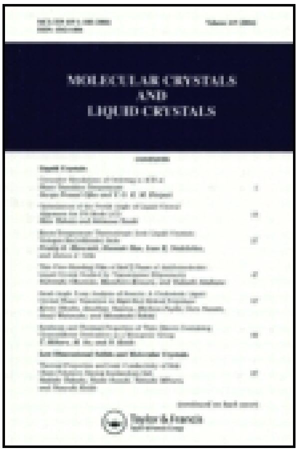

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Crystal Structure of 4,4′-Biphenylene-Bis(Oxycarbonylbutyric Acid)

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Crystal Structure of 4,4′-Biphenylene-Bis(Oxycarbonylbutyric Acid)

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4,4′-biphenylene-bis(oxycarbonylbutyric acid), $C_{22}H_{22}O_8$, a dicarboxylic acid containing a mesogenic core, has been synthesized and its crystal and molecular structure has been determined at room temperature by direct methods. Crystals are monoclinic, space group $P2_1/c$, a = 19.548(2) Å, b = 8.309(2) Å, c = 18.968(6) Å, ß = 99.24(2)°, with six molecules in the unit cell. The structure was refined by full matrix least squares method to R = 0.060 for 3285 observed independent reflections having $I > 3\sigma(I)$. Molecules with two different conformations are present in the unit cell. The main conformational difference regards the dihedral angle between the planes of the phenyl rings in the biphenyl moiety, which is 0° in the centrosymmetric molecules and 25.0(3)° in the other molecules. Molecules are bonded along extended rows through hydrogen bonds between carboxylic groups. Centrosymmetric molecules form rows of linear symmetry *ti*, whereas rows of symmetry *t*1 are formed by the noncentrosymmetric molecules.

INTRODUCTION

In previous papers[1,2] we have reported investigations on the phase behaviour and the crystal structure of some α,ω-dicarboxylic acids containing a mesogenic core, as possible model compounds for the crystal packing of linear semiflexible polymers exhibiting liquid crystalline properties.

As a continuation of this research program, we report in the present paper a structural investigation of the dicarboxylic acid 4,4′-biphenylene-bis(oxycarbonylbutyric acid), having formula

$$HOOC\text{-}(CH_2)_3\text{-}COO\text{-}C_6H_4\text{-}C_6H_4\text{-}OOC\text{-}(CH_2)_3\text{-}COOH,$$

which may be considered as a model compound for the crystal structure of semiflexible polyesters prepared from 4,4′-dihydroxybiphenyl and aliphatic dicarboxylic acids. These polymers, which have been extensively studied by Krigbaum et al.,[3] exhibit a very peculiar odd-even effect, in that polymers having an odd number of methylenic groups in the monomer units are nematogenic, whereas those having an even number, which title compound should be properly regarded as a model for, exhibit a highly ordered smectic *H* phase. This and other differences (e.g., the higher crystallinity and the wider temperature range of stability of the mesophase found for the even terms) have been correlated with the different molecular geometry of polymers having different parity. In particular, the co-directionality of biphenyl moieties (which reduces the bulkiness about the chain axis) and the trans arrangement of carbonyl dipoles in the fully extended conformation of the even polymers have been pointed out,[3] as possible features favouring the stability of the smectic phase.

EXPERIMENTAL PART

The title compound was synthesized by esterification of 4,4′-dihydroxybiphenyl with glutaric anhydride. 3.0 g (16.1 mmol) of 4,4′-dihydroxybiphenyl were dissolved in 250 ml of dioxane, and to this solution 0.80 g (35 mmol) of metallic sodium were added. The mixture was heated and stirred until no further development of H_2 was observed. The excess of sodium was then destroyed by addition of methanol. To the resulting solution was added, under stirring, a large excess of glutaric anhydride (15.0 g, 131 mmol). The reaction mixture was allowed to stir, at 70°C, for 15 minutes, then was poured into a large volume of water ($\approx 1 l$) and acidified with glacial acetic acid. The solid residue was filtered, washed with water and recrystallized one time from ethanol-water and twice from ethanol giving pure title compound.

The proton NMR spectrum of the title compound, recorded on a Varian XL200 spectrometer, is consistent with its formula.

Phase transition temperatures and enthalpies were determined by differential calorimetric analysis (Perkin Elmer DSC7, scanning rate 10 K/min, N_2 atmosphere). Optical observations were made using a Linkam microfurnace (N_2 atmosphere) combined with a Leitz polarizing microscope. X-ray diffraction patterns of the different solid phases exhibited by the compound were registered photographically (flat film camera, CuKα radiation).

