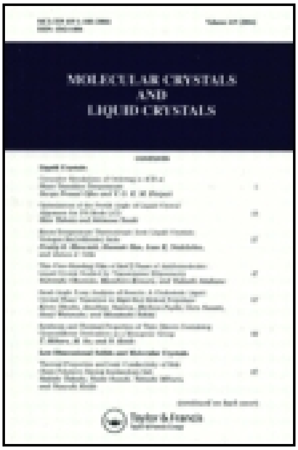

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The Crystal and Molecular Structure of a Reentrant Nematogen: 4-Cyanophenyl-3-methyl-4′-(4″-n-undecyloxy cinnamoyloxy) benzoate (11 CPMCB)[†]

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The crystal and molecular structure of 4-cyanophenyl-3-methyl-4′-(4″-n-undecyloxycinnamoyloxy)benzoate (11 CPMCB), $C_{35}H_{39}O_5N$, has been determined at room temperature by direct methods. The compound, which exhibits a reentrant nematic phase, crystallizes in the triclinic space group $P\bar{1}$, $a = 10.368$, $b = 10.846$, $c = 16.750$ Å, $\alpha = 97.90$, $\beta = 100.28$, $\gamma = 118.68°$, with two molecules in the unit cell. The structure has been refined to $R = 0.106$, using photographically observed data. The 11 CPMCB molecules pack in a well-imbricated antiparallel arrangement with their alkoxy chains fully extended. The molecular packing in the crystal is discussed with reference to the reentrant behavior of the compound.

INTRODUCTION

4-cyanophenyl-3-methyl-4′-(4″-n-undecyloxy cinnamoyloxy)benzoate (11 CPMCB) exhibits reentrant nematic behavior at atmospheric pressure. This compound was first synthesized and characterized by Urs and Sadashiva[1] and undergoes the following phase transitions:

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

$$\begin{tikzcd}
\text{solid} \arrow[r, "102.4^\circ\text{C}"] & \text{reentrant nematic} \arrow[r, "107^\circ\text{C}"] & \text{smectic A} \arrow[d, "153.2^\circ\text{C}"] \\
& \text{isotropic} & \text{nematic} \arrow[l, "193.6^\circ\text{C}"']
\end{tikzcd}$$

The analysis of the crystal and molecular structure of 11 CPMCB was undertaken (a) to make a comparison of its molecular packing with those known to exist in nematogenic and smectogenic crystals, and (b) to attempt to understand its reentrant property in terms of the molecular arrangement in the crystal. This paper reports the first crystal structure determination of a reentrant nematogen.

Experimental

Mr. M. Subramanya Raj Urs synthesized the compound and kindly provided the transparent white needle-like crystals used in the analysis. Oscillation and Weissenberg photographs revealed the crystal to be triclinic. The space group $P\bar{1}$ was selected on the basis of the E-value statistics and was later confirmed by the successful least-squares refinement. The unit cell parameters were refined using high angle reflections from projection Weissenberg photographs. The crystal data are listed in Table I.

Three-dimensional intensity data were collected photographically using CuKα radiation. The diffracted spots were rather diffused and the data did not extend to high Bragg angles, so that only 1735 independent reflections could be recorded. The intensities were estimated visually and corrected for Lorentz-polarization factors and spot-shape effect. No absorption correction was applied.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by direct methods using the computer program MULTAN-80.[2] The E-map corresponding to the best solution of MULTAN revealed all the non-hydrogen atoms.

The atomic parameters were refined by full-matrix least-squares technique using the SHELX-76 program system.[3] Four cycles of refinement with isotropic thermal parameters gave an R-value ($\Sigma|\Delta F|/\Sigma|F_0|$) of 0.189. Further refinement with anisotropic thermal parameters reduced the R-factor to 0.136. At this stage, the hydrogen atoms were introduced in their theoretically calculated positions and assigned isotropic thermal parameters (U's) one unit (i.e., 0.01 Å^2) greater than the equivalent isotropic

