The crystal structure of poly(trimethylene terephthalate) by X-ray and electron diffraction

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The crystal structure of poly(trimethylene terephthalate), $[C_6H_4{-}CO{-}O{-}(CH_2)_3{-}O{-}CO]_n$ has been determined by a combination of electron diffraction, X-ray diffraction and packing analyses.

Single crystals having a parallelogram shape were grown from a nitrobenzene solution. Seen in the electron microscope they consist of platelets about 80 Å thick. Single crystal electron diffraction and X-ray fibre diffraction patterns show that the chain molecules are normal to the base plane of the single crystal. For both single crystal and fibre the unit cell of poly(trimethylene terephthalate) is triclinic with parameters: a = 4.637 Å, b = 6.266 Å, c = 18.64 Å (fibre axis), α = 98.4°, β = 93.0°, γ = = 111.1°. The space group is $P\bar{1}$, and the calculated crystalline density: 1.387 g/cm^3. Conformational energies were calculated for the monomeric repeating unit using semi-empirical methods. The starting geometry of the residue was derived from previous studies on relevant model compounds. The several plausible molecular models thus obtained were examined by packing and X-ray analyses. The structure consists of rigid planar terephthaloyl residues alternating with a more flexible trimethylene sequence. This $O{-}CH_2{-}CH_2{-}CH_2{-}O$ segment of the chain has a *trans-gauche-gauche-trans* conformation.

INTRODUCTION

Some members of the terephthalate polyester series have been examined by X-ray diffraction in the past. The crystal structure of poly(ethylene terephthalate)[1] and the reversible crystalline transformations occurring between two forms of poly(tetramethylene terephthalate)[2–4], and poly(pentamethylene terephthalate)[5] have been examined. The unit cell dimensions of poly(hexamethylene terephthalate)[6,7] and poly(decamethylene terephthalate)[8] have also been reported. The lattice parameters of poly(trimethylene terephthalate), abbreviated as 3GT in this study, have not been reported so far, although a fibre repeat of 9.1 Å has been established[9,10].

The present investigation is part of a study of the relationships between the structures of polymers and the related oligomers. In a series of papers we recently reported accurate crystallographic studies on small molecules which can be considered as polymeric fragments[11–14]. In this manner, ethylene glycol dibenzoate and dimethyl terephthalate are models for poly(ethylene terephthalate). It was thus shown that the so-called shrinkage of the poly(ethylene terephthalate) fibre could be accounted for by a peculiar geometry in the ethylene glycol part of the molecule. In the course of these studies it was found that not only accurate bond distances and angles could be obtained but also the conformational angles which could be applied to the polymer were available. Along this line the structure determination of the unknown 3GT polymer: $[C_6H_4{-}CO{-}O{-}(CH_2)_3{-}O{-}CO]_n$ has been undertaken. For this purpose the crystal structure of two model compounds namely: trimethylene glycol dibenzoate and trimethylene glycol di-*para* chlorobenzoate have been resolved using conventional X-ray diffraction methods on small molecules[15,16].

Ordinary fibre diffraction diagrams yield at best 5 to 10 equatorial (hk0) diffraction spots while the electron diffractogram from a lamellar single crystal shows at least 5 times as many base plane diffraction data. From this additional information we may expect much greater accuracy in the cell dimensions and much greater certainty in the space group assignment. Electron diffraction patterns have often been obtained from polymer single crystals grown from solution. However, the use of electron diffraction in the elucidation of a polymeric structure has rarely been attempted[17]. In the series of aromatic polyesters under investigation, only single crystals of poly(ethylene terephthalate)[18,19] have been reported.

The purpose of the present study is to show how the information derived from the study of relevant model compounds and the combined use of single crystal and fibre data is a useful approach to elucidate the 3-dimensional structure of a polymer.

EXPERIMENTAL

Sample preparation

3GT polymer chips with an intrinsic viscosity of 0.90 dl/g were a gift of the Eastman Kodak Company, Rochester[20]. Single crystals of 3GT suitable for electron diffraction were successfully grown in the following manner. The polymer was first dissolved in nitrobenzene at 170°C. The solution containing about 0.05% polymer by wt. was filtered to remove all solid residues. The clear solution was slowly cooled

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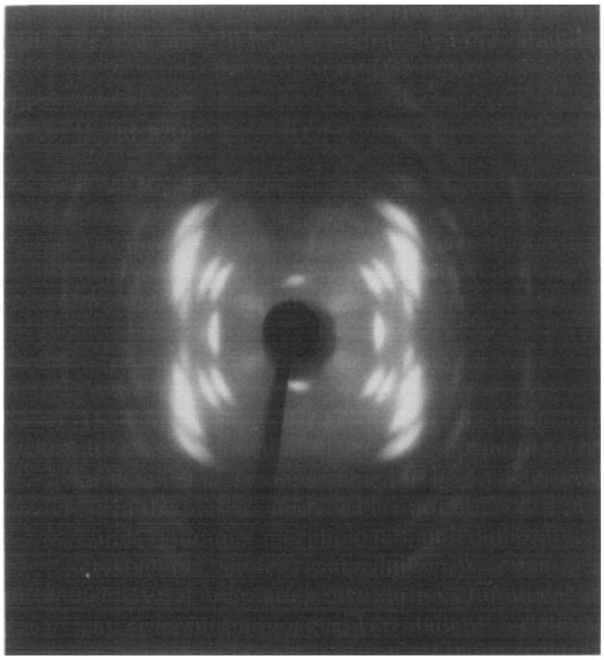

