesogens. According to the classic rule first suggested by Vorländer,[5] the molecules of calamitic liquid crystals should have a large length-to-breadth ratio X; the addition of lateral groups decreases X and consequently the stability of mesophases. Normally, larger laterally attached substituents lead to lower clearing temperatures. However, there are a limited number of compounds deviating from this rule.[6,7]

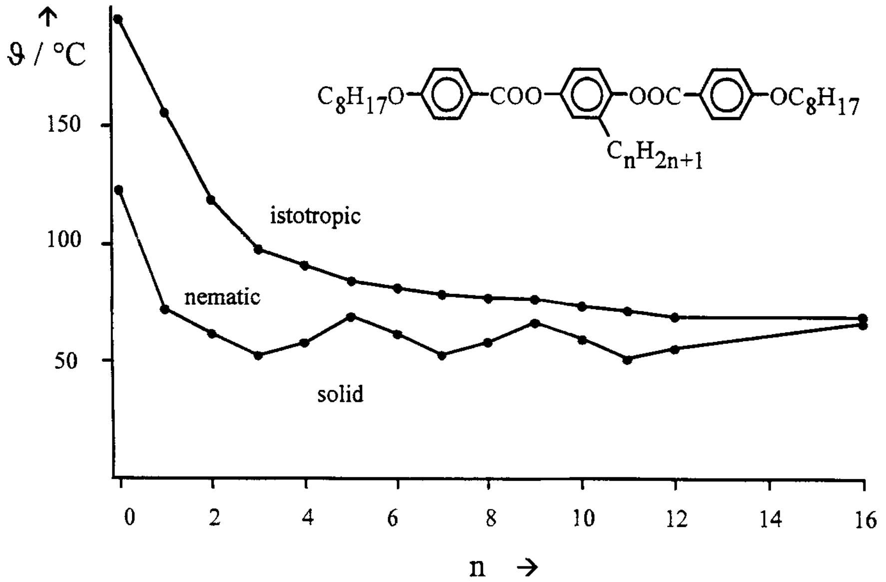

FIGURE 1 Transition temperatures in the homologous series of the 2-*n*-alkyl-1,4-phenylene bis(4-*n*-octyloxybenzoates).

In Figure 1 the phase behaviour of the 2-*n*-alkyl-1, 4-phenylene bis(4-*n*-octyloxybenzoates) is displayed. Transition temperatures are plotted against the number of carbon atoms in the lateral chain. All members of this series are nematic after melting. As expected, the clearing points decrease dramatically on substituting the 2-H atom by a methyl, ethyl or propyl group. However, further lengthening of the alkyl chain leads to a less pronounced depression of the clearing temperatures and, surprisingly, the later homologues tend to a limiting value. This form of clearing-point curve is also typical of other homologous series of laterally alkyl-branched substances.[1,3,8] On the basis of molecular statistical theories of the hard rod or of the van der Waals type, the graph shown in Figure 1 would mean that with increasing lateral alkyl group size the ratio X decreases and tends to a constant value for long chain members of the series. Therefore, for the interpretation of the nematic behaviour of the compounds the conformation of their laterally attached alkyl chains is of great importance because it directly influences the ratio X. From this point of view, the trend to a saturation value of the clearing temperatures should indicate that the lateral chain is approximately parallel to the molecular long axis.

The 2-*n*-alkyl-1,4-phenylene bis(4-*n*-octyloxybenzoates) represent one of the most intensively investigated homologous series of liquid crystals. Transition enthalpies and entropies, viscosities, densities and phase transition volumes, order parameters of dissolved dyes, optical refractive indices and the pressure dependence of clearing temperatures were measured.[9,10,11] Some results, e.g. those of miscibility[10] and X-ray studies[12] support the assumption of a non-linear conformation of the lateral alkyl group.