TABLE I

Crystal Data

Molecular Formula		$C_{35}H_{39}O_5N$
Molecular weight		553.7
a	=	10.368 ± 0.008 Å
b	=	10.846 ± 0.008 Å
c	=	16.750 ± 0.010 Å
α	=	97.90 ± 0.2°
β	=	100.28 ± 0.3°
γ	=	118.68 ± 0.3°
Space group		$P\bar{1}$
V	=	1571.59 $Å^3$
$F(000)$	=	592
$\mu(\mathrm{CuK}\alpha)$	=	5.4 cm^{-1}
Z	=	2
D_c	=	1.17 $\mathrm{gm\,cm}^{-3}$
D_m(flotation)	=	1.14 ± 0.03 $\mathrm{gm \cdot cm}^{-3}$

value of the corresponding carbon atoms. Due to the lack of sufficient data, the hydrogen atoms were not refined, but their contribution was included in the structure factor calculations. The final R was 0.106

$$\left(R_g = \left[\frac{\Sigma(|\Delta F| \cdot |\Delta F|)}{\Sigma(|F_0| \cdot |F_0|)}\right]^{1/2} \text{was } 0.088\right).$$

The final positional parameters and isotropic equivalents of the anisotropic thermal parameters of all the non-hydrogen atoms are listed in Table II. The atom numbering scheme is indicated in Figure 1. The tables of structure factors and a list of the parameters of the hydrogen atoms in their ideal positions are available with the author and will be supplied on request. The structure determination and refinement were carried out on the DEC-1090 computer at Indian Institute of Science, Bangalore.

RESULTS AND DISCUSSION

The bond lengths and angles involving the non-hydrogen atoms are listed in Table III. Within the limits of experimenta error, the molecular dimensions are normal ($\Delta \leq 3\sigma$). In the phenyl rings, the average value of the C—C lengths is 1.39 (0.02) Å and the C—C—C angles average to 120 (1)°. In the alkoxy chain, the average C—C distance is 1.52 (0.02) Å.

The least-squares mean planes through various groups of atoms have been calculated with respect to an orthogonal coordinate system. Table IV

TABLE II

Final fractional atomic coordinates ($\times 10^3$) with e.s.d.'s in parentheses and isotropic equivalents ($\times 10^3$) of the anisotropic thermal parameters

Atom	x	y	z	U_{eq} (Å^2)
N(1)	−304(2)	412(1)	192(1)	92
C(2)	−222(2)	388(1)	165(1)	72
C(3)	−123(2)	356(2)	128(1)	70
C(4)	−146(2)	214(2)	108(1)	77
C(5)	−51(2)	185(1)	76(1)	71
C(6)	72(2)	303(2)	61(1)	68
C(7)	102(2)	443(2)	80(1)	81
C(8)	6(2)	470(1)	113(1)	78
O(9)	179(1)	274(1)	34(1)	80
C(10)	190(2)	287(1)	−47(1)	73
O(11)	111(1)	310(1)	−93(1)	89
C(12)	315(2)	262(1)	−61(1)	70
C(13)	392(2)	214(1)	−10(1)	71
C(14)	502(2)	193(1)	−29(1)	73
C(15)	526(2)	209(1)	−106(1)	66
C(16)	457(2)	257(1)	−161(1)	70
C(17)	344(2)	279(1)	−141(1)	73
C(18)	494(2)	278(2)	−243(1)	95
O(19)	641(1)	184(1)	−126(1)	75
C(20)	607(2)	42(2)	−148(1)	80
O(21)	480(1)	−53(1)	−147(1)	109
C(22)	723(2)	30(1)	−172(1)	69
C(23)	687(2)	−108(2)	−203(1)	73
C(24)	791(2)	−146(1)	−236(1)	70
C(25)	734(1)	−297(2)	−266(1)	79
C(26)	819(2)	−344(1)	−300(1)	79
C(27)	961(2)	−241(2)	−307(1)	74
C(28)	1018(2)	−90(2)	−278(1)	77
C(29)	929(2)	−49(1)	−245(1)	72
O(30)	1039(1)	−295(1)	−342(1)	84
C(31)	1185(2)	−194(1)	−352(1)	86
C(32)	1240(2)	−287(1)	−394(1)	73
C(33)	1390(2)	−192(1)	−412(1)	78
C(34)	1445(2)	−285(1)	−455(1)	77
C(35)	1595(2)	−197(1)	−477(1)	80
C(36)	1647(2)	−294(1)	−519(1)	81
C(37)	1802(2)	−204(1)	−537(1)	85
C(38)	1854(2)	−300(1)	−577(1)	86
C(39)	2002(2)	−219(1)	−599(1)	85
C(40)	2055(2)	−313(2)	−641(1)	108
C(41)	2204(2)	−229(1)	−660(1)	100