Single crystals suitable for X-ray studies were obtained by slow evaporation from ethanol as colourless prisms elongated in the *b* direction. Crystalline density was determined by flotation in carbon tetrachloride/*n*-heptane solution.

Preliminary Weissenberg and oscillation photographs indicated monoclinic $P2_1/c$ symmetry. Accurate cell parameters were obtained through a least square fit of the setting angles of 25, accurately centered, strong reflections, in the range $15° \leq \theta \leq 25°$, on an Enraf Nonius CAD-4 automated single crystal diffractometer, using graphite monochromated CuKα radiation. A set of crystallographic relevant parameters is reported in Table I. Data collection was performed in the range $2° \leq \theta \leq 70°$ with a max. $\sin \theta/\lambda = 0.6092$. Reflections were measured in the following ranges of indices: $0 \leq h \leq 23$, $0 \leq k \leq 10$, $-23 \leq l \leq 23$, in the ω/θ scan mode. Two standard reflections periodically measured during data collection showed only random fluctuations. Of the total of 5758 independent reflections collected, only 3285, having $I > 3\sigma(I)$, were considered as observed and used in structure analysis. Lorentz and polarization corrections were applied, no correction for absorption and extinction.

TABLE I

Crystal data of 4,4'-biphenylene-bis(oxycarbonylbutyric acid)

$C_{22}H_{22}O_8$
Formula weight= 414.42
Monoclinic
Space group $P2_1/c$
a= 19.548(2) Å
b= 8.309(3) Å
c= 18.968(6) Å
β= 99.24(2)°

V= 3041(9)$Å^3$
Z= 6
D_{calc} = 1.358 g/cm^3
D_{obs} = 1.35(1) g/cm^3
λ(CuKα) = 1.54178 Å
μ(CuKα) = 8.3 cm^{-1}
F(000) = 1308

Determination and Refinement of the Structure

The space group of the compound and the number of molecules in the unit cell ($Z = 6$) fix the independent structural unit as containing one molecule plus half of a centrosymmetric one.

The structure was solved by direct methods using SIR program,[4] and completed by standard Fourier methods. Coordinates and anisotropic thermal parameters of all non-H atoms were refined (on F) by full matrix least squares method. The positions of H atoms were determined on stereochemical grounds at each stage of the structure refinement, with exception of H atoms of carboxy groups, whose positions were defined on the basis of difference Fourier maps. To all H atoms were given isotropic thermal parameters equal to B_{eq}'s of the carrier atoms. H atoms were included in structure factors calculations but not refined. Final agreement factors are $R = 0.060$, $R_w = 0.060$ ($S = 1.580$). Largest parameter shift to error ratio in the last refinement cycle was less than 0.03. The final difference Fourier map showed no maxima higher than 0.23 $e \cdot Å^{-3}$. Unit weights were used throughout the refinement. Atomic scattering factors were taken from International Tables for X-Ray Crystallography,[5] programs from Enraf Nonius Structure Determination Package.[6] All calculations were performed on a Digital MicroVMS V4.7 computer. Additional material to this paper (list of observed and calculated structure factors, refined anisotropic thermal parameters of non-H atoms, coordinates and thermal parameters of H atoms) is available from the authors on request.

RESULTS AND DISCUSSION

The title compound is polymorphic in the solid state. In Figure 1 it is reported the DSC curve, on heating, of a sample formed by manually selected single crystals of the same kind used in the structural determination. It can be seen that the crystal phase whose structure is discussed here, called C_1, tranforms, at 443 K ($\Delta H = 9.5$ kJ/mol) into a second crystal phase, C_2 (the indented shape of the endothermic signal corresponding to the transition in the DSC scan may be accounted for the nature of the sample used, being formed by a few manually selected, large single crystals). The reverse transition, $C_2 \rightarrow C_1$, is not observed on cooling the phase C_2 and, moreover, the transition $C_1 \rightarrow C_2$ is not a topotactic one. The phase C_2 melts at 464 K giving a liquid crystal phase which, in turn, isotropizes at 470 K

