

The structure of poly(trimethylene terephthalate)

I. J. Desborough,* I. H. Hall and J. Z. Neisser

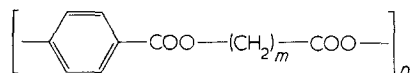
Department of Pure and Applied Physics, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

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The determination of the crystalline structure of oriented fibres of poly(trimethylene terephthalate) is described. The unit cell is triclinic with the following parameters: $a = 4.6\text{\AA}$, $b = 6.2\text{\AA}$, $c = 18.3\text{\AA}$, $\alpha = 98^\circ$, $\beta = 90^\circ$, $\gamma = 112^\circ$. Each cell contains two monomers of one polymer chain. Both methylene bonds are in the *gauche* conformation. The chain conformation and the packing of chains within the unit cell are discussed in detail and compared with other chemically similar materials, both monomeric and polymeric.

INTRODUCTION

Poly(trimethylene terephthalate) is a member of the family of polymers having the structural formula:



and abbreviated *mGT*. The best known member of this series is 2GT [poly(ethylene terephthalate)] which has been extensively studied. 4GT has been the subject of several recent structural studies¹⁻⁴ which have revealed the presence of *gauche* bonds in the conformation of the methylene section of the chain. Under stress, this transforms reversibly to the all-*trans* conformation. In 5GT also^{5,6} the conformation of the methylene sequence contains non-*trans* bonds when a specimen has been annealed free to retract. Under stress, this will again transform reversibly to the all-*trans* conformation. However, unlike 4GT, this conformation is also found, though only in mixture with the other form, in a stress-free fibre which has been annealed under stress.

Measurements of the crystallographic repeat of 3GT⁷ have indicated that, for this material also, the methylene bonds are not all *trans*, but it has not proved possible to produce a transformation to a *trans* conformation by application of stress; the fibre breaks before this is achieved. However, the crystalline lattice is unusually compliant.

These studies have led to a determination of the chain conformation of 3GT which is reported in the present paper.

EXPERIMENTAL

Material

3GT polymer chip was polymerized in the Department of Polymer and Fibre Science at UMIST and melt spun into coarse monofilament at 270°C. Lengths of monofilament were cold drawn and then annealed for 2 h at 185°C. The draw ratio was about 4:1.

* Present address: 29, Quakerfields, Westhoughton, Bolton, Lancs, UK

Recording of X-ray diffraction data

X-ray diffraction photographs were taken using nickel filtered $\text{CuK}\alpha$ radiation with a camera of the type described by Elliott⁸ and manufactured by G. and D. Searle Ltd. The essential feature of this camera is that a high intensity, highly monochromatic beam of X-rays of about 40 μm diameter is focused at the film position giving a diffraction photograph of good resolution with comparatively short exposure time. A cylindrical film holder of 30 mm radius was used, and the camera evacuated to eliminate air-scatter. The diffraction pattern obtained is shown in *Figure 1(b)*. The fibre axis was perpendicular to the X-ray beam, and co-axial with the film.

Determination of unit cell parameters

In *Figure 1* there appear to be meridional reflections and row lines parallel to the meridian. This suggests that the unit cell is at least monoclinic with the c -axis normal to the ab plane. Furthermore, there are no clearly defined layer lines. This was taken as an indication that the lines were very closely separated suggesting a helical structure with a long crystallographic repeat. Extensive attempts to construct a unit cell and index reflections on these assumptions were unsuccessful.

Very careful inspection of the diffraction photographs revealed that the row lines on which reflections lay were in fact not exactly parallel to the meridian, but inclined to it at a small angle, indicating that c^* was not exactly aligned along the meridian. The meridional reflection was not therefore truly meridional but consisted of two overlapping reflections each slightly displaced to either side of the meridian. As an alternative hypothesis, to explain the absence of layer lines, it was assumed that the unit cell was triclinic and aligned with c^* close to the fibre axis. Fibre symmetry was generated by rotation of cells about the fibre axis which now would not coincide with chain (or unit cell c -) axis.