Figure 1 X-ray fibre diagram of 3GT taken with CuKα Ni-filtered radiation

to 134°C and kept at this temperature for 12 h. The polymer that had crystallized, was filtered off and redissolved in nitrobenzene at 170°C. The new solution was slowly brought down to 139°C, and then cooled to 136°C at the rate of 1°C/12 h. When the solution reached 136°C a slight precipitation was observed. Single crystals of 3GT were obtained after keeping the temperature constant for 24 h. The fibres of 3GT were obtained from the white opaque polymer heated to become transparent at 210°C. The molten sample was quickly drawn and quenched to room temperature. The fibre was further elongated until a complete 'necking' was achieved. Finally the sample was annealed at 210°C for 12 h.

Electron and X-ray diffraction

Drops of the suspension of 3GT single crystals in nitrobenzene were evaporated on carbon grids. Micrographs and diffraction patterns were obtained with a Philips EM 300 electron microscope which was used at 80kV for imaging and 100kV for diffraction. For d spacing calibration some of the crystals were etched with evaporated gold. The thickness of the crystals was estimated to be about 80 Å. The intensities of the observed reflections were estimated by comparison with standard references. The structure factor magnitudes were derived from observed intensities, following the procedure outlined by Dorset[21]. The electron scattering factors for C, O and H atoms were taken from International Tables for X-ray Crystallography, Vol. IV[22].

X-ray diffraction photographs were taken with nickel filtered CuKα radiation in a Laue and a Weissenberg camera 57.3 mm in diameter using the multiple film technique. The diffracted intensities of the different films, visually estimated, were scaled and corrected for Lorentz and polarization factors. The X-ray scattering factors were obtained from Cromer & Waber[23] for C and O atoms, and from Stewart, Davidson and Simpson[24] for H atoms.

Conformational analysis

The potential energy calculated for a given conformation included the torsion energy about the different torsion angles, the non-bonded energies and the electrostatic interactions. Intrinsic torsional potential with a three-fold barrier of 2.8 kcal/mol was assigned to rotations about the CH_2–CH_2 bonds while the torsional barrier for the C–O bond was taken to be zero. The rotation between the carboxy and the benzene planes was not allowed, since for most benzoates[11–13], this angle reached at the most 4°. The all-*trans* planar conformation defines the starting position (all ϕ_i's = 180°). The sign of the torsion angle is given in adherence to the IUPAC Nomenclature[25]. The Van der Waals interactions between non-bonded atoms were evaluated using 6–12 potential functions, with the parameters proposed by Scott and Scheraga[26,27]. Electrostatic interactions were evaluated by assigning partial charges to the atoms using a Coulomb's law potential function[28]. The following values for the bond moments were used C–C = 0.0, C–O = 0.82, $\mathrm{C}{\simeq}$ = 0.39, C=O = 0.74 and C–H = 0.38 in debyes[29]. A value of 2.0 was assigned to the effective dielectric constant[30].

Energies were calculated at 2°C intervals in the neighbourhood of the minima and at intervals of 5°C elsewhere. Isoenergy contours are plotted at 1 kcal/mol intervals with respect to the minimum energy which is arbitrarily set to zero.

STRUCTURE DETERMINATION

Unit-cell dimensions and space group

The 2θ values of 42 reflections, up to the eighth layer-line, to a resolution of 1.42 Å, were obtained from an X-ray fibre diagram such as that of *Figure 1*. A unit-cell fitting these reflections was determined by trial and error and further refined by a least-squares procedure. The triclinic unit-cell dimensions thus derived are reported in *Table 1*. A list of the observed and calculated reticular distances is shown in *Table 2*. A crystal of 3GT and its electron diffractograms are shown in *Figure 2*. These electron diffraction patterns clearly indicate a $\bar{1}$ symmetry. This finding corroborates the assignment of a triclinic unit-cell to the X-ray fibre data. A comparison of the relevant reciprocal unit-cell dimensions derived from both the X-ray fibre diagram and the electron diffractogram is given in *Table 1*. The comparison of the density calculated from the unit-cell dimensions with the measured value obtained in a gradient column[31] (see *Table 1*) indicated that there are two monomers per unit-cell. Such a monomer is illustrated in *Figure 3*. As the molecule of 3GT possesses a centre of symmetry located on the centre of the terephthaloyl moiety, the $P\bar{1}$ space was assumed. The unit-cells of both poly(ethylene terephthalate)[1] and

Table 1 Crystal data for $[C_6H_4\text{–}CO\text{–}O\text{–}(CH_2)_3\text{–}O\text{–}CO]_n$, (3GT)

$[C_{11}H_{10}O_4]_n$ $M_r = 206.07$
Triclinic unit-cell, space group $P\bar{1}$

$a = 4.637(10)$	$b = 6.226(10)$	$c = 18.64(5)$Å (fibre axis)
$\alpha = 98.4(5)$	$\beta = 93.0(5)$	$\gamma = 111.1(5)°$
$V = 493.4 Å^3$	$d_0 = 1.35$	$d_c = 1.387 g/cm^3$
$Z = 2$	$\lambda CuK\alpha = 1.54178$Å	