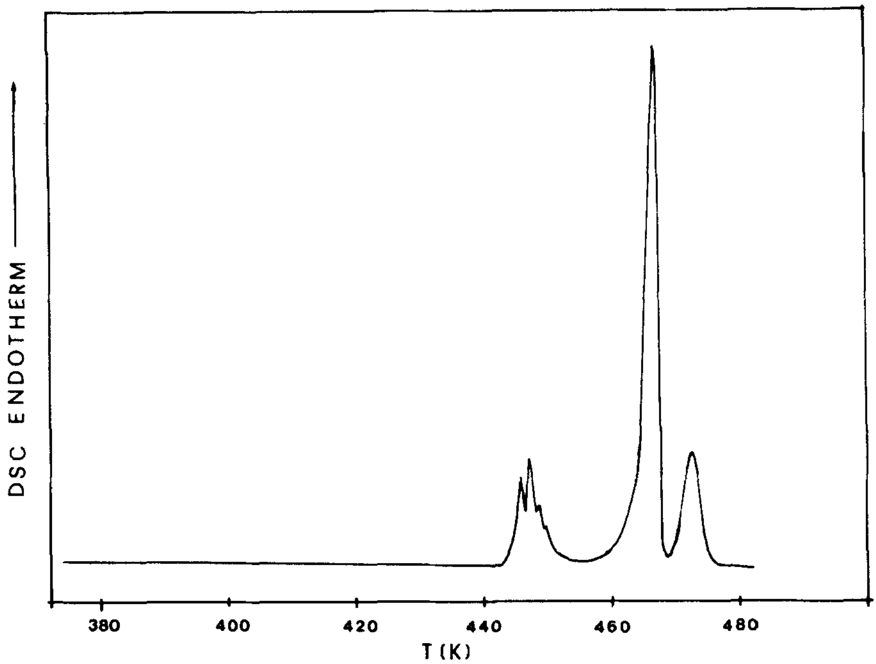

FIGURE 1 DSC thermogram, on heating, of the title compound recorded, at a scanning rate of 10 K/min, from a sample formed by a few, manually selected, large single crystals of the same kind used in the structure determination.

($\Delta H \approx 10$ kJ/mol). The DSC curve recorded for a microcrystalline sample obtained from ethanol and containing both crystal forms coincides with that reported in Figure 1, with exception for the enthalpic change at the $C_1 \rightarrow C_2$ transition, which is reduced by far.

After the melting transition, however, the compound is rather unstable and undergoes a large decomposition. This instability prevented the possibility of an accurate investigation of the nature of the liquid crystal phase. In fact, although the textures observed at the polarizing microscope clearly indicate an optically anisotropic behaviour (Figure 2), little significance may be attributed to the specific morphologies observed. Yet it has not been possible to record any X-ray diffraction pattern of the mesophase, because of the too long exposure time needed.

Final refined coordinates and equivalent temperature factors for the atoms of the independent structural unit are given in Table II; bond lengths, bond angles and torsion angles are reported in Table III. Atomic numbering and molecular geometry are shown in Figure 3.

Bond lengths and bond angles of the two crystallographically not equivalent molecules do not show significant differences from expected values, with exception of the C—O bond lengths of the carboxy group in the centrosymmetric molecule; the values of these latter hint the presence of a partial orientational disorder of the carboxy group. In fact, the difference Fourier map calculated for a model containing all non-H atoms anisotropically refined and H atoms in stereochemical positions, with exception of those bonded to O1 and O5, which were found in a

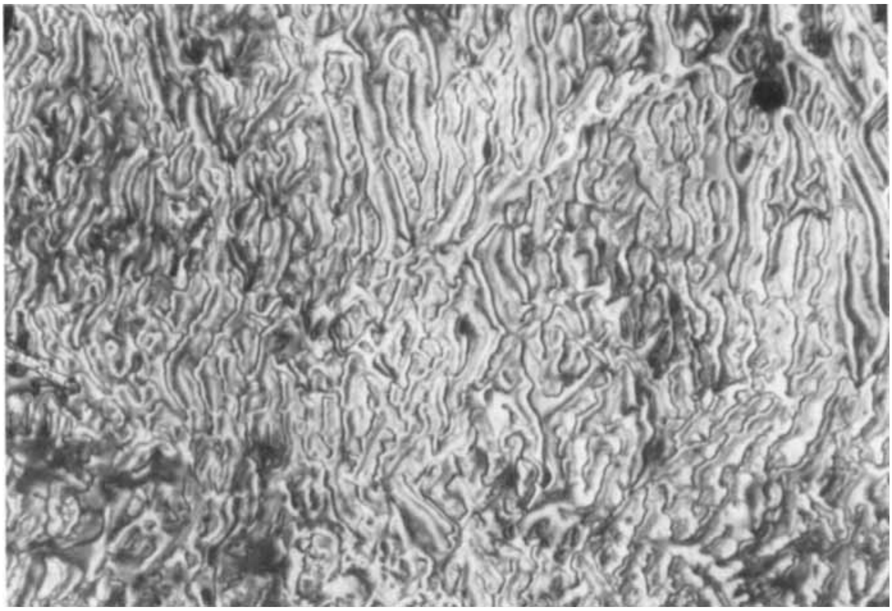

FIGURE 2 Optical texture of the liquid crystal phase at 463 K, on cooling. Crossed polarizers.

previous difference synthesis, showed electron density maxima in positions stereochemically compatible with a double location of the hydroxyl H atom, bonded to O1' and O2' (0.3 $e/Å^3$ and 0.19 $e/Å^3$ respectively).