According to NMR investigations[13] the bending of the lateral alkyl chain is generated by an accumulation of gauche conformations particularly between the carbon atoms three to six. This behaviour can be understand in terms of molecular statistical theories including molecular repulsion forces. Calculations concerning the influence of lateral side chains attached to thermotropic calamitic nematogens were made by Ballauf on the basis of the Flory lattice model.[14] He concluded that the decrease of the clearing temperatures by lateral substituents is caused by their influence on the molecular packing and the dilution of the anisotropic dispersion forces between the central nematic cores. However, for laterally long-chain substituted mesogens there is only little agreement between his theoretical predictions and the experimental data. One reason for this may be an insufficient consideration of the special conformations assumed by the lateral chains in the nematic state.

The problem of the orientation of the lateral long-chain substituents is also of interest for liquid crystalline polymers with mesogenic groups in the main chain. For such materials the extremely low solubilities and very high melting ranges can be avoided by the attachment of flexible lateral chains to the rigid backbone.[15,16] In many cases, homologous series of these laterally alkyl-substituted l.c. polymers have curves of the nematic-isotropic transition temperatures similar to those of the above-discussed low molecular mesogens. But for stiff-chain l.c. polymers intercalated layer structures with stretched lateral alkyl chains seem to be possible.[16,17]

For the above-mentioned and other related reasons, it seemed useful to have exact knowledge of both the molecular structure and packing of a laterally long-chain branched mesogenic compound. Such structural information can be obtained by X-ray analysis, although strictly valid only for the solid state. However, in the case of mesogens with large lateral substituents the number of such investigations is very small because of the difficulties of preparing suitable single crystals. To the best of our knowledge, only our own work on the crystal structures of 4-ethoxy-3′-(4-ethoxyphenyliminomethyl)-4′-(4-methoxybenzoyloxy)-azobenzene[18] and 4-nitrobenzyl 2,5-bis(4-ethoxybenzoyloxy)-benzoate[19] has been reported until now. In this paper we present the results of an X-ray analysis of 2-*n*-nonyl-1,4-phenylene bis(4-*n*-octyloxybenzoate) (abbreviated as NPOB in the following), the first structure of a three-ring mesogen with a lateral long-chain alkyl substituent. NPOB was first synthesized and characterized by Weissflog and Demus[20] and shows the following transition temperatures:

$$\text{Cr}\quad 67\,^{\circ}\text{C}\quad \text{N}\quad 77\,^{\circ}\text{C}\quad \text{Is}$$

EXPERIMENTAL

Optically clear, colorless crystals of NPOB obtained by recrystallization from a methanol/acetone mixture were mounted first on a Stoe STADI 4 diffractometer and investigated at room temperature. But the results of this structure analysis were unsatisfactory; the R value and estimated standard deviations were rather high. The carbon atoms of both terminal octyloxy groups had unusually high displacement parameters and, consequently, anomalous bond lengths and angles were observed. These phenomena are typical of a kind of disorder analysed in detail for terephthalylidene-bis-(4-*n*-butylaniline) (TBBA) by Doucet *et al.*[21] and generally interpreted as a 'partial melting' of the alkyl chains. Such disorder has also been observed by us in earlier investigations on crystalline mesogens.[22,23] Measurements were therefore repeated on a Siemens R3m/V diffractometer at low temperature (− 100 °C).

Relevant crystal data and details of X-ray analysis for both the room (RT) and low temperature (LT) investigations are summarized in Table I. Lattice parameters were derived by a least-squares treatment of the setting angles for 86 (RT) and 50 (LT) reflections, respectively. Data reduction was carried out applying Lorentz and polarization corrections but neglecting absorption and extinction effects. The structures were solved by direct methods. Full-matrix least-squares refinement on F was performed with anisotropic displacement parameters for the non-H atoms. The positions of the