This 'tilted crystal orientation', in which the unit cell is tilted away from its usual orientation with chain and fibre-axes coincident, has proved to be a common feature of

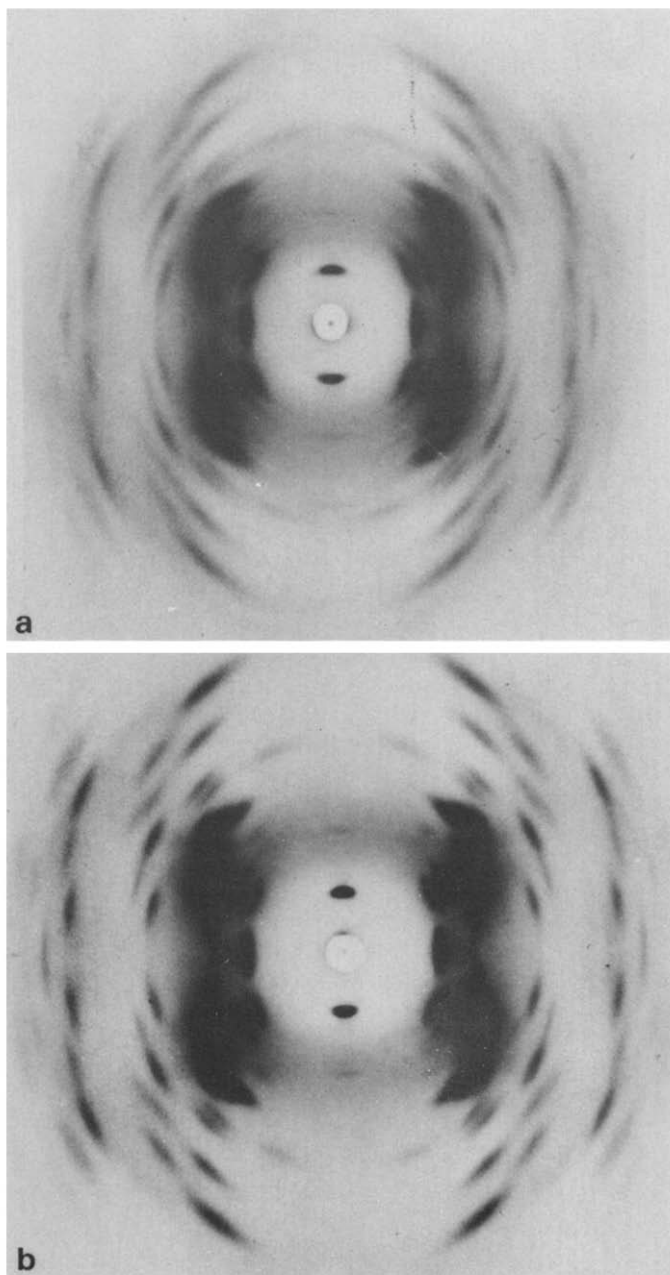


Figure 1 Diffraction patterns of 3GT. (a) Fibre drawn so as to reduce tilt, (b) fibre drawn to give 'tilted crystal' orientation

poly(n-glycol terephthalate) fibres^{9,1,6} and from the assumptions just described a satisfactory trial unit cell was constructed. The magnitude and direction of the tilt was determined following the method described by Daubeny *et al.*⁹.

The unit cell parameters were refined by minimizing the sum of the squares of the differences between the *d*-spacings calculated from the location of the diffraction spots and those calculated from the unit cell. This procedure had the advantage that the *d*-spacing can be calculated from the location of the reflection without knowing the values of the tilt parameters.

Determination of intensity of X-ray diffraction spots

The integrated intensity of each reflection was determined using an Optronix 'Photoscan' digital microdensitometer in conjunction with an Optronix 'Photowrite' machine. The technique has been fully described elsewhere¹⁰. As far as possible, allowance was made for background intensity, and intensity was apportioned between partly overlapping reflections. Where this could not be done, the reflections were treated as an overlapping group, and because of the absence of well-defined layer lines some of these groups included members from different lines.

Near-meridional reflections were not used because of the uncertainty of their Lorentz factors.

Determination of chain conformation

Comparison of the density calculated from the unit cell dimensions with the measured value indicated that there were two monomers per unit cell. The magnitude of the cell dimensions showed that there was one molecular chain per cell with two monomers per crystallographic repeat. Since these are unlikely to have different conformation angles they must be related either by a 2/1 screw axis along the chain axis, or by a centre of symmetry at the centre of the benzene rings (see Figure 2). The monomer is illustrated in Figure 2 which also defines the symbols used to specify particular angles and bonds.