lists the equations of these mean planes and the angles between the relevant pairs of planes. The phenyl rings A and C are inclined to each other at 10° 06′, whereas ring B is tilted away from them, making an angle of 64° 09′ with ring A and 74° 12′ with ring C. The carboxyl group (plane D)

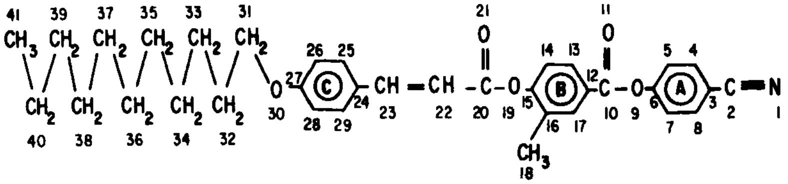

FIGURE 1 The structural formula of 11 CPMCB showing the numbering scheme for the atoms.

between the rings A and B is tilted away from ring A by 71° 05′ and makes an angle of 6° 57′ with ring B. The conformation of this part of the molecule is similar to that in phenyl benzoate,[4] 4′-nitrophenyl-4-n-octoxybenzoate[5] and 4′-cyanophenyl-4-n-pentoxybenzoate.[6] The —CH=CH—C(O)—O—group (plane E) is tilted away from ring B by 73° 02′ and makes an angle of 4° 42′ with ring C. The undecyloxy chain is fully extended. Figure 2 gives the perspective drawing of the 11 CPMCB molecule obtained using the ORTEP program.[7]

Figures 3 and 4 show the molecular packing in the *ac*- and *bc*-planes respectively. The short intermolecular contacts for non-hydrogen atoms are listed in Table V. The 11 CPMCB molecules associate in antiparallel pairs making an angle of about 25° with the *a*-axis. The molecular arrangement could be described as imbricated, wherein the end of one molecule falls near the central portion of its neighbor. This mode of molecular packing is typical of a nematogenic crystal (see, e.g., Refs. 8 and 9). Neighboring molecules in the unit cell are staggered with respect to each other along their long molecular axes. This results in alternate layers of phenyl ring systems and undecyloxy chains stacked on top of one another parallel to the *ab*-plane at $z = 0$ and $z = \frac{1}{2}$ respectively (see Figures 3 and 4). Another interesting feature is that all the short intermolecular contacts (<3.7 Å) are between atoms in the ring systems (with two of the contacts being less than the sum of the van der Waals' radii of the corresponding atoms). Thus, the layers consisting of phenyl ring systems form high density regions and alternate with the low density regions of undecyloxy chains. A density wave in the molecular arrangement is found to occur in the crystal structures of most smectogenic compounds[‡] and could be interpreted as a smectogenic feature. Consequently, though the 11 CPMCB molecules pack in a well-imbricated arrangement (hence the K–N_{re} transition), there is an inher-

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[‡] Such a density modulation often results in a perfect layer-like packing as found in the crystal structures of ethyl *p*-azoxy-benzoate[10] and TBBA.[11]

