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## Liquid Crystals

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### A comparative study of mesogenic structures. The crystal structures of bis[(4-butoxycarbonyl)-phenyl]terephthalate and bis[(4-valeroyloxy)-phenyl]terephthalate

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**A comparative study of mesogenic structures**  
**The crystal structures of bis[(4-butoxycarbonyl)-phenyl]terephthalate**  
**and bis[(4-valeroyloxy)-phenyl]terephthalate**

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Smectogenic bis[(4-butoxycarbonyl)-phenyl]terephthalate (B-A) and nematogenic bis[(4-valeroyloxy)-phenyl]terephthalate (V-A) have been synthesized and their crystal and molecular structure have been determined, at room temperature, by direct methods. Crystals of B-A are triclinic, space group  $P\bar{1}$ ,  $a = 5.914(1) \text{ \AA}$ ,  $b = 8.532(1) \text{ \AA}$ ,  $c = 13.647(2) \text{ \AA}$ ,  $\alpha = 102.07(1)^\circ$ ,  $\beta = 92.73(2)^\circ$ ,  $\gamma = 73.21(2)^\circ$  with one molecule per unit cell. Crystals of V-A are monoclinic, space group  $P2_1/c$ ,  $a = 32.318(5) \text{ \AA}$ ,  $b = 5.350(3) \text{ \AA}$ ,  $c = 7.987(2) \text{ \AA}$ ,  $\beta = 92.84(2)^\circ$  with two molecules per unit cell. The structures were refined by the full matrix least squares method, to  $R = 0.050$  for B-A and  $R = 0.071$  for V-A. Molecules of B-A and V-A are centrosymmetric (point group  $C_i$ ) and show some differences in the structure of the phenyl terephthalate moiety, which are probably due to the different electron withdrawing effects of the terminal substituents linked to the phenyl rings. The crystal packing of the two compounds is different. Molecules of V-A are packed in layers with their long molecular axes normal to the layer surface, while in B-A molecular layers are formed in which the long molecular axes are highly tilted with respect to the layer normal.

### 1. Introduction

The mesophase behaviour of linear semiflexible polymers, i.e. polymers with a regular alternation along the chain of rigid and flexible sections, may be varied through a number of structural features. These include the nature of the rigid group, the nature and the length of the flexible spacer and the nature of the group linking the rigid and flexible sections. In addition seemingly secondary structural factors may actually have a strong influence on mesomorphism. This is the case for linear semiflexible polymers containing an ester linkage,  $-\text{COO}-$ , between rigid and flexible sections. In several cases, in fact, it was found that when the ester group is linked to the rigid moiety through an alkoxy oxygen, nematic phases are obtained, while, if the ester group is linked through the carbonyl carbon, the tendency to give nematic phases is drastically reduced, and smectic mesomorphism is preferred [1].

The conformational analysis of the two corresponding classes of polymers has shown some differences [2]; in particular a significant statistical population of highly extended conformers was found for systems containing the ester group linked at the mesogen through an alkoxy oxygen, while, in the reversed orientation of the ester group, the fraction of highly extended conformers of appreciable population is considerably smaller.

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We have performed a complete crystal structure analysis of the constitutional isomers



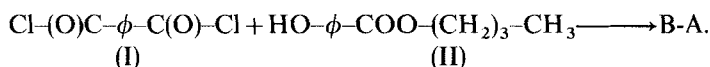
and



which are called B-A and V-A respectively ( $-\text{A}-=\phi-\text{OOC}-\phi-\text{COO}-\phi-$ ,  $-\phi- = p$ -phenylene). The choice of these compounds, which contain a rigid group to be found either in mesogenic polymers [1] or in low molar mass compounds [3, 4], was suggested by their different liquid-crystalline behaviour and by the possibility of finding correlations between molecular structure, crystal packing and mesogenic features.