Values for bond lengths and angles were assumed to be the same as those in comparable low molecular weight compounds, and so only the chain conformation angles and the orientation of the molecules within the unit cell remained to be determined. The values assumed are shown in Table 1 and were chosen using the studies of Pérez and Brisse¹¹⁻¹⁴ as a guide. In these the methylene bond has been found to be shorter than 1.54Å, in some compounds being as short

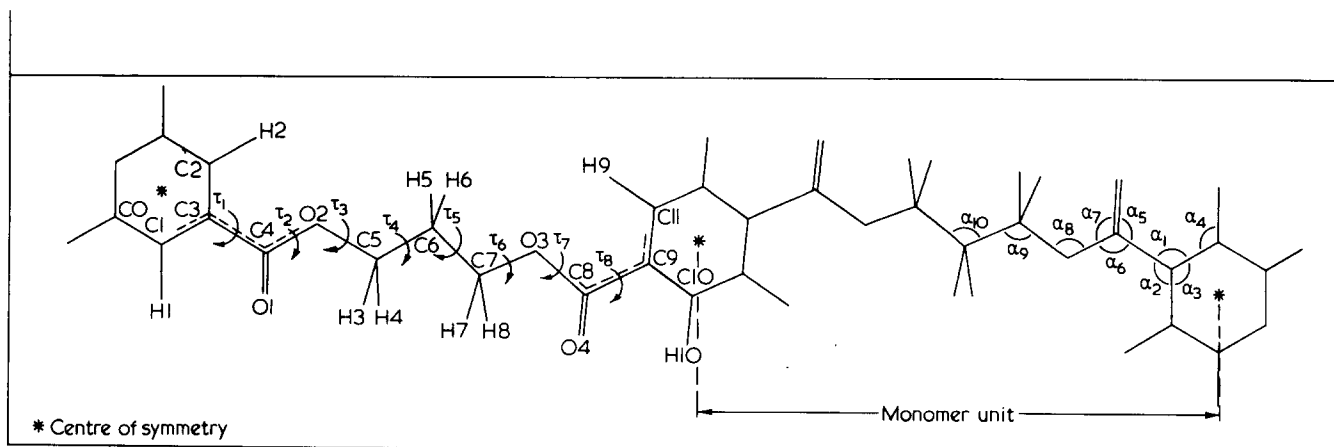


Figure 2 Crystallographic repeat of 3GT.

Table 1 Values assumed for bond lengths and angles

Bond	Length (Å)
C ₀ -C ₁	1.39
C ₁ -C ₃	1.39
C ₂ -C ₃	1.39
H ₁ -C ₁	1.07
H ₂ -C ₂	1.07
C ₄ -C ₃	1.48
O ₁ -C ₄	1.21
O ₂ -C ₄	1.34
C ₅ -O ₂	1.44
H ₃ -C ₅	1.03
C ₆ -C ₅	1.50
	Angle (degrees)
α_1	120
α_2	120
α_3	120
α_4	120
α_5	125
α_6	113
α_7	122
α_8	116
α_9	106
α_{10}	113

as 1.50Å. Consequently, conformations were tried having values of both 1.54Å and 1.50Å for this bond.

To construct trial models, the 'Linked Atom Least Squares'¹⁶ Structure Refinement System for Helical Polymers' (LALS) was used. In using this computer program (which was kindly made available by Professor Arnott) to build models, values of bond angles and lengths are fixed and trial values of the conformation angles are inserted. These are then refined so that the model meets the required crystallographic repeat length and other symmetry constraints. Particular conformation angles can be fixed, and weighting schemes used so that some angles change preferentially to others.

τ_1 , τ_2 , τ_7 and τ_8 are close to 180° in all similar structures. τ_1 and τ_8 were therefore fixed at this value but τ_2 and τ_7 weighted to restrain their movement from it. Combinations of *trans* and \pm *gauche* were chosen for the methylene bonds τ_4 and τ_5 , and these were also weighted to restrain movement. Neither τ_3 nor τ_6 have consistent values in similar structures and so these were allowed to vary freely.

Initial trial models having all possible combinations of *trans* and \pm *gauche* for τ_4 and τ_5 were used, and both the 2/1 screw axis and the centrosymmetric conformation were investigated for each model. For the centrosymmetric case, all the trial models adjusted themselves to meet the crystallographic constraints with only small movements of the strongly restrained angles. However, for those models with the 2/1 screw axis, it was only in those with both methylene bonds in one of the *gauche* conformations that these bonds remained near to their initial values, and for these models τ_2 and τ_7 varied appreciably from 180°. Thus even at this early stage the models with a 2/1 screw axis looked very unpromising. They were, however, taken forward to the next stage of model construction.