Reciprocal unit-cell (comparison of X-ray and electron diffraction results)

X-ray fibre diagram	electron diffractogram
$a^* = 0.2327 Å^{-1}$	$a^* = 0.2363 Å^{-1}$
$b^* = 0.1744$	$b^* = 0.1761$
$\gamma^* = 68.9°$	$\gamma^* = 69°$

Table 2 Comparison of the observed and calculated X-ray *d*-spacings

Layer line	d_0	d_c	hkl	Layer line	d_0	d_c	hkl
0	5.682	5.717	010	4	3.314	3.329 3.301	$10\bar{4}$ 014
	4.268	4.298 4.286	100 $\bar{1}10$		3.125	3.160 3.100	$1\bar{1}4$ $\bar{1}14$
	2.112	2.149 2.143	200 $\bar{2}20$		3.013	2.970	104
	1.899	1.906	030		2.565	2.695 2.644 2.598	$11\bar{4}$ $0\bar{2}4$ $1\bar{2}4$
	1.420	1.429 1.429	040 $\bar{3}30$		2.369	2.363 2.308 2.252	$\bar{1}24$ 114 024
1	4.091	4.191 4.155 4.082	$1\bar{1}1$ $\bar{1}11$ 101		1.960	1.971 1.956 1.927	$1\bar{3}4$ $2\bar{2}4$ 224
	2.836	2.854 2.837	$\bar{1}21$ 111	5	2.807	2.959 2.863 2.812 2.759	$10\bar{5}$ 015 $1\bar{1}5$ $\bar{1}15$
	2.276	2.312 2.283	$\bar{2}11$ $2\bar{1}1$		2.664	2.644 2.515	105 $11\bar{5}$
	1.530	1.534 1.526	$\bar{3}11$ $\bar{3}21$		2.377	2.418	$1\bar{2}5$
2	9.065	9.160	002		1.912	1.914 1.901	$2\bar{1}5$ $1\bar{3}5$
	5.171	5.288	$0\bar{1}2$	6	2.958	3.053	006
	4.515	4.505	012		2.816	2.917	$0\bar{1}6$
	3.853	4.075 3.911 3.854	$10\bar{2}$ $1\bar{1}2$ $\bar{1}12$		2.484	2.515 2.510 2.366	016 $1\bar{1}6$ 106
	3.766	3.731	102		2.211	2.327 2.299 2.236	$11\bar{6}$ $0\bar{2}6$ $1\bar{2}6$
	2.864	2.956 2.885 2.877	$11\bar{2}$ $1\bar{2}2$ $0\bar{2}2$		1.715	1.738	$\bar{2}26$
	2.601	2.601	022	7	2.142	2.215 2.130	$\bar{1}17$ 107
	2.044	2.086 2.078 2.058 2.041	$12\bar{2}$ $\bar{2}22$ $1\bar{3}2$ 202		1.691	1.692 1.689	$2\bar{1}7$ $0\bar{3}7$
	1.805	1.803	032	8	2.051	2.007 2.004	018 $\bar{1}18$
	1.717	1.720	212		1.635	1.650 1.641	028 $1\bar{3}8$
3	3.534	3.719 3.540 3.477	$10\bar{3}$ $1\bar{1}3$ $\bar{1}13$				
	3.358	3.341	103				
	1.947	2.026 2.010	$1\bar{3}3$ $\bar{2}23$				
	1.709	1.734 1.690	033 $\bar{2}33$				

poly(tetramethylene terephthalate)[2–4], contain only one monomer unit and the terephthaloyl residues as well as the middle of CH_2–CH_2 bonds are located on the inversion centres along *c* of the P1 space group. Since in 3GT there is an odd number of methylene groups, there cannot be any centre of symmetry in the middle of the trimethylene part of the chain. Therefore, to satisfy the space group requirements the two monomer units should be strung along the *c* dimension.

Determination of the chain conformations

The chain passing through the unit-cell was constructed using the following procedure. The geometrical data for the terephthaloyl residue was taken from a previous study of dimethyl terephthalate[14], while the trimethylene part of the monomer was constructed using the geometrical data averaged from the two model compounds: trimethylene glycol dibenzoate[15] and trimethylene glycol di-*para* chlorobenzoate[16]. The molecular geometry of the trimethylene moiety departs significantly from that expected for C(sp^3) atoms. The C(18)–C(39) distance is 1.504 (3) Å, while the O(12)–C(18)–C(38) angle is 106.8. The values of the bond lengths and bond angles are shown on *Figure 3*. In the above mentioned model compounds, the central methylene group was found to lie on a two-fold axis of rotation. In order to keep the number of variables as low as possible, such an internal symmetry was assumed throughout the conformational analysis of the 3GT monomeric unit. This assumption is supported by the nearly perfect coincidence between one half of the fibre repeat and the equivalent distance observed in the model compounds. With this assumption the number of torsion angles necessary to define the chain conformation is reduced to the two angles: $\phi_1 = \phi_{1'}$ = C(17)–O(12)–C(18)–C(38) and $\phi_2 = \phi_{2'}$ = O(12)–C(18)–C(38)–C(18′). On the (ϕ_1, ϕ_2) energy map computed for this situation