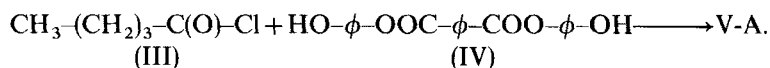
## 2. Experimental

Compound B-A was prepared according to the scheme



Compound (II), butyl-*p*-hydroxybenzoate ( $T_m = 343$  K), was prepared by Fischer esterification of *p*-hydroxybenzoic acid and *n*-butanol. The dichloride (I) (10 per cent less than the stoichiometric amount), previously dissolved in a few ml of anhydrous chloroform, was added dropwise under stirring to a solution of (II) in dry pyridine. The mixture was allowed to stir, at ambient temperature, for half an hour. B-A was then precipitated from the reaction mixture, in quantitative yield, by addition of ethanol; the raw product was purified by column chromatography (silica gel,  $\text{CHCl}_3$  as eluent) and finally recrystallized from a chloroform/ethanol mixture. The synthesis of B-A, following a different route, has already been described in the literature [4]. It should also be noted that melting and clearing temperatures of B-A reported in [4] are sensibly lower (7–8 K) than those found by us; in the same paper, moreover, the solid state polymorphism of the compound is not mentioned explicitly.

Compound V-A was prepared according to



Compound (IV), bis[[4-hydroxy)-phenyl]terephthalate ( $T_m = 591$  K), was prepared by esterification of hydroquinone and terephthaloyl chloride (molar ratio 10:1); it was dissolved in dry pyridine and to this solution, under stirring, valeroyl chloride (10 per cent in excess of the stoichiometric amount) was added. V-A was then collected from the reaction mixture by precipitation with ethanol and was purified by column chromatography as for B-A.

The transition temperatures were determined by differential scanning calorimetric analysis (Perkin-Elmer DSC 2, heating rate 10 K/min). Optical observations were made using a Mettler FP 5 microfurnace combined with a Leitz polarizing microscope. The X-ray diffraction patterns of the mesophases were recorded photographically ( $\text{CuK}_\alpha$  radiation) using a flat film camera equipped with a microfurnace to allow temperature control. The samples were sealed in Lindemann capillaries under nitrogen atmosphere.

Single crystals suitable for X-ray studies were obtained by evaporation from chloroform/*n*-hexane solutions for B-A (colourless prisms) and by evaporation from anhydrous acetone solutions for V-A (colourless prisms elongated in the *b* direction); Weissenberg and oscillation photographs showed triclinic symmetry for B-A and monoclinic  $P2_1/c$  symmetry for V-A.

Accurate cell parameters for both compounds were obtained through a least squares fit of the setting angles of 25, accurately centred, strong reflections, in the range  $15^\circ < 2\theta < 25^\circ$ , on an Enraf Nonius CAD-4 automated single crystal diffractometer, using graphite monochromated  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). A set of crystallographic relevant parameters is reported for both compounds in table 1. Data collection was performed in the range  $2^\circ < \theta < 60^\circ$  with a maximum value for  $\sin \theta / \lambda$  of  $0.561 \text{ \AA}^{-1}$ . Reflections were measured in the following ranges of indices:  $-6 \leq h \leq +6$ ,  $-9 \leq k \leq +9$ ,  $0 \leq l \leq 15$  for B-A, in the  $\omega/\theta$  scan mode;  $-36 \leq h \leq +36$ ,  $0 \leq k \leq 6$ ,  $0 \leq l \leq 8$ , for V-A, in the  $\omega$  scan mode. Two standard reflections periodically measured during data collection showed only random fluctuations in both cases. 1913 independent reflections were collected for B-A and 2024 for V-A. 180 reflections for B-A and 732 for V-A, having  $I < 3\sigma(I)$ , were not considered in the structural analysis. Lorentz and polarization corrections were applied, no corrections for absorption. A correction for secondary extinction was applied only for B-A (the final refined value of the extinction coefficient,  $g$  [5], is  $1.44(1) \times 10^{-5}$ ).

### 2.1. Determination and refinement of the structures

The space group of V-A,  $P2_1/c$ , and the number of molecules in the unit cell ( $Z = 2$ ), unequivocally fix the independent structural unit which is half a molecule. The same holds for compound B-A ( $Z = 1$ ), if we take  $P\bar{1}$  as the space group, as suggested by the E value statistics. Therefore, molecules of B-A and V-A are centrosymmetric (point group  $C_i$ ) with an inversion centre at the middle of the terephthaloyl moiety. The structures were solved by direct methods (Multan82 [6]). The E-map calculated with the set of phases having the highest combined figure of merit given by Multan showed all non-hydrogen atoms for both structures. Refinement (on  $F$ ), by the full matrix least squares method, was initially performed with individual isotropic thermal parameters for all

Table 1. Crystal data for compounds B-A and V-A.