In the models so far constructed the chain is placed in the unit cell with the centre of a benzene ring at the origin, and with the chain axis coinciding with the *c*-axis. Another facility of the computer program is now used, so that the

orientation of the chain about the *c*-axis is varied to minimize the 'contact distances' (this was the difference between the separation of the centre of a pair of atoms and the sum of their Van der Waals radii for those atoms whose separation is the smaller of those quantities. The Van der Waals radii were taken to be 1.7Å for carbon, 1.4Å for oxygen and 1.0Å for hydrogen). The chain conformation was also allowed to make small adjustments to minimize these distances. When the best orientation had been found the *R*-factor ($R = \sum |F_o - F_c| / \sum |F_o|$) was determined for all observed reflections and the separations of all pairs of atoms (both inter and intra molecular) were calculated.

For all models having 2/1 symmetry, the packing was unsatisfactory with large contact distances for some pairs of atoms and the *R*-factors were high. For the centrosymmetric models, only one (that with the *-gauche -gauche* conformation in the methylene sequence) had both a reasonably low *R*-factor and satisfactory packing. Subsequent investigation was therefore confined to this.

Refinement was effected by varying the conformation angles and the orientation of the chain within the unit cell. This was done so that the constraints of symmetry and chain repeat length were satisfied, and the sum of the squares of the differences between observed and calculated structure factors was minimized. This facility was a further feature of the same computer program. For the refinement, structure factors were weighted to prevent the strongest reflections dominating the procedure^{2,17}, and unobserved reflections were given an intensity which, it was estimated, would be just visible above background in the region of the film in which they would be located were they visible. They were included in the refinement if the calculated intensity was greater than this, but otherwise were omitted.

The convention used for measuring the conformation angle τ is illustrated in Figure 3. To understand this diagram, imagine the molecule is being built by starting at H₁ (Figure 2) and successively adding atoms. Suppose that C₄ has been reached, and O₂ is about to be added. Its position will be determined by three parameters, the bond length C₄-O₂, the bond angle α_6 , and the conformation angle τ_1 . Suppose that the section of chain C₁-C₃-C₄-O₂ is held so that C₃-C₄ (the bond about which τ_1 is measured) is normal to the plane of the diagram with C₁-C₃ (the section already built) above the plane and C₄-O₂ (the section about to be built) below. τ_1 is then measured as shown. It is positive if measured clockwise, negative if anticlockwise.

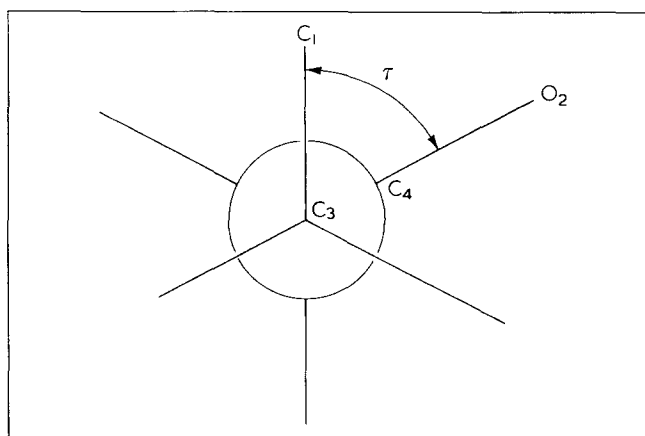
Figure 3 Convention for measuring conformation angle τ

Table 2 Unit cell parameters

a (Å)	4.5(9)
b (Å)	6.2(1)
c (Å)	18.3(1)
α (degrees)	98.(0)
β (degrees)	90.(0)
γ (degrees)	111.(7)
Volume (Å ³)	479.(4)
Density (g.cm ⁻³)	1.43
Measured density (g.cm ⁻³)	1.35

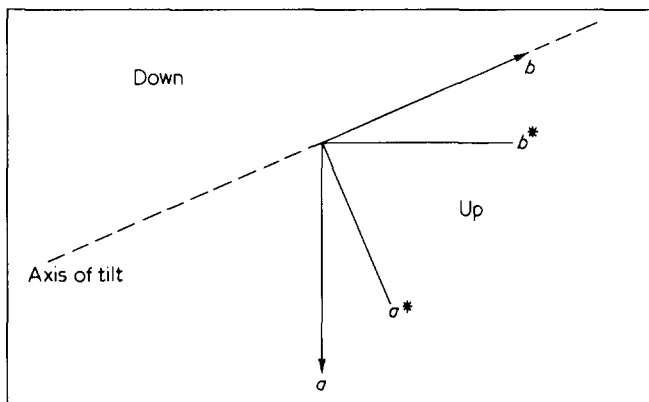


Figure 4 Projection of unit cell down c -axis, showing axes about which tilting occurs

RESULTS

Unit cell

Unit cell parameters are given in Table 2.

