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Crystal Structure of a Mesogenic Twin

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The compound under study is a double mesogen in which two rigid p-terphenyl-based units are laterally connected by a carbonate linker. The cystal structure has been determined and reported. Here some crystallogra-phic calculations have been done to correlate the structure – property relationship of the compound. The six rings are found to be in different conformations. No two rings are coplanar. The four decycloxy side chains are maximally extended. Molecules of the compound are packed along the crystallographic a-axis. The molecular arrangement is a precursor of smectic phase. Texture study has been performed and supercooling region was found. The layer spacing and intermolecular distance during the entire mesomorphic range have been studied from X-ray diffraction technique.

Keywords: Mesogenic twin; smectic A phase; smectic layer periodicity

INTRODUCTION

The liquid crystalline compound bis - (4,4" - dicycloxy - p - terphenyl - 2' - yl) methyl carbonate has been undertaken for study. The title compound has been reported as a new type of twin mesogen . It is considered to be prepolymer synthesized by Jens Andersch and Carsten Tschierske [1]. The title compound is a double mesogen in which two rigid p-terphenyl-based units are connected laterally by a carbonate linker. We have solved the crystal structure of the title compound. Here we report some significant data to analyse the mesomorphic behaviour. From X-ray diffraction technique we have studied the smectic A phase. The texture study has also been done.

EXPERIMENTAL DETAILS

Crystal data

Transparent plate shaped crystals were obtained by means of slow evaporation from a solution of methanol at 296 (2) K. The crystal structure of the compound has been solved at 123 (2) K by us with the help of the program SHELXS - 93. SHELXL - 93 is used to refine the structure. The structure has been reported as an electronic paper [2]. Here we are not giving the crystal data for solution and refinement. Some relevant data to analyse the structure-property relationship are listed in Table 1.

TABLE 1 Summary of crystal data

Parameter	
Molecular Formula	$C_{79}H_{110}O_7$
Molecular weight g/mol^{-1}	1171.67
Crystal system/ Lattice type	Monoclinic/ Centrosymmetric
Space group	$P2_1/C$
a/Å	33.654 (9) $\alpha = 90.00^o$
b/Å	30.229 (8) $\beta = 94.74$ (1)^o
c/Å	6.798(2) $\chi = 90.00^o$
V/Å^3	6892.3(3)
D_c/gcm^{-3}	1.129
Z	4
R value	0.0729

Texture study

The phase transition of the compound has been studied by observing textures under crossed polarizers with a polarizing microscope of magnification 150x. The transition temperatures agree well with the literature values during heating [1] but during cooling we get supercooled smectic A phase over a wide range of temperature. A typical fan shaped texture of SmA has been observed during heating and cooling both and it becomes supercooled at 60°C. The transition temperatures of the compound is given below :

Solid (105° C) SmA (116 ° C) Isotropic

X-ray diffraction study

X-ray diffraction photographs of the title compound during the entire mesomorphic range were taken. By heating the sample slowly to the isotropic state and then cooling it down to the desired temperature we have obtained the photographs. We could not align the sample by usual magnetic field. The photographs obtained have the inner and outer rings . In order to determine the parameters, the photographs were scanned linearly by an optical micro densitometer (VEB Carl Zeiss Jena, Model MD 100)

RESULTS AND DISCUSSIONS

Structure - Property Relationship :

Figure 1 shows the perspective drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have an arbitrary radius. From crystal data we have calculated the various parameters by using the UNIX version of PARST [3]. The compound C79 H110 O7 consists of six rings. The puckering parameters of the six rings calculated using the method of Cremer and Pople [4] appear in Table 2. The rings A, D and E were found to be in twist-boat conformations. The rings B and C were in boat conformations. Only the ring F was in chair conformation. The dihedral angles of any two rings are calculated. No two attached rings are found to be coplanar. The normals to the least squares mean plane through O_1 to C_{10} makes an angle 23.04 (0.10) Å with the attached ring A. The normals to the least squares mean plane through O_2 to C_{20} makes an angle 13.37 (0.09) Å with the attached ring C. The mean planes through O_3 to C_{30} and through O_4 to C_{40} make angles 71.05 (0.08) Å and 1.99 (0.10) Å with their attached rings respectively. The dihedral angles of any two attached rings and of the chain part with the attached ring are listed in Table 3. Molecules of the compound are packed along the crystallographic a-axis.

Table 2 Ring - puckering parameters (Å, °) for six rings

Ring *	q2	q3	QT	θ
A	0.018 (4)	-0.005 (3)	0.019 (4)	105.21 (10)
B	0.036 (3)	0.012 (3)	0.038 (3)	71.65 (4)
C	0.030 (4)	0.004 (4)	0.030 (4)	82.68 (7)
D	0.032 (2)	-0.003 (2)	0.032 (2)	95.52 (4)
E	0.040 (3)	0.004 (3)	0.040 (3)	84.57 (4)
F	0.004 (3)	0.006 (3)	0.008 (3)	33.25 (23)

* Ring A : C_{41} to C_{46}, Ring B : C_{47} to C_{52}, Ring C : C_{53} to C_{58}, Ring D : C_{59} to C_{64}, Ring E : C_{65} to C_{70}, Ring F : C_{71} to C_{76}.