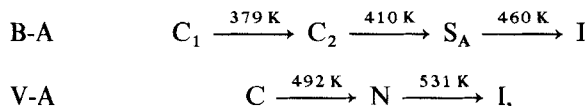
	B-A	V-A
	$\text{C}_{30}\text{H}_{28}\text{O}_8$ 518.57	
Formula weight		
Space group	Triclinic $P\bar{1}$	Monoclinic $P2_1/c$
$a/\text{\AA}$	5.914(1)	32.318(5)
$b/\text{\AA}$	8.532(1)	5.350(3)
$c/\text{\AA}$	13.647(2)	7.987(2)
$\alpha/^\circ$	102.07(1)	90
$\beta/^\circ$	92.73(2)	92.84(2)
$\gamma/^\circ$	73.21(2)	90
$V/\text{\AA}^3$	645(4)	1379(2)
$Z$	1	2
$D_x/\text{g cm}^{-3}$	1.336	1.248
$\mu(\text{Cu-K}\alpha)/\text{cm}^{-1}$	7.6	7.1
$F(000)$	274	548

non-hydrogen atoms and then with individual anisotropic ones. When convergence was achieved, hydrogen atoms were introduced in positions defined on stereochemical grounds. All hydrogen atoms were given isotropic thermal parameters equal to those of the carrier atoms. Hydrogen atoms were included in structure factor calculations but not refined. The analysis was terminated at  $R=0.050$  ( $R_w=0.055$ ,  $S=0.55$ ) for B-A and at  $R=0.071$  ( $R_w=0.058$ ,  $S=0.92$ ) for V-A. The largest parameter shift-to-error ratio in the last refinement cycle was less than 0.03 in both cases. The final difference Fourier maps showed no maxima higher than  $0.16 \text{ e} \text{ \AA}^{-3}$ . Unit weights were used for both compounds throughout the refinement. The rather high  $R$  value for V-A may be due to the poor quality of the crystal and, also, to the high thermal motion affecting the terminal aliphatic chain. Atomic scattering factors were taken from International Tables for X-ray Crystallography [7] and the programs from the Enraf Nonius Structure Determination Package [8].

Additional material to this paper, including lists of observed and calculated structure factors, anisotropic thermal parameters, coordinates and thermal parameters of hydrogen atoms, has been deposited as a Supplementary Publication with the British Library Document Supply Centre. Copies of these tables which comprise 23 pages may be obtained from the British Library, Lending Division, by quoting the number SUP 16519 according to the procedure described at the end of this issue.

### 3. Results and discussion

The mesophase behaviour of compounds B-A and V-A is consistent with the pattern described in the Introduction: B-A is smectogenic and V-A is nematogenic. The phase transitions are



(C=solid phase,  $S_A$ =smectic A phase, N=nematic phase, I=isotropic liquid) the numbers are the transition temperatures as determined in a DSC heating cycle.

The difference in the transition temperatures between the compounds is relevant: the smectic A phase of B-A becomes isotropic at a temperature far below the melting point of V-A. Yet, the thermal stability interval of the mesophase is larger in B-A.

The identification of the liquid crystal phases was based upon optical observations (fan and homeotropic textures for the smectic A phase of B-A and a schlieren texture for the nematic phase of V-A) and X-ray diffraction measurements. Compound B-A exhibits solid state polymorphism; the crystal phase whose structure is discussed in this paper is the low temperature one ( $C_1$ ). Its transformation to  $C_2$  does not occur topotactically.

Final refined coordinates and equivalent thermal parameters of the crystallographically independent half molecules of B-A and V-A are reported in table 2; bond lengths, bond angles and torsion angles are given in table 3. Molecular models and relative lettering are reported in figure 1.