Systematic misorientation of chain axes

The crystallites are tilted about an axis which lies in the a^*b^* plane, along the line of intersection of this plane with the bc plane. The magnitude of tilt is such that the chain axes are, on average, inclined at an angle of 3° to the fibre axis. Its sense is such that the positive a -axis moves up (see Figure 4). The $(\bar{1}20)$ plane is normal to the tilt axis and will remain vertical on tilting.

Different modes of sample preparation yield different diffraction patterns. For example, the pattern in Figure 1(a), which shows clearer evidence of layer lines, was obtained from a sample which had been drawn manually at a temperature of about 170°C , separating its ends at a speed of about 0.5×10^{-2} m/sec. If this speed was further reduced, maintaining the other conditions, the pattern reverted to that of Figure 1(b). Pin and plate drawing at commercial speeds, the temperature being 60°C and 90°C respectively, led to patterns similar to that of Figure 1(a).

These diffraction patterns could be indexed satisfactorily with the unit cell given in Table 2, but it was necessary to alter the tilt parameters. The direction of the tilt axis and the sense of tilt were unaltered, but the magnitude was reduced to 1° .

Chain conformation

Parameters defining the chain conformation together with the R -factor of the structure (calculated on observed reflections only) are given in Table 3. The angles θ , ϕ , ψ

define the inclination of the benzene rings with respect to the unit cell edges. The suffix 1 refers to the ring at the origin, 2 to the other. If the molecule is placed in the unit cell so that the chain axis coincides with the c -axis and the normal to the benzene ring inclined towards the positive c -direction lies in the (010) plane in the positive a -direction, then θ is the rotation about the chain axis required to bring the molecule into its correct orientation and is positive if this rotation is anticlockwise looking in the negative c -direction. ϕ is the angle between C_3C_4 and the c -axis; ψ is the angle the normal to the benzene ring makes with the c -axis.

The separation of all pairs of non-bonded atoms has been compared with the sums of their Van der Waals radii. All separations which are less than this sum, both within and between molecules, are given in Table 4.

The chain conformations and packing within the unit cell are illustrated in Figures 5–7. Fractional atomic coordinates are given in Table 5. Calculated and observed d -spacings and structure factors are given in Table 6.

Table 3 Parameters defining chain conformation

τ_1 (degrees)	-170.(2)
τ_2 (degrees)	-169.(6)
τ_3 (degrees)	167.(4)
τ_4 (degrees)	-73.(7)
τ_5 (degrees)	-61.(9)
τ_6 (degrees)	-152.(8)
τ_7 (degrees)	-176.(8)
τ_8 (degrees)	166.(4)
θ_1 (degrees)	-170.(8)
θ_2 (degrees)	-5.(3)
ϕ_1 (degrees)	40.(9)
ϕ_2 (degrees)	46.(8)
ψ_1 (degrees)	52.(7)
ψ_2 (degrees)	51.(5)
R	27.9

Table 4 Amount by which atomic separations are less than the sum of Van der Waals radii

(a) Within a molecule		Sum of radii Separation (Å)
Atom pair		
O_1-C_1		0.22
O_2-C_2		0.39
O_2-H_2		0.07
C_5-O_1		0.47
H_3-C_4		0.16
C_7-O_2		0.11
C_7-H_3		0.05
O_3-C_5		0.24
C_8-H_7		0.21
O_4-C_7		0.47
O_4-H_7		0.08
$C_{10}-O_4$		0.21
$C_{11}-O_3$		0.39
$H_{10}-O_3$		0.03
(b) Between molecules		Sum of radii Separation (Å)
Atom pair	Unit cell translation	
O_1-C_7	$a = 0 \quad b = 1$	0.29