The molecular arrangement is a precursor of a smectic phase. Figure 2 is a projection along the crystallographic c-axis. The Crystal packing in the ab plane may be described as an assembly of molecular layers piled up along the crystallographic a-axis ; stimulating Smectic A type arrangement. The thickness of the layers of each half of the twin is close to the value of the 'a' parameter.

In the most extended conformations the length of the molecule of one half of the twin mesogen (C_{10} - C_{20}) is found to be 38.21 Å and the other half (C_{30} - C_{40}) is 37.60 Å. The chain length was calculated and enlisted in Table 4.

TABLE 3 Dihedral angles (degree) formed between normals to least squares mean planes

Planes *	Dihedral Angle
P(1) & P(2)	33.01(7)
P(2) & P(3)	41.68(8)
P(4) & P(5)	53.14(8)
P(5) & P(6)	21.36(9)
P(1) & P(7)	23.04(10)
P(3) & P(8)	13.37(9)
P(4) & P(9)	71.05(8)
P(6) & P(10)	1.99(10)
P(2) & P(11)	28.45(6)
P(5) & P(11)	63.64(6)

Defination of planes :

P(1) = C_{41} to C_{46}, P(2) = C_{47} to C_{52}, P(3) = C_{53} to C_{58}, P(4) = C_{59} to C_{64}, P(5) = C_{65} to C_{70}, P(6) = C_{71} to C_{76}, P(7) = O_1 to C_{10}, P(8) = O_2 to C_{20}, P(9) = O_3 to C_{30}, P(10) = O_4 to C_{40}, P(11) = O_5 to C_{79}.

From X-ray diffraction study we have obtained the smectic layer periodicity d . It is found to be 37 Å during the entire smectic phase. The intermolecular distance D was found to be 5 Å throughout the mesophase. The ratio of the smectic layer periodicity to the estimated molecular length was found to be approximately 1. Here the spacers and terminal chains separate such that the mesogenic units in one layer are all attached to the mesogenic units in the same adjacent layer resulting to a conventional monolayer smectic phase [5].

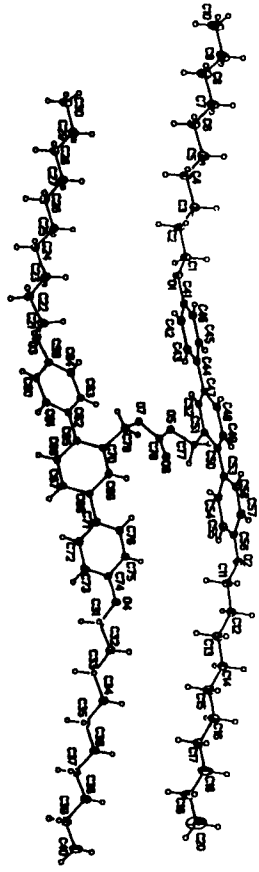

FIGURE 1 Perspective drawing of the compound showing the atomic numbering scheme. Displacement ellipsoids are shown at the 30% probability level and H atoms have an arbitratry radius.

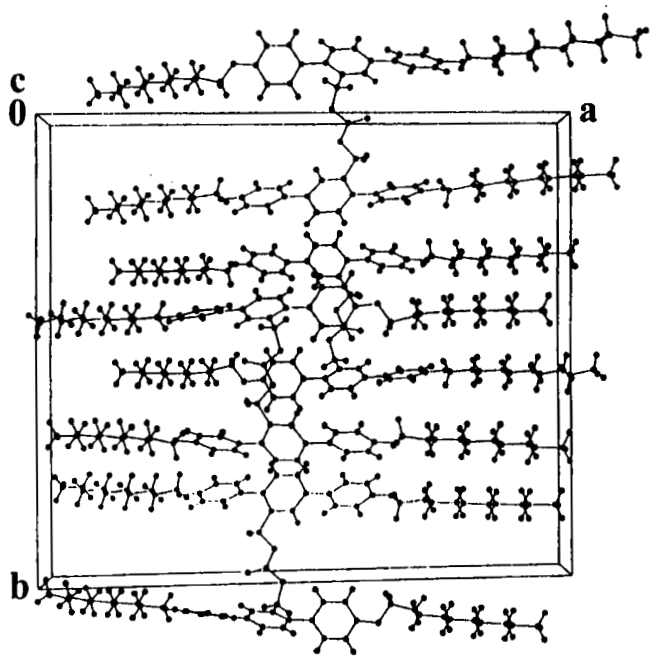

FIGURE 2 Molecular packing along [001]

TABLE 4 Molecular length (Å)

Atoms	Mol. length (Å)
From C_{10} to C_{20}	38.21
From C_{30} to C_{40}	37.59
From C_{51} to C_{70}	6.55
From C_{10} to C_{41}	13.77
From C_{20} to C_{56}	13.77
From C_{30} to C_{59}	13.13
From C_{40} to C_{74}	13.85

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