Substantial differences are found, on the other hand, in the conformation of the two molecules. The main difference concerns the dihedral angle between the planes of the phenyl rings in the biphenyl moiety, which is zero in the centrosymmetric molecule and 25.0(3)° in the other molecule. This difference is not surprising, because a variability in the conformation of the biphenyl moiety, depending on packing forces, is well established.[7] A further example of this variability, although occurring in two different crystal modifications, has been recently reported for a mesogenic compound containing 4,4'-dicarboxybiphenyl group.[8]

The major deviation from the trans planar conformation in the aliphatic chains is observed for the torsion angle around bond C2'—C1', which is of the gauche type (O1'-C1'-C2'-C3' = 130.0(5)°). This finding, which is consistent with the presumably low torsional barrier around bond C1'—C2',[9] is probably due to packing effects including the different mode of formation of hydrogen bond between centrosymmetric molecules (see below). Only minor deviations from the trans planarity are observed in the other torsion angles of the chains and this is substantially true also for the torsion angles around C—C bonds contiguous to carbonyl groups of the ester moieties (C3-C4-C5-O4 = 174.7(4)°, O5-C18-C19-C20 = 166.7(4)°, C3'-C4'-C5'-O4' = −162.9(4)°). To this respect we remind that conformational energy calculations performed on semiflexible polyesters containing a different mesogenic group[10] have shown that chain conformations having values of this torsion angle between the trans and the gauche states are low in energy and are

TABLE II

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

Atom	x	y	z	B_{eq} (Å^2)
O1	0.9401(2)	-0.1372(5)	0.5171(2)	6.10(9)
O2	0.8585(2)	0.0436(5)	0.5260(2)	6.72(9)
O3	0.6468(2)	0.0502(5)	0.3213(2)	8.0(1)
O4	0.6281(2)	-0.1787(4)	0.2603(2)	5.49(7)
O5	0.2085(2)	0.1566(4)	-0.0658(2)	5.25(8)
O6	0.2277(2)	0.0155(5)	-0.1607(2)	7.6(1)
O7	0.0081(2)	-0.0009(5)	-0.3642(2)	5.82(8)
O8	-0.0732(2)	0.1816(5)	-0.3554(2)	6.95(9)
O1'	0.0746(2)	-0.1091(6)	0.0043(2)	7.5(1)
O2'	0.0235(2)	-0.0131(5)	0.0912(2)	7.0(1)
O3'	0.2432(2)	0.0491(5)	0.3072(2)	8.8(1)
O4'	0.3097(2)	-0.1686(4)	0.3142(2)	5.93(8)
C1	0.8800(2)	-0.0701(6)	0.4958(2)	4.6(1)
C2	0.8392(2)	-0.1504(6)	0.4315(2)	4.3(1)
C3	0.7704(2)	-0.0692(6)	0.4036(2)	4.8(1)
C4	0.7296(2)	-0.1659(6)	0.3430(2)	4.3(1)
C5	0.6647(2)	-0.0815(6)	0.3091(2)	4.5(1)
C6	0.5683(2)	-0.1180(6)	0.2165(2)	4.6(1)
C7	0.5762(2)	-0.0239(7)	0.1579(3)	5.0(1)
C8	0.5168(2)	0.0201(6)	0.1115(2)	4.7(1)
C9	0.4511(2)	-0.0268(6)	0.1234(2)	3.82(9)
C10	0.4455(2)	-0.1210(6)	0.1833(2)	4.3(1)
C11	0.5047(2)	-0.1673(6)	0.2305(2)	4.8(1)
C12	0.3873(2)	0.0182(6)	0.0724(2)	3.69(9)
C13	0.3274(2)	-0.0749(6)	0.0658(2)	4.1(1)
C14	0.2682(2)	-0.0317(6)	0.0182(2)	4.6(1)
C15	0.2704(2)	0.1041(6)	-0.0233(2)	4.4(1)
C16	0.3283(2)	0.1978(7)	-0.0189(2)	5.0(1)
C17	0.3871(2)	0.1546(6)	0.0297(2)	4.7(1)
C18	0.1919(2)	0.1039(6)	-0.1337(2)	4.3(1)
C19	0.1250(2)	0.1805(6)	-0.1668(2)	4.5(1)
C20	0.0928(2)	0.1016(6)	-0.2367(2)	4.5(1)
C21	0.0254(2)	0.1884(7)	-0.2674(2)	4.9(1)
C22	-0.0133(2)	0.1126(6)	-0.3341(2)	4.5(1)
C1'	0.0691(2)	-0.0941(6)	0.0697(2)	4.8(1)
C2'	0.1217(2)	-0.1848(6)	0.1212(2)	4.8(1)
C3'	0.1571(2)	-0.0806(6)	0.1825(2)	4.9(1)
C4'	0.2103(2)	-0.1810(6)	0.2307(3)	5.2(1)
C5'	0.2537(2)	-0.0835(6)	0.2882(2)	4.9(1)
C6'	0.3599(2)	-0.1059(6)	0.3684(2)	4.5(1)
C7'	0.4091(3)	-0.0038(7)	0.3514(2)	5.2(1)
C8'	0.4647(2)	-0.0372(6)	0.4035(2)	4.6(1)
C9'	0.4697(2)	-0.0211(5)	0.4724(2)	3.71(9)
C10'	0.4172(3)	-0.1167(8)	0.4879(3)	7.9(1)
C11'	0.3621(3)	-0.1617(8)	0.4357(3)	8.2(2)