TABLE III

(a) Bond lengths (Å) with standard deviations in parentheses

Atoms	Distance	Atoms	Distance
N(1)–C(2)	1.14(3)	C(20)–C(22)	1.40(3)
C(2)–C(3)	1.44(3)	C(22)–C(23)	1.35(2)
C(3)–C(4)	1.42(2)	C(23)–C(24)	1.49(3)
C(4)–C(5)	1.35(3)	C(24)–C(25)	1.43(2)
C(5)–C(6)	1.40(2)	C(25)–C(26)	1.37(3)
C(6)–C(7)	1.37(3)	C(26)–C(27)	1.40(2)
C(7)–C(8)	1.34(3)	C(27)–C(28)	1.42(2)
C(3)–C(8)	1.42(2)	C(28)–C(29)	1.37(3)
C(6)–O(9)	1.42(2)	C(29)–C(24)	1.36(2)
O(9)–C(10)	1.40(2)	C(27)–O(30)	1.36(2)
C(10)–O(11)	1.17(3)	O(30)–C(31)	1.44(2)
C(10)–C(12)	1.49(3)	C(31)–C(32)	1.52(3)
C(12)–C(13)	1.39(3)	C(32)–C(33)	1.51(2)
C(13)–C(14)	1.35(3)	C(33)–C(34)	1.54(2)
C(14)–C(15)	1.38(2)	C(34)–C(35)	1.53(2)
C(15)–C(16)	1.37(3)	C(35)–C(36)	1.54(2)
C(16)–C(17)	1.39(3)	C(36)–C(37)	1.54(2)
C(16)–C(18)	1.52(2)	C(37)–C(38)	1.53(3)
C(17)–C(12)	1.45(2)	C(38)–C(39)	1.50(2)
C(15)–O(19)	1.43(2)	C(39)–C(40)	1.52(3)
O(19)–C(20)	1.38(2)	C(40)–C(41)	1.49(2)
C(20)–O(21)	1.23(2)		

(b) Bond angles (°) with standard deviations in parentheses

N(1)–C(2)–C(3)	177(1)	O(19)–C(20)–O(21)	117(2)
C(2)–C(3)–C(4)	123(1)	O(19)–C(20)–C(22)	113(1)
C(2)–C(3)–C(8)	120(2)	O(21)–C(20)–C(22)	130(2)
C(3)–C(4)–C(5)	122(1)	C(20)–C(22)–C(23)	115(1)
C(4)–C(5)–C(6)	116(1)	C(22)–C(23)–C(24)	124(1)
C(5)–C(6)–C(7)	124(2)	C(23)–C(24)–C(25)	116(1)
C(6)–C(7)–C(8)	119(1)	C(23)–C(24)–C(29)	126(1)
C(7)–C(8)–C(3)	121(2)	C(24)–C(25)–C(26)	121(1)
C(8)–C(3)–C(4)	118(2)	C(25)–C(26)–C(27)	120(1)
C(5)–C(6)–O(9)	116(2)	C(26)–C(27)–C(28)	120(2)
C(7)–C(6)–O(9)	120(1)	C(27)–C(28)–C(29)	118(1)
C(6)–O(9)–C(10)	116(1)	C(28)–C(29)–C(24)	123(1)
O(9)–C(10)–O(11)	124(2)	C(29)–C(24)–C(25)	118(2)
O(9)–C(10)–C(12)	107(2)	C(26)–C(27)–O(30)	117(1)
O(11)–C(10)–C(12)	129(2)	C(28)–C(27)–O(30)	123(1)
C(10)–C(12)–C(13)	127(2)	C(27)–O(30)–C(31)	119(1)
C(10)–C(12)–C(17)	114(2)	O(30)–C(31)–C(32)	106(1)
C(12)–C(13)–C(14)	123(2)	C(31)–C(32)–C(33)	111(1)
C(13)–C(14)–C(15)	117(2)	C(32)–C(33)–C(34)	111(1)
C(14)–C(15)–C(16)	125(2)	C(33)–C(34)–C(35)	114(1)
C(15)–C(16)–C(17)	118(2)	C(34)–C(35)–C(36)	113(1)
C(16)–C(17)–C(18)	118(2)	C(35)–C(36)–C(37)	112(1)
C(17)–C(12)–C(13)	119(2)	C(36)–C(37)–C(38)	112(1)
C(14)–C(15)–O(19)	116(2)	C(37)–C(38)–C(39)	114(1)
C(16)–C(15)–O(19)	119(2)	C(38)–C(39)–C(40)	116(2)
C(15)–O(19)–C(20)	118(1)	C(39)–C(40)–C(41)	114(2)

TABLE IV

(a) Equations of the various least-squares mean planes defined as $px + qy + rz = s$ (where x, y, z form an orthonormal system with x along the a-axis and y-axis in the ab-plane).