Consistent with their mesogenic properties, molecules of B-A and V-A have a strongly anisometric shape, with a long axis, measured between the two terminal carbon atoms, of  $28.517(6) \text{ \AA}$  for B-A and  $29.64(1) \text{ \AA}$  for V-A. The value found for B-A is fully compatible with the layer periodicity of the smectic A phase, which is  $30.4(5) \text{ \AA}$  at 428 K. The terminal aliphatic chains are, substantially, in the all-*trans* planar

Table 2. Refined positional parameters and equivalent temperature factors with e.s.d.'s in parentheses.  $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab \cos \gamma B_{12} + ac \cos \beta B_{13} + bc \cos \alpha B_{23}]$ .

Atom	x	y	z	$B_{eq} (\text{\AA}^2)$
B-A				
O1	0.4038(3)	-0.9743(2)	0.3225(2)	4.40(5)
O2	0.7698(4)	-1.0121(3)	0.2681(2)	5.70(6)
O3	0.2283(3)	-0.3370(2)	0.1309(2)	4.01(4)
O4	-0.1385(4)	-0.3469(2)	0.0821(2)	5.19(5)
C1	0.1437(7)	-1.3206(4)	0.5114(3)	5.94(9)
C2	0.3506(6)	-1.3038(4)	0.4569(2)	4.39(7)
C3	0.2794(6)	-1.1488(4)	0.4105(3)	4.39(7)
C4	0.4858(6)	-1.1330(3)	0.3559(2)	4.39(7)
C5	0.5670(5)	-0.9306(3)	0.2783(2)	3.67(7)
C6	0.4657(5)	-0.7715(3)	0.2427(2)	3.17(6)
C7	0.6135(5)	-0.7187(3)	0.1887(2)	3.63(6)
C8	0.5264(5)	-0.5751(3)	0.1506(2)	3.65(6)
C9	0.2929(5)	-0.4847(3)	0.1677(2)	3.33(6)
C10	0.1415(5)	-0.5313(3)	0.2232(2)	3.75(6)
C11	0.2304(5)	-0.6771(3)	0.2598(2)	3.66(6)
C12	0.0176(5)	-0.2827(3)	0.0868(2)	3.45(6)
C13	0.0123(5)	-0.1357(3)	0.0431(2)	3.03(6)
C14	0.1923(5)	-0.0577(3)	0.0593(2)	3.43(6)
C15	-0.1785(5)	-0.0782(3)	-0.0162(2)	3.38(6)
V-A				
O1	-0.2726(1)	0.0706(7)	-0.3063(4)	7.19(9)
O2	-0.3002(1)	-0.180(1)	-0.1248(6)	16.0(2)
O3	-0.11101(9)	-0.0621(6)	-0.0729(4)	5.66(7)
O4	-0.0915(1)	0.2683(8)	-0.2218(5)	9.5(1)
C1	-0.4567(3)	-0.061(3)	-0.280(2)	26.6(7)
C2	-0.4212(2)	0.038(2)	-0.345(1)	18.0(4)
C3	-0.3816(2)	-0.060(2)	-0.255(1)	14.4(3)
C4	-0.3441(2)	0.043(2)	-0.3284(8)	10.6(2)
C5	-0.3048(2)	-0.041(1)	-0.2377(7)	9.1(2)
C6	-0.2322(1)	0.025(1)	-0.2375(5)	6.0(1)
C7	-0.2107(2)	-0.1779(9)	-0.2947(5)	5.9(1)
C8	-0.1696(2)	-0.2033(9)	-0.2399(5)	5.7(1)
C9	-0.1527(1)	-0.0270(9)	-0.1308(5)	5.4(1)
C10	-0.1745(1)	0.1749(9)	-0.0721(5)	5.7(1)
C11	-0.2155(2)	-0.2004(9)	-0.1270(5)	6.1(1)
C12	-0.0824(1)	0.1000(9)	-0.1279(5)	6.0(1)
C13	-0.0403(1)	0.0445(8)	-0.0589(5)	5.1(1)
C14	-0.0313(1)	-0.1673(8)	0.0403(5)	5.5(1)
C15	-0.0088(1)	0.2090(9)	-0.0980(5)	5.6(1)

conformation. For compound V-A, in particular, the atoms of the aliphatic chain show very large thermal factors, which are highly anisotropic and increase with the separation from the carbonyl carbon to the end of the chain. The thermal parameters for atoms C1 and C2 correspond to root mean square vibration amplitudes larger than 0.5 Å in a direction which is approximately perpendicular to the plane of the zig-zag conformation. Probably because of the high thermal motion some bond lengths (in

Table 3. Bond lengths given in Å, bond angles in ° and torsion angles in ° with e.s.d.'s in parentheses.