compatible with the measured identity periods, provided the other torsion angles of the chain are in the trans state.

The torsion angles around ester bonds contiguous to the phenyl rings (C5-O4-C6-C7 = 79.4(5)°, C18-O5-C15-C16 = 95.4(5)°, C5'-O4'-C6'-C7' = −82.1(6)°) take values in the range expected on the basis of energetical considerations[11] and similar to those found by the authors in the crystal structure of other mesogenic esters.[12,13]

Crystal packing is shown in Figures 4 and 5. Molecules are bonded along extended

TABLE III

Bond lengths (Å), bond angles (°), and torsion angles (°) with e.s.d.'s in parentheses

O1-C1	1.305(5)	C2-C3	1.522(5)	C18-C19	1.499(5)
O2-C1	1.214(5)	C3-C4	1.520(5)	C19-C20	1.522(4)
O3-C5	1.183(5)	C4-C5	1.500(5)	C20-C21	1.532(5)
O4-C5	1.345(4)	C6-C7	1.388(5)	C21-C22	1.504(5)
O4-C6	1.415(4)	C6-C11	1.373(5)	C1'-C2'	1.502(5)
O5-C15	1.411(4)	C7-C8	1.389(5)	C2'-C3'	1.524(5)
O5-C18	1.350(4)	C8-C9	1.394(5)	C3'-C4'	1.518(5)
O6-C18	1.187(4)	C9-C10	1.399(5)	C4'-C5'	1.505(5)
O7-C22	1.212(5)	C9-C12	1.498(4)	C6'-C7'	1.359(5)
O8-C22	1.307(4)	C10-C11	1.398(5)	C6'-C11'	1.353(5)
O1'-C1'	1.270(4)	C12-C13	1.392(5)	C7'-C8'	1.389(5)
O2'-C1'	1.237(5)	C12-C17	1.393(5)	C8'-C9'	1.382(5)
O3'-C5'	1.187(5)	C13-C14	1.396(5)	C9'-C10'	1.367(5)
O4'-C5'	1.329(4)	C14-C15	1.380(6)	C10'-C11'	1.392(5)
O4'-C6'	1.403(4)	C15-C16	1.365(5)	C9'-C9'*	1.493(6)
C1-C2	1.501(5)	C16-C17	1.399(5)		

C5-O4-C6	119.3(3)	C15-C16-C17	118.6(4)
C15-O5-C18	119.8(3)	C12-C17-C16	121.2(4)
C5'-O4'-C6'	120.8(3)	O5-C18-O6	123.0(3)
O1-C1-O2	123.4(4)	O5-C18-C19	108.8(3)
O1-C1-C2	113.3(4)	O6-C18-C19	128.2(3)
O2-C1-C2	123.3(4)	C18-C19-C20	113.1(3)
C1-C2-C3	114.2(4)	C19-C20-C21	109.8(3)
C2-C3-C4	110.9(3)	C20-C21-C22	114.1(3)
C3-C4-C5	112.4(3)	O7-C22-O8	123.7(3)
O3-C5-O4	123.3(4)	O7-C22-C21	123.9(4)
O3-C5-C4	127.2(4)	O8-C22-C21	112.4(4)
O4-C5-C4	109.5(3)	O1'-C1'-O2'	123.7(4)
O4-C6-C7	118.9(4)	O1'-C1'-C2'	115.5(4)
O4-C6-C11	117.9(4)	O2'-C1'-C2'	120.8(4)
C7-C6-C11	122.9(3)	C1'-C2'-C3'	113.0(3)
C6-C7-C8	117.8(4)	C2'-C3'-C4'	109.3(3)
C7-C8-C9	121.4(4)	C3'-C4'-C5'	113.1(3)
C8-C9-C10	118.9(3)	O3'-C5'-O4'	123.5(4)
C8-C9-C12	121.2(3)	O3'-C5'-C4'	127.9(4)
C10-C9-C12	119.9(3)	O4'-C5'-C4'	108.5(4)
C9-C10-C11	120.6(4)	O4'-C6'-C7'	119.8(4)
C6-C11-C10	118.4(4)	O4'-C6'-C11'	118.5(4)
C9-C12-C13	121.4(3)	C7'-C6'-C11'	121.4(3)
C9-C12-C17	120.2(3)	C6'-C7'-C8'	119.2(4)
C13-C12-C17	118.4(3)	C7'-C8'-C9'	121.0(4)
C12-C13-C14	120.9(4)	C8'-C9'-C10'	117.8(3)
C13-C14-C15	118.7(4)	C9'-C10'-C11'	121.6(4)
O5-C15-C14	118.4(4)	C6'-C11'-C10'	118.9(4)
O5-C15-C16	119.0(4)	C8'-C9'-C9'*	120.6(4)
C14-C15-C16	122.2(3)	C10'-C9'-C9'*	121.6(4)