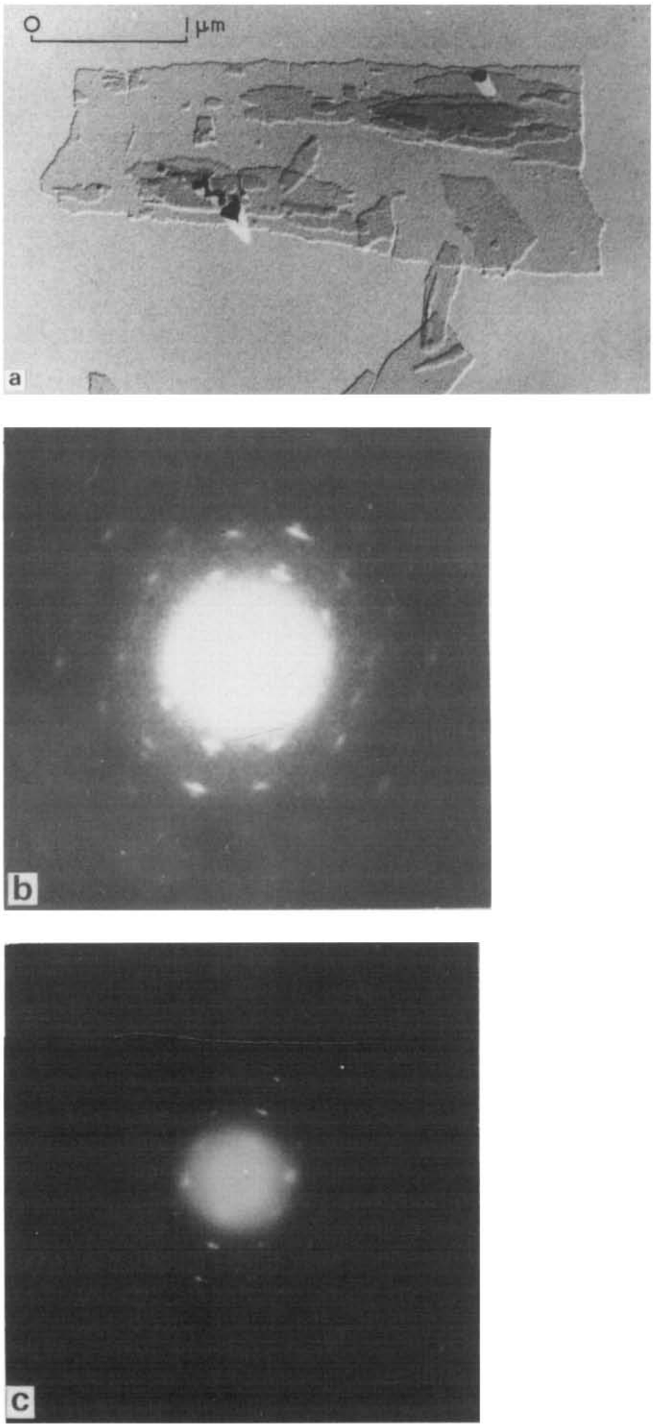

Figure 2 Top: 3GT single crystal. Bottom: Two electron diffractograms of 3GT taken with long and short exposure time to show the very large intensity differences

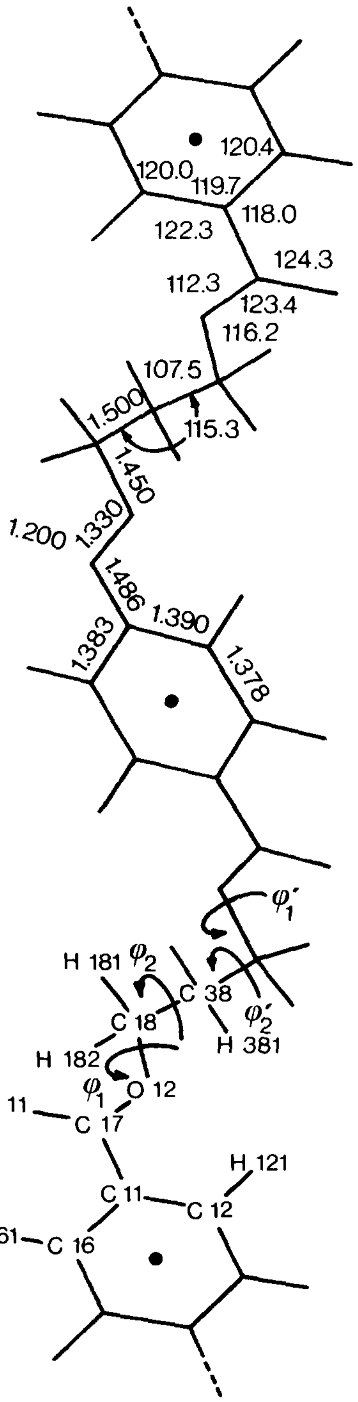

Figure 3 Bond distances and angles in the generation of the 3GT chain. Numbering of the atoms and indication of the torsion angles of interest

(*Figure 4*), the energy minima are represented by (+), whereas the solid state conformations found for the two model compounds are shown as black dots (●). The dotted lines correspond to combinations of ϕ_1 and ϕ_2 such that the fibre repeat is equal to one half of that of the polymer (9.32 Å). The (ϕ_1, ϕ_2) pairs for all the calculated energy minima are compared in *Table 3* with the actual conformations of the model compounds. Only two energetically favoured conformations can match the fibre repeat. These conformations, III and IV, are therefore good candidates for a possible chain conformation. It is worthwhile to observe that the conformations found from the crystal structures of model compounds are close to one of the energy minima and are almost lying on the fibre repeat curve.