TABLE I

Crystal data and details of intensity measurements and structure refinements

Compound	NPOB (room temperature)	NPOB (low temperature)
Chemical formula	$C_{45}H_{64}O_6$	
Molecular weight (g mol^{-1})	700.96	
Measuring temperature (°C)	25	− 100
Crystal description	colourless prism	
Crystal size (mm)	0.58 × 0.48 × 0.11	0.60 × 0.40 × 0.25
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	10.165(4)	9.878(2)
b(Å)	12.863(5)	12.700(3)
c(Å)	17.940(6)	17.830(4)
α(°)	69.65(2)	71.83(2)
β(°)	85.23(2)	84.58(2)
γ(°)	75.43(2)	76.11(2)
Unit cell volume (Å^3)	2128.54	2062.64
Molecules per unit cell	2	2
Measured density (Mg m^{-3})	1.08(1)	
Calculated density (Mg m^{-3})	1.094	1.129
Radiation	Mo K (α), λ = 0.71073 Å	Mo K (α), λ = 0.71073 Å
Absorption coefficient (mm^{-1})	0.40	
F(000)	764	
No. of reflections measured	11976	7860
No. of independent reflections	5928	7275
No. of observed reflections ($F_0 > 3.92\sigma(F_0)$)	2940	3382
Collection method	ω/θ-scan	ω-scan
R_{int}	0.052	0.037
θ_{max}	23	25
h,k,l (min/max)	$\bar{11},\bar{12},0/11,14,19$	$\bar{11},\bar{15},\bar{21}/1,14,21$
Variation of standards (%)	±3.5	±5
No. of reflections per parameter	6.9	7.3
R	0.108	0.056
wR	0.132	0.075
Weighting scheme	$w = 1.00/(\sigma^2(F_0) + 0.002\,F^2)$	$w = 1.12/\sigma^2(F_0) + 0.003\,F^2)$

H atoms were geometrically calculated and refined isotropically using the riding model.

All calculations were performed on an IBM RISC/6000-320 work station using the program packages SHELXS-86[24], SHELX-76[25] and EDIT[26]. Diagrams of the molecular structure and packing were plotted using programs ORTEP[27] and PLUTO.[28] Final atomic parameters of the low temperature structure are summarized in Table II. Those of the room temperature structure together with further details of both crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-400507 (LT) and CSD-400508 (RT), respectively, the names of the authors, and the journal citation.

RESULTS AND DISCUSSION

For mesogenic compounds, different solid crystalline modifications have often been found, apart from the liquid crystalline phases. However for NPOB, starting from room temperature, phase transitions could be observed neither on heating to the melting point nor on cooling to $-100\,^{\circ}$C. Apart from the disappearance of the above-mentioned disorder the low temperature structure is identical with that determined at room temperature. Because of the improved precision, all data and figures in the following discussion refer to the low temperature investigation.

Molecular structure

The molecular structure of NPOB, including the applied labelling scheme, is illustrated in Figure 2. Essential parameters of the molecular geometry are summarized in Tables III and IV. A realistic picture of the molecular shape can be visualized by the space-filling PLUTO model[28] shown in Figure 3, for which the van der Waals radii given by Bondi[29] were used. As can be seen from Figure 1, the molecule consists of four largely linear structural fragments: the central three-ring skeleton, the lateral and the two terminal substituents. The phenylene bis(benzoate) moiety (the mesogenic core) has a non-planar but optimally extended shape. This is based on the stereochemistry of the carboxylic group as a bridging structural component with parallel configuration, causing only a slight parallel displacement of the moieties it connects. The phenyl rings I (C9...C14), II (C16...C21) and III (C23...C28) and the carboxylic groups IV (C12, C15, O2, O3) and V (C23, C22, O4, O5) are planar within experimental error and make the following interplanar angles: I/IV 7.5, IV/II 111.2, II/V 82.5, V/III 2.1°. These values lie in the ranges observed in previous investigations of mesogenic phenyl benzoates in general[30] and on phenyl bis(benzoate) derivatives in particular.[31,32] However, there is a noticeable difference in the twist of the central phenyl ring relative to the other two phenyl rings (I/II 117.9, II/III 82.0°) which can be explained by the unsymmetrical substitution of ring II by the lateral nonyl group. The latter has a nearly perfect *all-trans* conformation and is inclined by 53.8° to the l.s. line through the main chain limited by atoms O1 and O6. The octyl chains are also completely staggered; one of them (C1...C8) has a tilt of 51.2° and nearly the same orientation as the nonyl group, whereas