C6-O4-C5-O3	5.8(7)	C9-C10-C11-C6	-0.0(8)
C6-O4-C5-C4	-173.6(4)	C9-C12-C13-C14	179.8(4)
C5-O4-C6-C7	79.5(5)	C17-C12-C13-C14	-0.8(6)
C5-O4-C6-C11	-106.2(5)	C9-C12-C17-C16	179.3(4)
C18-O5-C15-C14	-91.4(5)	C13-C12-C17-C16	-0.0(7)
C18-O5-C15-C16	95.4(5)	C12-C13-C14-C15	1.1(7)
C15-O5-C18-O6	-1.1(7)	C13-C14-C15-O5	-173.5(4)
C15-O5-C18-C19	-178.7(4)	C13-C14-C15-C16	-0.6(7)
C6'-O4'-C5'-O3'	1.8(7)	O5-C15-C16-C17	172.6(4)
C6'-O4'-C5'-C4'	179.4(4)	C14-C15-C16-C17	-0.3(7)
C5'-O4'-C6'-C7'	-82.1(6)	C15-C16-C17-C12	0.6(7)
C5'-O4'-C6'-C11'	104.3(6)	O5-C18-C19-C20	-166.7(4)
O1-C1-C2-C3	-177.3(4)	O6-C18-C19-C20	15.8(7)
O2-C1-C2-C3	4.5(7)	C18-C19-C20-C21	-179.2(4)
C1-C2-C3-C4	-175.0(4)	C19-C20-C21-C22	-175.9(4)
C2-C3-C4-C5	-174.2(4)	C20-C21-C22-O7	-4.5(7)
C3-C4-C5-O3	5.9(7)	C20-C21-C22-O8	174.7(4)
C3-C4-C5-O4	-174.7(4)	O1'-C1'-C2'-C3'	130.0(5)
O4-C6-C7-C8	173.4(4)	O2'-C1'-C2'-C3'	-51.0(6)
C11-C6-C7-C8	-0.6(8)	C1'-C2'-C3'-C4'	-178.7(4)
O4-C6-C11-C10	-173.8(4)	C2'-C3'-C4'-C5'	173.5(4)
C7-C6-C11-C10	0.3(7)	C3'-C4'-C5'-O3'	14.5(7)
C6-C7-C8-C9	0.7(8)	C3'-C4'-C5'-O4'	-162.9(4)
C7-C8-C9-C10	-0.4(7)	O4'-C6'-C7'-C8'	-169.8(4)
C7-C8-C9-C12	-178.8(5)	C11'-C6'-C7'-C8'	3.5(8)
C8-C9-C10-C11	0.1(8)	O4'-C6'-C11'-C10'	171.5(5)
C12-C9-C10-C11	178.5(4)	C7'-C6'-C11'-C10'	-1.9(9)
C8-C9-C12-C13	153.6(4)	C6'-C7'-C8'-C9'	-1.6(8)
C8-C9-C12-C17	-25.7(6)	C7'-C8'-C9'-C10'	-1.7(7)
C10-C9-C12-C13	-24.8(6)	C8'-C9'-C10'-C11'	3.3(8)
C10-C9-C12-C17	155.9(4)	C9'-C10'-C11'-C6'	-1.6(9)