Packing analysis

In the P$\bar{1}$ space group, the chain of 3GT can only have the centre of the terephthaloyl residues located on the centres of symmetry along *c*. Since the chain is treated as a rigid body, the only packing parameter is the chain rotation around *c*. Starting from an arbitrary position the orientation of the chain within the unit-cell is arrived at by minimization of the interchain energy using the procedure described by Williams[32] and modified by Sarko and Zugenmaier[33]. In order to avoid local minima, different starting positions are chosen. The degree of interaction between atoms of adjacent chains is measured by the packing index: R_p =

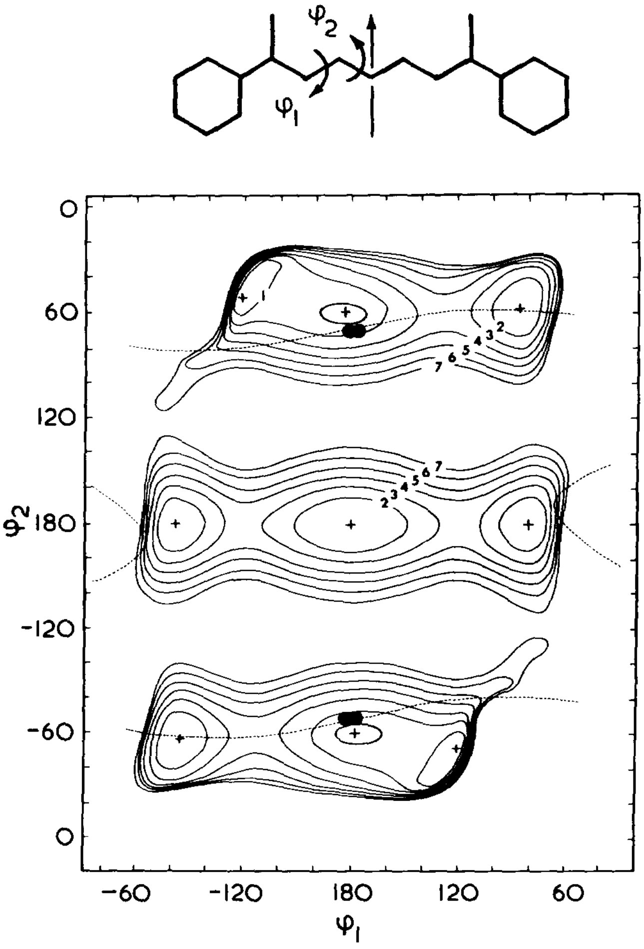

Figure 4 Energy map for 3GT. The energy minima are shown by (+) while the (O) correspond to the conformations found in the model compounds

Table 3 Conformational analysis of 3GT

Conformation	ϕ_1	ϕ_2	Energy, kcal/mol
I	180	180	1.73
II	±80	180	1.53
III	±175	±60	1.10
IV	±80	±55	0.91
V	±125	∓50	0.00

Experimental values from model compounds

	ϕ_1	ϕ_2
trimethylene glycol dibenzoate	±176.8	∓66.8
trimethylene glycol di-*para* chlorobenzoate	±176.7	±66.3

Table 4 Fractional atomic coordinates (x 10^4) of the chain of 3GT

	X	Y	Z
O(12)	–4287	404	1525
O(12′)	–4862	–1459	3316
O(11)	–1057	4076	1508
O(11′)	–3742	4629	3414
C(16)	–1322	–2392	–246
C(11)	–978	998	606
C(17)	–2077	2016	1257
C(18)	–5530	1208	2163
C(38)	–7961	–918	2357
C(18′)	–6711	–2620	2620
C(17′)	–3520	–2661	3650
C(11′)	–1688	–1306	4356
C(16′)	–111	–2233	4788
C(12)	–2300	–1394	360
C(12′)	–1578	947	4579
H(121)	–3960	–2401	619
H(161)	2277	4119	424
H(181)	–3835	1573	2577
H(182)	–6495	2336	2048
H(381)	–9194	–434	2728
H(381′)	–9595	–1734	1933
H(182′)	–8469	–4062	2684
H(181′)	–5381	–3036	2262
H(161′)	–191	–3879	4626
H(121′)	–2716	1630	4268

$\Sigma w(d_0 - d_{ij})^2$ where d_0 is a reference distance while d_{ij} is the actual distance between atoms *i* and *j* in different chains while *w* is a weighting factor. The values of d_0 and *w* used here were those of Williams[32]. When attempts were made to pack the chain whose conformation is defined by ($\phi_1 = \pm 80°$, $\phi_2 = \pm 55°$), the minimum value reached by R_p was 259 kcal/mol. The interactions were much less important when the chain with the other possible conformation ($\phi_1 = \pm 175°$, $\phi_2 = \mp 60°$) was used. In this case the R_p value reached is of the order of 40 kcal/mol. This indicates that this is the most likely conformation for the chain of 3GT. In order to minimize further the interactions, another chain was built so that its conformational angles ($\phi_1 = 180°$, $\phi_2 = -67°$) would give a fibre repeat matching exactly that of the polymer. The packing analysis of this new chain yielded two orientations, differing in projection by only 169°, having comparable R_p values ($R_{p_1} = 29$, $R_{p_2} = 36$ kcal/mol).