B-A			
O1–C4	1.462(4)	C6–C7	1.393(5)
O1–C5	1.339(4)	C6–C11	1.394(4)
O2–C5	1.198(3)	C7–C8	1.383(4)
O3–C9	1.398(3)	C8–C9	1.377(4)
O3–C12	1.357(3)	C9–C10	1.390(5)
O4–C12	1.195(4)	C10–C11	1.390(4)
C1–C2	1.518(6)	C12–C13	1.491(4)
C2–C3	1.527(5)	C13–C14	1.397(4)
C3–C4	1.512(4)	C13–C15	1.388(4)
C5–C6	1.488(4)	C14–C15*	1.387(4)
C4–O1–C5	115.8(2)	O3–C9–C8	114.1(3)
C9–O3–C12	122.6(2)	O3–C9–C10	123.5(2)
C1–C2–C3	111.4(2)	C8–C9–C10	122.3(3)
C2–C3–C4	111.2(2)	C9–C10–C11	118.0(2)
O1–C4–C3	106.4(2)	C6–C11–C10	120.7(3)
O1–C5–O2	123.3(3)	O3–C12–O4	124.4(3)
O1–C5–C6	112.1(2)	O3–C12–C13	110.4(3)
O2–C5–C6	124.6(3)	O4–C12–C13	125.2(3)
C5–C6–C7	117.8(2)	C12–C13–C14	122.1(2)
C5–C6–C11	122.6(3)	C12–C13–C15	117.7(3)
C7–C6–C11	119.6(3)	C14–C13–C15	120.3(3)
C6–C7–C8	120.2(2)	C13–C14–C15*	119.5(2)
C7–C8–C9	119.1(3)	C13–C15–C14*	120.2(3)
C5–O1–C4–C3	175.4(2)	C11–C6–C7–C8	–1.1(4)
C4–O1–C5–O2	–1.8(4)	C5–C6–C11–C10	–178.4(3)
C4–O1–C5–C6	177.5(2)	C7–C6–C11–C10	0.2(4)
C12–O3–C9–C8	140.9(3)	C6–C7–C8–C9	0.6(4)
C12–O3–C9–C10	–43.7(4)	C7–C8–C9–O3	176.4(2)
C9–O3–C12–O4	6.0(4)	C7–C8–C9–C10	0.9(4)
C9–O3–C12–C13	–172.3(2)	O3–C9–C10–C11	–176.8(3)
C1–C2–C3–C4	–179.8(3)	C8–C9–C10–C11	–1.8(4)
C2–C3–C4–O1	–175.2(2)	C9–C10–C11–C6	1.2(4)
O1–C5–C6–C7	–175.3(2)	O3–C12–C13–C14	–7.5(4)
O1–C5–C6–C11	3.4(4)	O3–C12–C13–C15	171.7(2)
O2–C5–C6–C7	4.0(4)	O4–C12–C13–C14	174.1(3)
O2–C5–C6–C11	–177.3(3)	O4–C12–C13–C15	–6.6(4)
C5–C6–C7–C8	177.6(3)		
V-A			
O1–C5	1.340(7)	C6–C7	1.380(7)
O1–C6	1.411(5)	C6–C11	1.379(7)
O2–C5	1.174(8)	C7–C8	1.385(7)
O3–C9	1.415(5)	C8–C9	1.378(6)
O3–C12	1.356(6)	C9–C10	1.384(7)
O4–C12	1.199(6)	C10–C11	1.381(7)
C1–C2	1.39(1)	C12–C13	1.474(6)
C2–C3	1.53(1)	C13–C14	1.405(6)
C3–C4	1.48(1)	C13–C15	1.391(6)
C4–C5	1.500(8)	C14–C15*	1.374(6)

Table 3 (continued).