TABLE II

Final fractional atomic coordinates and equivalent thermal parameters (Å^2) for non-H atoms
$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_i$

Atom	x/a	y/b	z/c	U_{eq}
C1	−0.8022(6)	2.1728(5)	−0.1260(3)	0.09(2)
C2	−0.7326(6)	2.0921(5)	−0.0548(3)	0.09(2)
C3	−0.8100(5)	2.0321(4)	0.0103(3)	0.08(2)
C4	−0.7384(5)	1.9487(4)	0.0813(3)	0.07(2)
C5	−0.8260(5)	1.8942(4)	0.1476(3)	0.07(2)
C6	−0.7501(5)	1.8021(4)	0.2155(3)	0.06(1)
C7	−0.8446(5)	1.7512(4)	0.2822(3)	0.06(1)
C8	−0.7649(5)	1.6519(4)	0.3464(3)	0.06(1)
C9	−0.6188(4)	1.4679(3)	0.3539(2)	0.04(1)
C10	−0.5585(4)	1.3905(3)	0.3130(2)	0.04(1)
C11	−0.4683(4)	1.2904(3)	0.3510(2)	0.04(1)
C12	−0.4370(4)	1.2657(3)	0.4307(2)	0.04(1)
C13	−0.4984(4)	1.3444(3)	0.4702(2)	0.04(1)
C14	−0.5888(4)	1.4448(3)	0.4328(2)	0.05(1)
C15	−0.3435(4)	1.1588(3)	0.4744(2)	0.04(1)
C16	−0.2225(4)	0.9752(3)	0.4666(2)	0.04(1)
C17	−0.0911(4)	0.9479(3)	0.4354(2)	0.04(1)
C18	−0.0156(4)	0.8353(3)	0.4664(2)	0.04(1)
C19	−0.0737(4)	0.7592(3)	0.5246(2)	0.04(1)
C20	−0.2048(4)	0.7876(3)	0.5565(2)	0.04(1)
C21	−0.2816(4)	0.8980(3)	0.5261(2)	0.05(1)
C22	0.1003(4)	0.6223(3)	0.6066(2)	0.04(1)
C23	0.1793(4)	0.5033(3)	0.6287(2)	0.04(1)
C24	0.1571(4)	0.4210(3)	0.5977(2)	0.04(1)
C25	0.2384(4)	0.3116(3)	0.6196(2)	0.05(1)
C26	0.3447(4)	0.2840(3)	0.6735(2)	0.04(1)
C27	0.3653(4)	0.3651(3)	0.7055(2)	0.04(1)
C28	0.2839(4)	0.4733(3)	0.6833(2)	0.05(1)
C29	0.4177(5)	0.0922(3)	0.6661(2)	0.05(1)
C30	0.5177(5)	−0.0158(3)	0.7084(2)	0.05(1)
C31	0.4804(5)	−0.0596(4)	0.7956(3)	0.05(1)
C32	0.5681(5)	−0.1750(4)	0.8397(3)	0.06(1)
C33	0.5208(5)	−0.2148(4)	0.9258(3)	0.06(1)
C34	0.6033(5)	−0.3286(4)	0.9741(3)	0.07(1)
C35	0.5514(5)	−0.3634(4)	1.0600(3)	0.07(2)
C36	0.6319(6)	−0.4774(4)	1.1090(3)	0.08(2)
C37	−0.0294(4)	1.0331(3)	0.3701(2)	0.04(1)
C38	−0.0951(4)	1.0631(3)	0.2899(2)	0.04(1)
C39	−0.0355(5)	1.1535(4)	0.2261(2)	0.05(1)
C40	−0.1072(5)	1.1901(4)	0.1471(2)	0.05(1)
C41	−0.0516(5)	1.2816(4)	0.0835(2)	0.06(1)
C42	−0.1224(5)	1.3154(4)	0.0039(2)	0.06(1)
C43	−0.0736(5)	1.4126(4)	−0.0593(2)	0.06(1)
C44	−0.1414(5)	1.4442(4)	−0.1386(2)	0.06(2)
C45	−0.0916(6)	1.5388(5)	−0.2016(3)	0.08(2)
O1	−0.7034(3)	1.5647(2)	0.3107(2)	0.05(1)
O2	−0.3056(3)	1.1368(2)	0.5411(2)	0.05(1)
O3	−0.3074(3)	1.0841(2)	0.4313(2)	0.05(1)
O4	0.0021(3)	0.6449(2)	0.5513(2)	0.05(1)
O5	0.1182(3)	0.6943(2)	0.6324(2)	0.06(1)
O6	0.4313(3)	0.1796(2)	0.6986(2)	0.05(1)