X-ray diffraction

Using the two sets of coordinates obtained in the packing analysis, the scale factor was refined for various values of the overall isotropic temperature factor B. The quantity minimized was $\Sigma(||F_0| - |F_c||)^2$. In the case where two or three reflections occurred on the same spot of the fibre diagram (similar *d* spacing), the sum of the contributing F_c's was compared to the corresponding F_o.

For the chain in an orientation corresponding to R_p = 29 kcal/mol, the lowest value reached by the *R* factor, $R = \Sigma\Delta F/\Sigma F_0$, was 0.38 with B = 10 Å^2. However, for the other chain orientation for which R_p = 36 kcal/mol and having the coordinates listed in *Table 4*, *R* was lowered to 0.31 with B = 12 Å^2. This orientation significantly improving the $|F_o| - |F_c|$ agreement was taken to be the correct orientation of 3GT chains in the unit-cell. In a manner similar to that used by Mencik[2], the F_o values corresponding to multiple reflections were split in the proportion of the contributing F_c values and the refinement was resumed with an overall anisotropic temperature factor. The *R* value reached was 0.255 for all the observed reflections. The $F_o - F_c$ list including observed and unobserved reflections is shown in *Table 5*.

Using the same set of coordinates, the electron diffraction amplitudes were computed and are compared in *Table 6* with the observed amplitudes.

DISCUSSION

Description of the structure

The *R* factor of 0.255 obtained for this structure is somewhat high by modern standards. It should be remembered, however, that an internal two-fold symmetry within the monomeric unit was imposed and maintained throughout this study. Furthermore no refinement incorporating variations of bond distances, bond angles and torsion angles was attempted. The proposed model for the structure of 3GT is reasonable, as the intramolecular geometry of the chain belongs to one of the energetically favoured regions of the conformational map, and no drastic short contacts are observed between neighbouring chains. The shortest of the intermolecular distances, that between C(18) and O(11) was also found to be short in the crystal structure of one model compound: trimethylene glycol dibenzoate[16].

The packing of the polymer chains of 3GT is shown by the stereoscopic pairs of *Figure 5*. It can be visualized that the structure is made up of two different parts: the rigid terephthaloyl residues alternating with the more flexible sequence of the trimethylene groups. Two consecutive terephthaloyl planes along *c* form between them an angle of 75°. This angle can be related to the angle between the branches of the X feature observed on the fibre diagram. This feature is characteristic of the diffraction of helical structures. This, of course shows that the terephthaloyl planes are the major contributors to the electron density distribution of the structure. The flexible part consists of a three methylene group sequence end has a $\mathrm{T\bar{G}\bar{G}T}$ conformation. Because of the existence of a centre of symmetry at *c*/2 the following monomer has the TGGT conformation. Seen in projection along *c*, the chain of 3GT has an elliptical envelope (*Figure 6*), on the outer edge of which are located the carboxylic groups.

Single crystals and morphology

One point of interest is to compare the structural similarities in the single crystal and the fibre. The *d* spacings of the observed electron diffraction spots in *Figure 2* correspond to those of reflections from the (hkO) planes. The *d* spacings and the intensities of such reflections agree, within experimental errors, with those of the X-ray fibre diagram. From this observation, it is concluded that the crystal structure is the same in both morphologies. A quite different situation was observed in the case of poly(ethylene terephthalate) where the chain molecules were found to be inclined at about 25–35° to the normal to the basal plane of the single crystals[18].

Another point of interest would be to confirm that quasikinematical electron diffraction intensity data can be obtained from thin organic microcrystals. One way to ascertain this point is to make a comparison between structure analyses by X-ray and electron diffractions. For such a comparison the most important consideration is the number of reflections which can be obtained. In this res-

Table 5 Comparison between the observed and calculated X-ray structure amplitudes