C5–O1–C6	119.1(4)	O3–C9–C8	117.2(4)
C9–O3–C12	117.5(3)	O3–C9–C10	119.1(4)
C1–C2–C3	112(1)	C8–C9–C10	123.8(4)
C2–C3–C4	111.7(7)	C9–C10–C11	117.8(4)
C3–C4–C5	112.9(6)	C6–C11–C10	118.4(4)
O1–C5–O2	121.7(5)	O3–C12–O4	122.2(4)
O1–C5–C4	109.0(5)	O3–C12–C13	112.4(4)
O2–C5–C4	129.3(6)	O4–C12–C13	125.4(4)
O1–C6–C7	118.5(4)	C12–C13–C14	122.3(4)
O1–C6–C11	117.3(4)	C12–C13–C15	117.4(4)
C7–C6–C11	124.0(5)	C14–C13–C15	120.3(4)
C6–C7–C8	117.6(4)	C13–C14–C15*	119.0(4)
C7–C8–C9	118.4(4)	C13–C15–C14*	120.7(4)
C6–O1–C5–O2	–2.2(9)	C11–C6–C7–C8	–1.4(7)
C6–O1–C5–C4	178.1(5)	O1–C6–C11–C10	–173.0(4)
C5–O1–C6–C7	87.6(6)	C7–C6–C11–C10	1.3(7)
C5–O1–C6–C11	–97.8(6)	C6–C7–C8–C9	0.7(6)
C12–O3–C9–C8	110.5(4)	C7–C8–C9–O3	178.1(4)
C12–O3–C9–C10	–71.4(5)	C7–C8–C9–C10	0.1(7)
C9–O3–C12–O4	0.1(6)	O3–C9–C10–C11	–178.2(4)
C9–O3–C12–C13	179.9(3)	C8–C9–C10–C11	–0.2(7)
C1–C2–C3–C4	179(1)	C9–C10–C11–C6	–0.4(6)
C2–C3–C4–C5	177.3(7)	O3–C12–C13–C14	5.3(6)
C3–C4–C5–O1	–177.0(6)	O3–C12–C13–C15	–175.8(4)
C3–C4–C5–O2	3(1)	O4–C12–C13–C14	–175.0(4)
O1–C6–C7–C8	172.8(4)	O4–C12–C13–C15	3.9(7)

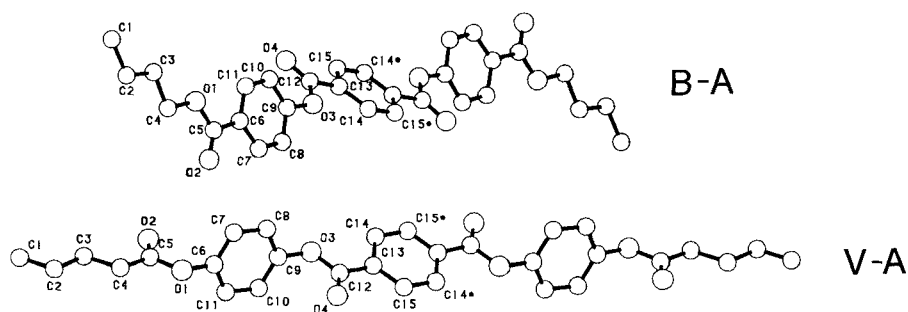


Figure 1. A stereoview of molecules B-A and V-A.

particular C1–C2) are shorter than the standard values. The orientation of the terminal aliphatic chain with respect to the adjacent phenyl ring is different in the two compounds. In B-A, owing to the partial double bond character of the bond C5–C6, the plane containing the carbon atoms of the chain is nearly coplanar with the phenyl ring, while it is almost orthogonal in V-A. Qualitatively, this is a consequence of the different rotational freedom around the bond contiguous to the phenyl ring. However, some influence of the crystal packing on the definition of the specific value ( $87.6(6)^\circ$ ) found for the torsional angle C5–O1–C6–C7 in V-A cannot be excluded. As far as the structural parameters of the phenylene terephthalate moiety are concerned, the geometry of the terephthaloyloxy group is similar in both compounds, showing a slight deviation from