Plane	Atoms in the plane	p	q	r	s	r.m.s. displacement in Å
A	Phenyl ring A	−0.38745	0.06440	−0.91964	−0.34099	0.006
B	Phenyl ring B	−0.21378	−0.86972	−0.44484	−2.39271	0.019
C	Phenyl ring C	−0.35316	0.23670	−0.90512	−0.09507	0.010
D	C(6),O(9),C(10), O(11),C(12)	−0.17424	−0.92281	−0.34359	−2.55652	0.022
E	O(19),C(20),O(21), C(22),C(23)	−0.28074	0.21221	−0.93603	0.61996	0.038

(b) Angles between the mean planes

Planes	Angle
A & B	64°09′
B & C	74°12′
A & C	10°06′
A & D	71°05′
B & D	6°57′
B & E	73°02′
C & E	4°42′

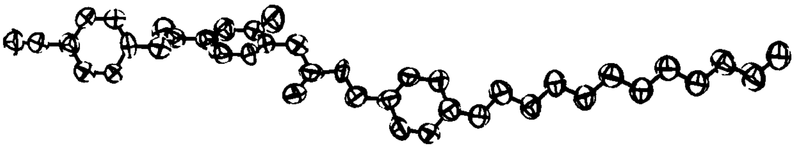

FIGURE 2 Perspective view of the 11 CPMCB molecule.

ent layer-like characteristic which perhaps manifests itself at higher temperatures as the smectic phase. This explanation of the reentrant behavior also suggests that the reentrant nematic phase consists of pairs of associated molecules formed by dipole interactions between cyano groups and that the smectic phase should be bilayered.

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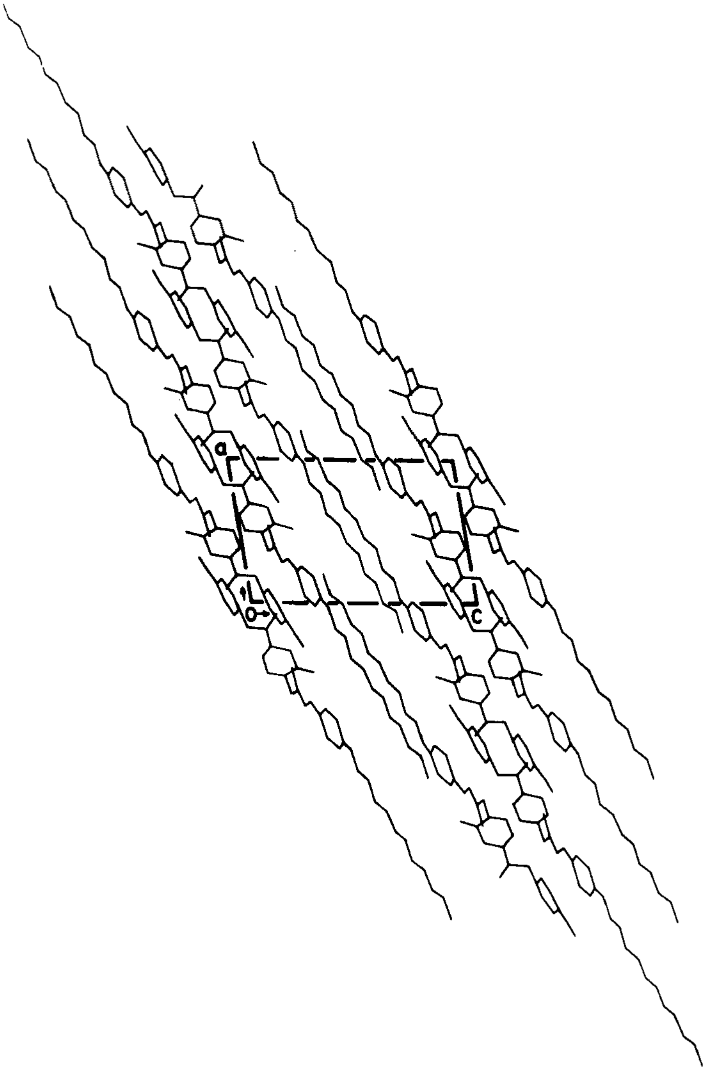

FIGURE 3 Molecular arrangement in the *ac*-plane.