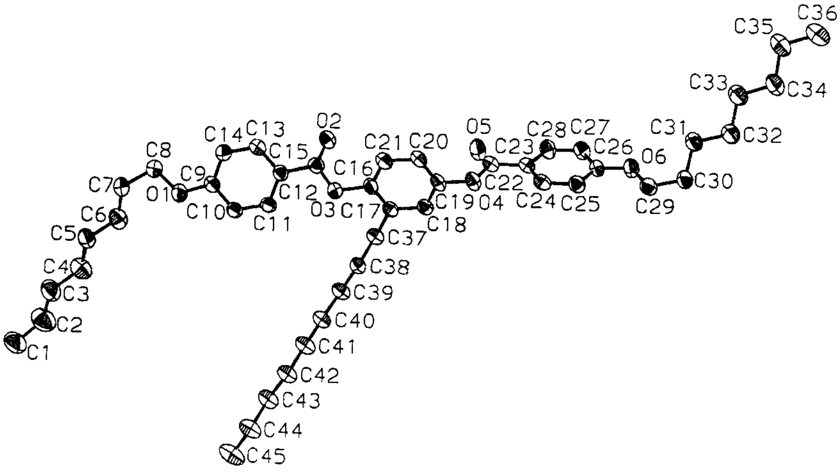

FIGURE 2 Molecular structure of NPOB with atom numbering.

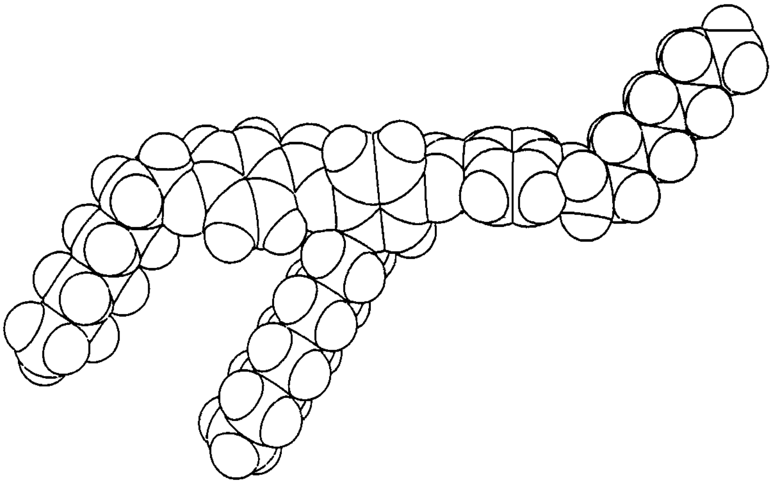

FIGURE 3 Space filling model of the molecular structure of NPOB.

the other one (C29...C36) is somewhat less inclined with a tilt of 41.8°. The approximately parallel arrangement of the three alkyl chains is made possible by the *gauche* conformations C6-C7-C8-O1 -63.5° and O6-C29-C30-C31 65.2°.