the *trans* planar conformation of O4–C12–C13–C14, owing to the repulsion between O4 and the hydrogen atom bonded to C15 (O4⋯C15 = 2.838(4) Å for B-A and 2.821(6) Å for V-A). The other structural parameters of the phenylene terephthalate moiety are, however, significantly different in the two compounds. In fact, for V-A, the torsional angle around bond C9–O3 (C12–O3–C9–C10 =  $-71.4(5)^\circ$ ) is close to the idealized value of  $-68.4^\circ$  as reported by Coulter and Windle [9], while for B-A a significantly smaller torsional angle is observed (C12–O3–C9–C10 =  $-43.7(4)^\circ$ ). Moreover, in B-A, a torsional angle around bond C12–O3, which deviates from the *trans* planar conformation (C9–O3–C12–C13 =  $-172.3(2)^\circ$  in B-A as compared to the value of  $179.9(3)^\circ$  in V-A) and, also, larger values of the bond angles C9–O3–C12 ( $122.6(2)^\circ$  in B-A, as compared to the value of  $117.5(3)^\circ$  in V-A) and O3–C9–C10 ( $123.5(2)^\circ$  in B-A,  $119.1(4)^\circ$  in V-A) are observed, presumably a result, at least partially of the repulsion between O4 and the hydrogen atom bonded to C10. It should be noted that these differences, which might be related, to some extent, with crystal packing, are also consistent with the different electronic character of the substituents in the para position with respect to the terephthaloyloxy moiety, that is CH<sub>3</sub>–(CH<sub>2</sub>)<sub>3</sub>–COO– for V-A and CH<sub>3</sub>–(CH<sub>2</sub>)<sub>3</sub>–OOC– for B-A. The electron withdrawing effect of the ROOC– substituent in B-A (as compared to the electron releasing effect of the RCOO– group in V-A) should enhance, in fact, the double bond character of the bond C9–O3, thus causing a decrease in the torsional angle, in order to obtain a better  $\pi$  interaction between C9 and O3, and should decrease the bond order and the rigidity of torsion around the bond C12–O3 [9]. The crystal packing of the two compounds is shown in figures 2 and 3. A common feature is the parallel arrangement of the long molecular axes which is, again, consistent with the mesogenic character of the compounds.

The packing of V-A may be described as an assembly of molecular layers piled up along *a*. The long molecular axes are perpendicular to the layer, thus recalling a smectic A type arrangement. Compound V-A, however, is nematogenic, and it should be noted that the crystal structures of nematogenic rod-like compounds reported in the literature show, almost invariably, imbricated packing of the molecules. In the *a* direction, layers of V-A molecules are packed by aliphatic–aliphatic van der Waals interactions and no intercalation occurs between the alkyl tails of molecules belonging to consecutive layers. This is consistent with the large thermal parameters observed for the atoms of the chain and with the difficulty that we experienced in growing single crystals well developed along *a*. Within each layer the packing shows lateral correspondence between chemically homologous molecular sections (aromatic–aromatic, aliphatic–aliphatic). The main features of the lateral packing of V-A, as can be deduced from figure 4, are phenyl face to phenyl edge and carbonyl carbon to

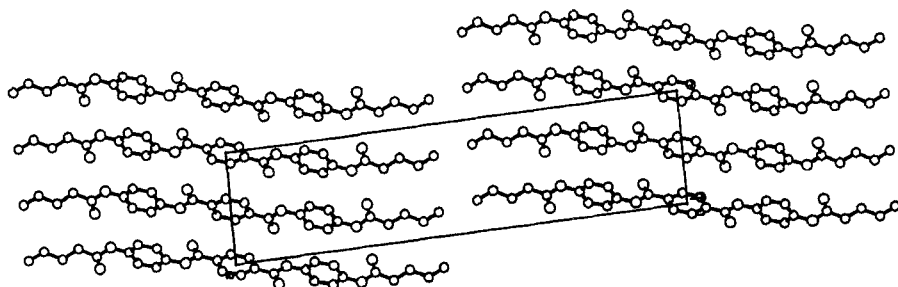


Figure 2. The crystal packing of V-A viewed along *b*.