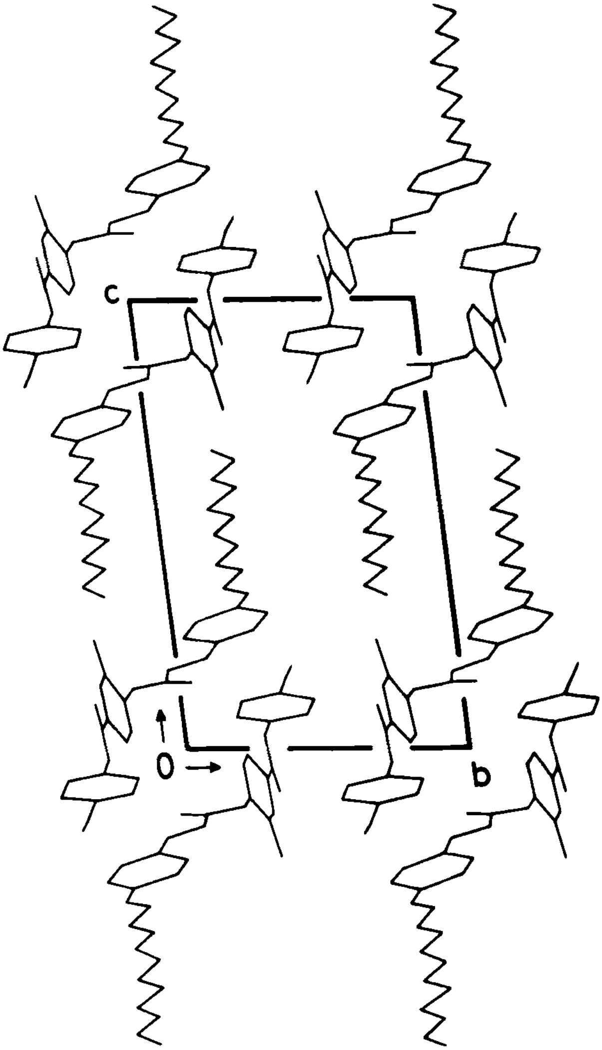

FIGURE 4 Molecular arrangement in the *bc*-plane.

TABLE V

Intermolecular contacts

From atom at x, y, z	To atom	At	Distance (Å)
O(11)	N(1)	$-x, 1-y, -z$	3.54
O(21)	N(1)	$-x, -y, -z$	3.31
C(14)	C(2)	$1+x, y, z$	3.50
O(11)	C(2)	$-x, 1-y, -z$	3.39
O(21)	C(2)	$-x, -y, -z$	3.25
C(14)	C(3)	$1+x, y, z$	3.70
O(21)	C(4)	$-x, -y, -z$	3.27
C(27)	C(4)	$1-x, -y, -z$	3.43
C(28)	C(4)	$1-x, -y, -z$	3.62
C(24)	C(5)	$1-x, -y, -z$	3.67
C(28)	C(5)	$1-x, -y, -z$	3.69
C(29)	C(5)	$1-x, -y, -z$	3.68
C(25)	C(6)	$1-x, -y, -z$	3.68
C(8)	C(7)	$-x, 1-y, -z$	3.63
O(19)	C(7)	$1-x, 1-y, -z$	3.48
O(11)	C(8)	$-x, 1-y, -z$	3.18
C(22)	O(11)	$1+x, y, z$	3.52
O(21)	C(14)	$1-x, -y, -z$	3.51

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