All bond lengths and angles in NPOB (cf. Table III) are in good agreement with standard values and require no comment.

Crystal structure

The packing of the NPOB molecules in the crystal is illustrated in Figures 4 and 5 in two different projections. It is characterized by a perfectly parallel alignment of the

TABLE III

Selected bond lengths (Å) and angles (°) for the non-hydrogen atoms (esd's in parentheses)

Atoms	Distance (Å)	Atoms	Distance (Å)	Atoms	Angle (°)	Atoms	Angle (°)
				Carboxylic groups			
C15—O2	1.208(5)	C22—O5	1.197(5)	C12—C15—O2	125.2(3)	C23—C22—O5	125.2(3)
C15—O3	1.363(5)	C22—O4	1.366(5)	C12—C15—O3	111.8(3)	C23—C22—O4	112.9(3)
C15—C12	1.476(6)	C22—C23	1.473(6)	O2—C15—O3	123.0(3)	O4—C22—O5	121.8(3)
O3—C16	1.419(5)	O4—C19	1.417(5)	C15—O3—C16	118.6(3)	C22—O4—C19	115.9(3)
				Octyloxy groups			
C9—O1	1.357(5)	C26—O6	1.359(5)	C9—O1—C8	119.3(3)	C26—O6—C29	118.8(3)
O1—C8	1.429(5)	O6—C29	1.440(5)	O1—C8—C7	106.8(3)	O6—C29—C30	107.6(3)
mean values for C1...C8		mean values for C29...C36		mean values for C1...C8		mean values for C29...C36	
C—C	1.48(3)	C—C	1.52(1)	C—C—C	117(4)	C—C—C	114(1)
				Nonyl group			
		C17—C37	1.515(6)	C16—C17—C37	122.4(3)	C18—C17—C37	121.0(3)
				mean values for C37...C45			
		C—C	1.524(7)	C—C—C	113.5(4)		
				Mean values for benzene rings			
Ring I (C9...C14)		Ring III (C23...C28)		Ring I (C9...C14)		Ring III (C23...C28)	
C—C	1.389(9)	C—C	1.387(9)	C—C—C	120(1)	C—C—C	120(1)
		Ring II (C16...C21)		Ring II (C16...C21)			
		C—C	1.38(1)	C—C—C	120(3)		

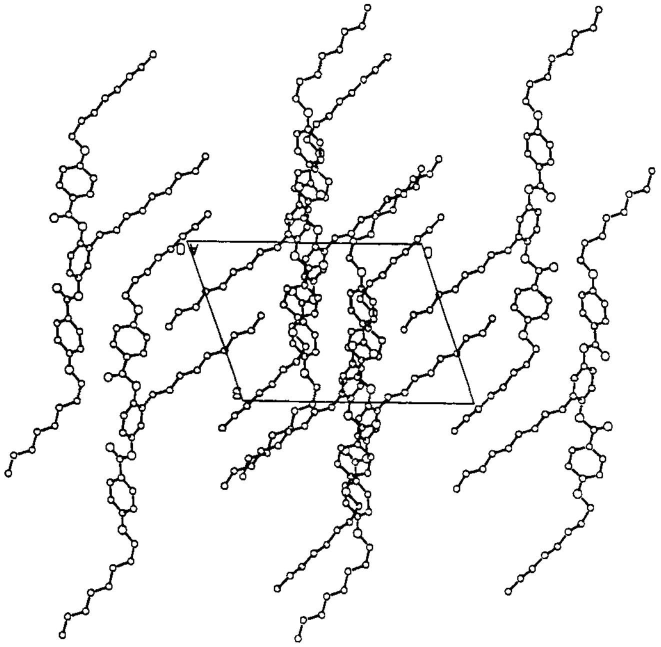

FIGURE 4 Crystal packing of NPOB projected along [100].