hkl	*Fo*	$\lvert Fc\rvert$	hkl	*Fo*	$\lvert Fc\rvert$	hkl	*Fo*	$\lvert Fc\rvert$	hkl	*Fo*	$\lvert Fc\rvert$
010	11.16	10.00	012	12.03	8.87	$1\bar{3}3$	4.71	3.37	$2\bar{1}5$	8.27	3.68
						$\bar{2}23$		0.76	$1\bar{3}5$		2.29
100	2.90	0.66	$10\bar{2}$	26.94	7.75						
$\bar{1}10$		1.72	$1\bar{1}2$		8.83	203		0.06	006	2.73	3.19
			$\bar{1}12$		6.87	$0\bar{3}3$		0.84			
110		0.57							$10\bar{6}$		0.00
$\bar{1}20$		2.18	102	13.71	9.47	033	3.96	2.56			
020		1.82				$\bar{2}33$		0.36	$0\bar{1}6$	3.63	2.06
$\bar{2}10$		0.87	$11\bar{2}$	6.32	1.52						
			$1\bar{2}2$		4.05	004		0.56	016	7.43	1.19
200	2.79	0.39	$0\bar{2}2$		0.94	$0\bar{1}4$		0.83	$1\bar{1}6$		1.16
$\bar{2}20$		1.10							106		4.44
			$\bar{1}22$		1.25	$10\bar{4}$	7.55	2.59			
120		0.43	112		1.41	014		5.85	$\bar{1}16$		0.08
$\bar{1}30$		1.38									
			023	3.90	3.28	$1\bar{1}4$	14.26	7.45	$11\bar{6}$	6.00	0.61
030	6.06	3.64				$\bar{1}14$		1.34	$1\bar{2}6$		2.25
			$\bar{2}12$		1.09				$0\bar{2}6$		0.80
040	2.64	0.58	$2\bar{1}2$		2.34	104	3.60	3.70			
$\bar{3}30$		0.20							$\bar{1}26$	***	0.76
			$20\bar{2}$		1.52	$11\bar{4}$	6.75	3.08	116		5.47
001		1.39	$2\bar{2}2$		0.65	$0\bar{2}4$		2.54	026		0.85
$0\bar{1}1$		1.56				$1\bar{2}4$		5.24			
011	***	4.74	$12\bar{2}$	6.31	2.23				226	5.10	0.33
$10\bar{1}$		1.64	$\bar{2}22$		1.47	$\bar{1}24$	5.25	2.55			
			$1\bar{3}2$		2.19	114		2.70	007		0.12
$1\bar{1}1$		2.28	202		1.06	024		2.16	$10\bar{7}$		0.28
$\bar{1}11$	8.45	4.27							$1\bar{1}7$		1.64
101		5.34	$\bar{1}32$		2.21	214		0.06	017		0.27
			$0\bar{3}2$		0.88	$20\bar{4}$		0.44			
$11\bar{1}$		1.43	122		0.02	$2\bar{1}4$		3.04	$\bar{1}17$	8.82	2.07
$1\bar{2}1$		0.69				$12\bar{4}$		1.04	107		5.28
$0\bar{2}1$		0.15	032	1.56	2.48						
						$1\bar{3}4$	6.65	0.52	$11\bar{7}$		0.19
$\bar{1}21$	3.69	1.73	212	2.31	3.49	$2\bar{2}4$		4.70	$0\bar{2}7$		0.20
111		4.75				$\bar{2}24$		1.08	$1\bar{2}7$		2.76
			003		0.99						
021		0.94	$0\bar{1}3$		0.89	$0\bar{3}4$		1.44	$2\bar{1}7$	3.30	1.08
			013	***	5.35	005		0.12	$0\bar{3}7$		0.50
$\bar{2}11$	1.88	0.22				$0\bar{1}5$		0.15			
$2\bar{1}1$		0.49	$10\bar{3}$	28.26	10.15				008		0.34
			$1\bar{1}3$		16.68	$10\bar{5}$	5.25	1.72	$0\bar{1}8$		0.47
$20\bar{1}$		0.39	$\bar{1}13$		1.94	015		2.14	$10\bar{8}$		0.04
$3\bar{2}1$		0.20				$1\bar{1}5$		3.05	$1\bar{1}8$		0.12
$\bar{2}21$		2.20	103	5.82	5.45	$\bar{1}15$		0.90			
201		0.93									
$12\bar{1}$		2.26	$11\bar{3}$		1.69	105	5.47	5.22			
$1\bar{3}1$		3.13	$0\bar{2}3$		1.26	$11\bar{5}$		3.15			
$\bar{1}31$		0.29	$1\bar{2}3$		2.57				018	2.87	2.20
121		1.39	$\bar{1}23$		0.77	$0\bar{2}5$		0.48	$\bar{1}18$		1.12
$0\bar{3}1$		1.98	113		1.02						
			023		1 95	$1\bar{2}5$	5.17	2.43	$11\bar{8}$		0.02
$\bar{3}11$	2.51	0.32	$\bar{2}13$		0.32				$0\bar{2}8$		1.04
$\bar{3}21$		0.53	$2\bar{1}3$		1.50	$\bar{1}25$		0.28	108		0.04
			$20\bar{3}$		0.62	115		1.82	$1\bar{2}8$		0.85
002	2.16	1.15	$12\bar{3}$		1.07	025		0.57			
			$2\bar{2}3$		0.66	$\bar{2}15$		0.90	028	2.40	0.22
$0\bar{1}2$	11.04	12.14				$20\bar{5}$		0.77	$1\bar{3}8$		0.82
						$12\bar{5}$		0.08			

pect, the electron diffraction data available in this study are really limited. The great majority of the reflections have a very weak intensity; only a few are very strong. This feature is due to the helical structure of the 3GT chains.

Based on the results of the electron diffraction pattern it is obvious that the chain molecules are oriented perpendicular to the base plane of the single crystals. In view of the lamellar thickness (80 Å) and the average degree of polymerization (estimated to be about 120), the 3GT chain must necessarily be folded in the platelet as in other polymer single crystals. The correlation of the electron micrograph and the selected area electron diffraction pattern (*Figure 2*) indicates that the longer side of the parallelogram corresponds approximately to the a^* dimension and the shorter side to the b^* dimension of the reciprocal unit-cell. A study of the projection of the structure onto the *ab* plane corroborates this observation. As mentioned earlier, the overall feature of such a projection is an elliptical envelope. The long axis of the ellipse, corresponding to the maximum distribution of matter, is oriented parallel to the *x* axis. Since this preferential orientation remains unchanged by symmetry translation, the growth planes of the crystal are of the (0 1 0) type. Indeed the (0 1 0) reflection is found to be the strongest among the (h k O) reflections.