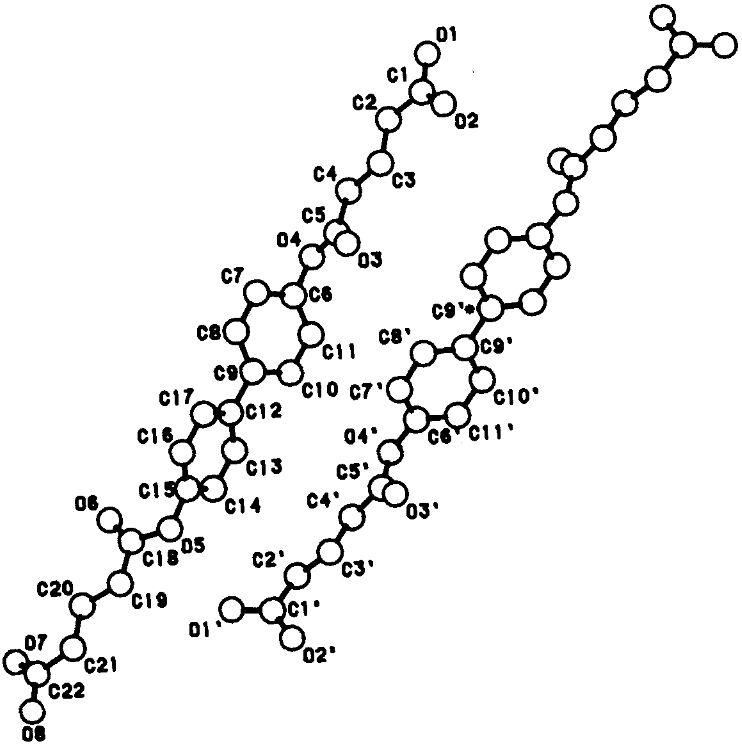

FIGURE 3 Drawing of the two independent molecules showing atomic numbering.

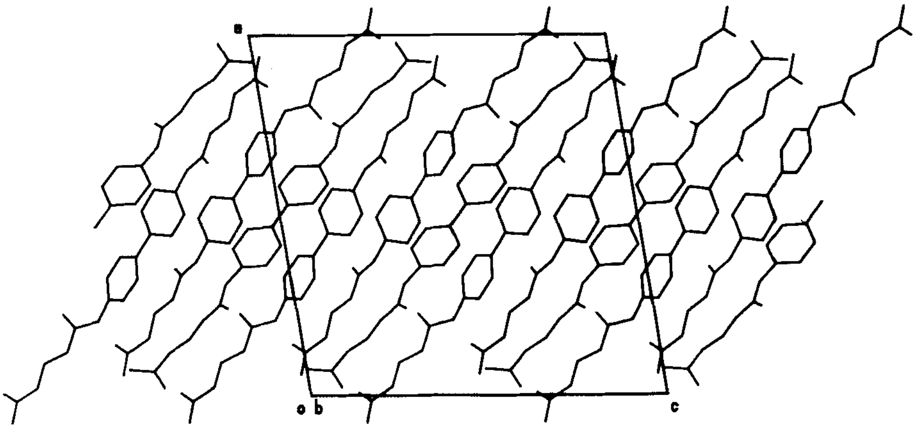

FIGURE 4 Crystal packing along [010].

rows through hydrogen bonds between carboxylic groups, thus simulating long polymeric chains in which the molecules are the "monomeric units". Intermolecular distances between oxygen atoms related by hydrogen bond (Table IV) are in good agreement with values reported in the literature[14]; the cyclic hydrogen bonded