molecules by the three lattice translations and the inversion centres of the space group. As can be seen in Figure 4, the molecules are arranged in rows parallel to [010]. Since both the lateral and terminal alkyl chains are also essentially parallel to each other, but considerably inclined to the long axis of the three-ring molecular backbone, the rows

TABLE IV

Selected torsion angles (°)

Atoms	Torsion angle (°)	Atoms	Torsion angle (°)
Carboxylic groups			
C11—C12—C15—O2	174.5(4)	C24—C23—C22—O5	−179.8(4)
C11—C12—C15—O3	−7.6(4)	C24—C23—C22—O4	−0.4(4)
C12—C15—O3—C16	−177.3(4)	C23—C22—O4—C19	−177.3(4)
O2—C15—O3—C16	0.5(4)	O5—C22—O4—C19	2.1(4)
C15—O3—C16—C17	−114.7(4)	C22—O4—C19—C20	−99.5(4)
Octyloxygroups			
C9—O1—C8—C7	176.2(4)	C26—O6—C29—C30	−175.7(4)
O1—C8—C7—C6	−63.5(4)	O6—C29—C30—C31	65.2(4)
Nonyl group			
C21—C16—C17—C37	179.5(5)	C19—C18—C17—C37	−179.2(4)

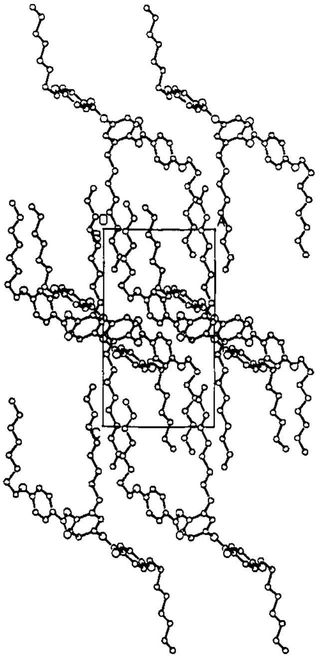

FIGURE 5 Crystal packing of NPOB projected along [010].

can be described as comb-like with an antiparallel orientation of the three teeth of each comb fragment in ratio 2:1. Each row is interlocked by its alkyl chains with the two neighbouring rows related to it by inversion centres.

Another striking feature of the crystal structure is that two different regions can be clearly discerned in it: One is located around $z/c = 1/2$ and comprises the benzene rings and carboxylic groups, whereas the other extends from $z/c = -1/4$ to $1/4$ and contains the non-polar hydrocarbon chains.

It can be concluded that the molecular structure of NPOB observed in the solid state is not consistent with the model of the bent laterally attached alkyl chain discussed for nematic phase in the introduction. Moreover, the molecular packing in the crystal, characterized by a pronounced interlocking of the hooked molecules, is apparently not the ideal precursor of the nematic phase. Therefore, the melting of the substance must be connected with a drastic change in the molecular conformation, especially concerning the lateral long-chain alkyl substituent. In this connection it is noteworthy that for the 2-*n*-alkyl-1,4-phenylene bis(4-*n*-octyloxybenzoates) after melting the existence of cybotactic groups as units of short range order has been proved by X-ray studies[12] despite the fact that the compounds do not form smectic phases. The model for the molecular packing within the cybotactic groups proceeds from the assumption that the alkyl chains have considerable flexibility for the members of the homologous series with $n \geq 5$.[12]

Judging from non-H intermolecular atomic distances there is no indication of other than normal van der Waals forces within the crystal lattice.

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