Table 6 Observed and calculated structure factors of the electron diffractogram of 3GT

hkl	*Fo*	|*Fc*|	hkl	*Fo*	|*Fc*|
100	66	19	020	81	116
200	25	40	120	36	5
300	40	27	320	7	5
$\bar{3}10$	10	33	$\bar{3}30$	40	31
$\bar{2}10$	17	81	$\bar{2}30$	32	22
$\bar{1}10$	59	30	$\bar{1}30$	40	26
010	324	351	030	79	117
110	41	23	130	10	18
210	10	56			
310	7	1	$\bar{3}40$	10	22
			$\bar{2}40$	17	0
$\bar{3}20$	10	39	$\bar{1}40$	17	12
$\bar{2}20$	36	34	040	10	5
$\bar{1}20$	44	4			

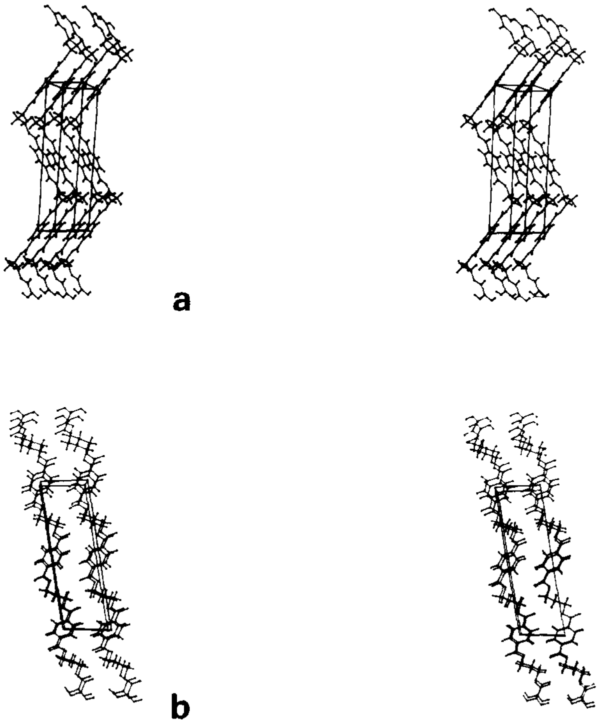

Figure 5 Stereo pairs of the 3GT chains in their unit-cell

Relationships between the structure and mechanical properties

The present structural data allow some insight into the understanding of the mechanical behaviour of 3GT polymer fibres. It has been reported that when subjected to mechanical tensile stress, the crystalline regions in 3GT respond immediately as the overall strain increases[10]. It was then assumed that upon longitudinal extension some twist of the *gauche* towards the *trans* conformation should occur. This assumption appears to be confirmed by the present results. The conformation of the 3GT polymer chain is such that only departure from the *gauche* conformation of the trimethylene groups would result in an extension of the chain. As depicted in *Figure 4* departure of ϕ_2 angle from the *gauche* conformation up to a value of about $-100°$ is feasible without any drastic energetic gain. In terms of chain extension this would correspond to a maximum value of the fibre repeat of 22.70 Å. In fact the highest extension reached in the above mentioned experiments[10] corresponds to a fibre repeat of 20.0 Å. Such an extension can be arrived at by a slight rotation of ϕ_2 angle from -67 to $-80°$. Thus the conformational arrangement within the trimethylene sequence of 3GT allows for a certain flexibility of the chain which deforms as though it were a coiled spring.

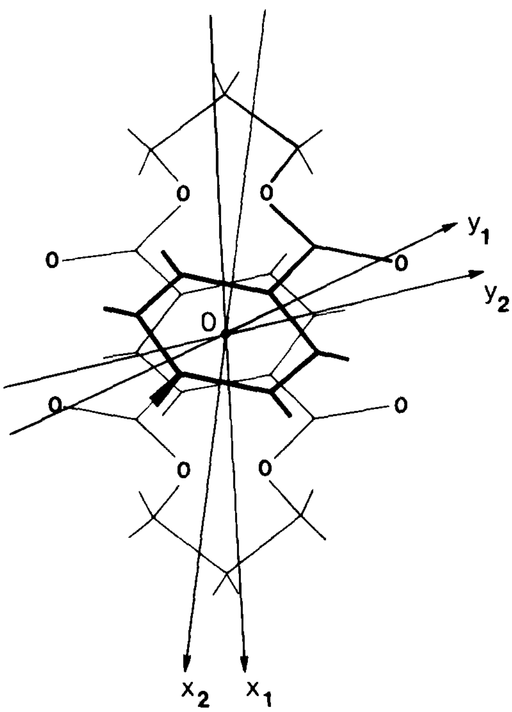

Figure 6 Projection of a chain of 3GT along *c*

At this stage it should be emphasized that any further twist towards an all-*trans* conformation of the chain would tend to align in a parallel fashion the dipole moments of the carboxyl groups. Since the dipolar contribution to the total energy as shown in *Figure 4* had not been taken into account it must be stressed that the energy associated with an all-*trans* conformation is certainly underestimated. As such, the all-*trans* conformation appears to be a very unlikely stable arrangement.

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