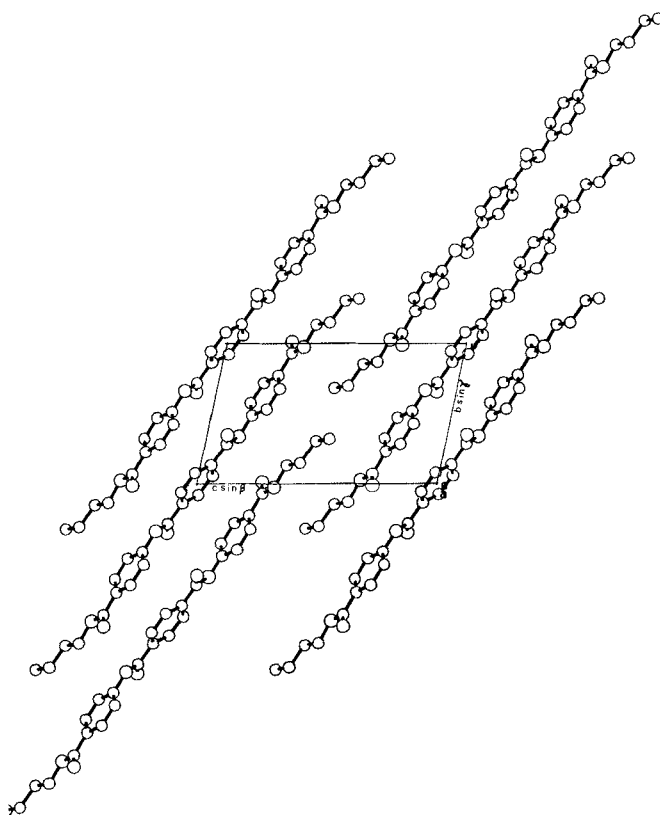


Figure 3. The crystal packing of B-A viewed along  $a$ .

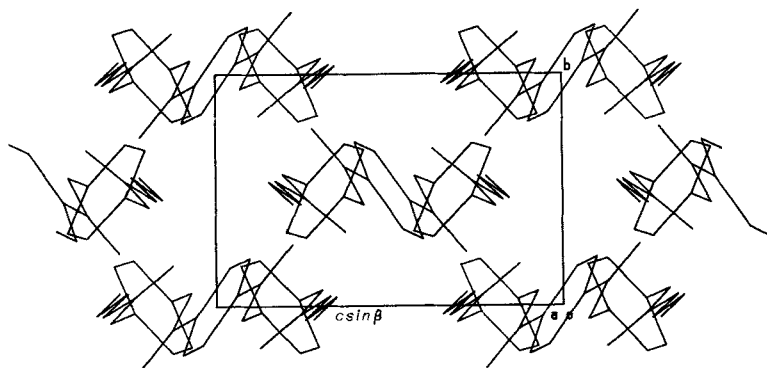


Figure 4. The crystal packing of V-A viewed along  $a$ .

carbonyl oxygen contacts. These features have also been found in the room temperature crystal structure of poly(*p*-phenylene terephthalate) [10], whose lateral packing resembles, very closely, that of V-A.

The crystal packing of B-A shows significantly different features. Elementary translations along *a* and *b* axes generate molecular layers which pile up along *c*. Within each layer, the long molecular axes are strictly parallel to each other and highly tilted with respect to the layer normal. Translation along *b* corresponds to a shift in the direction of the long molecular axis so that the terephthaloyloxy group of a molecule comes in contact with *p*-oxybenzoate moieties of the neighbouring molecules, still maintaining some phenyl face to phenyl edge and carbonyl carbon to carbonyl oxygen contacts. This packing does not appear to be in any immediate relation to the smectic A nature of the liquid crystal phase exhibited by B-A. We note, however, that the crystal phase which actually melts to give the smectic phase is C<sub>2</sub>; in this respect, the presence in the diffraction pattern of the phase C<sub>2</sub> of diffraction orders corresponding to a periodicity of 26.6(5) Å at 398 K, could be indicative, in the most simple hypothesis, of a layered structure in which the long molecular axes are still tilted with respect to the layer normal ( $\approx 30^\circ$ ) but to a lesser extent than in phase C<sub>1</sub>.

In conclusion, a different crystal packing between B-A and V-A is not at all surprising, on account of the differences distinguishing their molecular structure (in particular the different torsional angle around the bond O3-C9 and the different orientations of the terminal ester group with respect to the phenyl ring). However, no simple and direct correlation is visible between crystal packing and the liquid-crystalline structure exhibited. Furthermore, the evidently too simple expectation of an imbricated pattern for the crystal packing of nematogenic V-A and of a normal layered packing for smectogenic B-A is exactly contradicted.

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