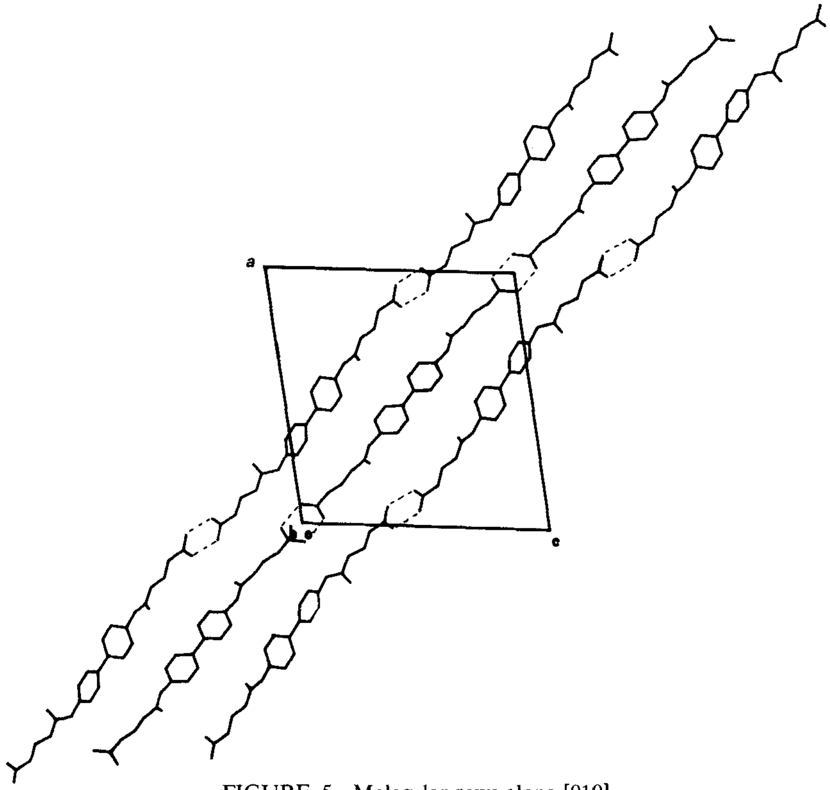

FIGURE 5 Molecular rows along [010].

TABLE IV

Hydrogen bond distances

$O1\cdots O7^{(i)}$	2.675(3)Å
$O2\cdots O8^{(i)}$	2.683(4)Å
$O1'\cdots O2'^{(ii)}$	2.622(4)Å

Symmetry codes:
(i) x+1, y, z+1;
(ii)-x, -y, -z.

dimers (C1, O1, O2, C22(*i*), O7(*i*), O8(*i*) and C1', O1', O2', C1'(*ii*), O1'(*ii*), O2'(*ii*)) are planar within 0.04 Å and 0.03 Å, respectively.

Rows of two different kinds are present in the structure: one, belonging to the line repetition group *t*1, is formed by the noncentrosymmetric molecules, being repeated, along the row, by translation, while the other, having linear symmetry *ti*, is formed by the centrosymmetric molecules, which are repeated, along the row, by inversion centers. The overall length of the molecule, taken as the distance between the two terminal carboxy groups, is almost coincident in the two cases (C1···C22 = 21.604(5) Å, C1′···C1′* = 21.550(5) Å.

All molecular rows are strictly parallel to each other; they are normal to the *b* axis and parallel to the $\vec{a} + \vec{c}$ axis. It is interesting to note how the basic postulate of polymer crystallography (i.e., that polymer chain axes have to be parallel to each other in the crystal lattice) is fully verified in the present structure, which is peculiar, on the other hand, for having rows of different conformation in the same lattice. The waviness of the rows, however, is very similar in the two cases (σ = 23.2(1)° for rows *t*1 and σ = 20.3(1)° for rows *ti*, where the angle σ is defined, according to Reference 15, in such a way that 180°-σ is the angle between the lines C6–C15 and C15–C6(*i*) for rows *t*1 and between the lines C6′–C6′* and C6′*–C6′(*i*) for rows *ti*) and this may acount for the co-crystallization in the same crystal lattice with parallel orientation of the chain axes.

The crystal packing may also be described as a sequence of triplets of molecular layers parallel to the (101) plane. Each triplet is formed by a layer of molecular rows of *ti* symmetry sandwiched between two layers containing rows of *t*1 type, almost equally stacked along $\vec{a} + \vec{c}$. This implies contacts between biphenyl moieties, with a herring bone type packing of the phenyl rings viewed end-on (Figure 6) in which phenyl face to phenyl edge and carbonyl carbon to carbonyl oxygen are the most relevent lateral contacts. Identical pattern is obtained with successive triplets by translation of $\vec{c}/2$.

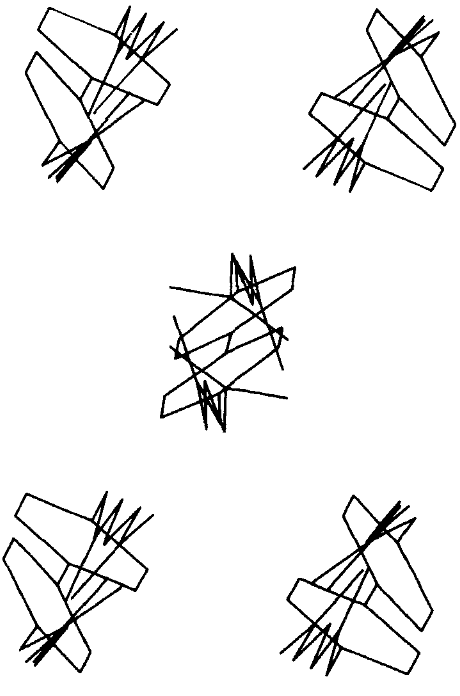

FIGURE 6 Crystal packing along [101].

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