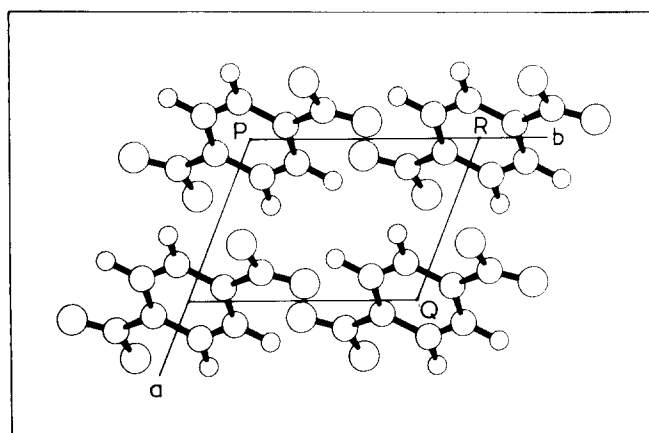
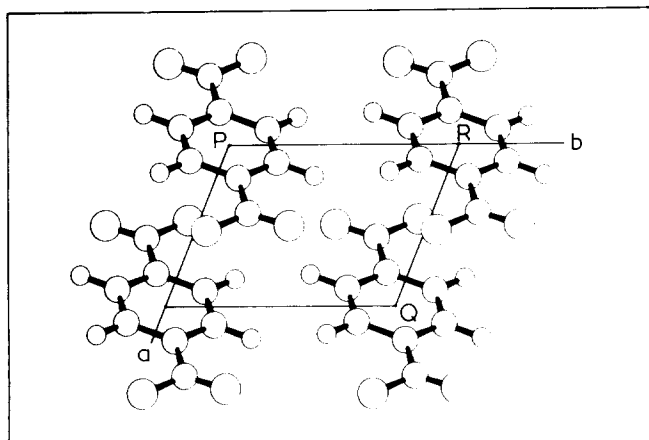


Figure 5 Projection of terephthaloyl residues down *c*-axis. (a) Residue including C₁–C₄, (b) residue including C₈–C₁₁

DISCUSSION

Systematic misorientation of chain axes

This misorientation has now been found in 2⁹, 3, 4¹ and 5⁶ GT and so seems to be a common feature of this chemical system. However, there is no common feature in the direction of the tilt axis, or in the sense of tilt and so that there is no indication of the structural feature responsible.

Conformation angles

Neither terephthaloyl unit deviates very much from planarity ($\tau_1 = 170^\circ$, $\tau_8 = 166^\circ$) but the value of τ_8 is further from 180° than is usual in chemically similar polymers. Only in the β -phase of 5GT⁶ is a greater deviation found. τ_2 (and its equivalent τ_7) is usually close to 180° in similar structures. The deviations here ($\tau_2 = -170^\circ$, $\tau_7 = -177^\circ$), whilst small, are larger than those found in other materials, except 5GT. The value of τ_3 (and τ_6) varies widely between different compounds (though tending to cluster around certain values⁶) suggesting that the conformation of this part of the molecule is not well determined energetically. The values obtained here lie near to the clusters of values found in similar compounds. Both methylene bonds ($\tau_4 = -74^\circ$, $\tau_5 = -62^\circ$) are close to *gauche*.

Intra-molecular atomic separations

The first three of the short atomic separations listed in Table 4a arise from the planarity of the terephthaloyl residue. Although the second residue is slightly less planar, the

equivalent separations (the last three in the Table) are very similar. The separation C₅–O₁ arises from the planarity of the section C₃C₄O₂C₅ and the equivalent separation in the other part of the molecule is again closely similar. H₃–C₄ (and its equivalent C₈–H₇) arises from the value of τ_3 , and the equivalent separations in both parts of the molecule are again similar, although the equivalent conformation angles are rather different. O₄–H₇ arises from the combination of τ_6 and τ_7 , and this separation is short in only one part of the molecule. The shortenings of all the above separations are very similar in all compounds which have been studied^{1,6}. The remaining short separations are a consequence of the *gauche* conformation of the methylene sequence; as this conformation angle approaches 60° the C–O separation shortens whilst that between C and H improves.

Molecular shape and packing

From Table 3, it will be seen that the values of ϕ and ψ are very similar for the two benzene rings, and that the values of θ differ by about 170° , suggesting that the two terephthaloyl residues are approximately related by a 2/1 screw axis. However, from Figures 5 and 6 it will be seen that this is not so. If it was, the rotation of one of the benzene rings in its plane to generate the angle ϕ would need to be in the opposite sense. The methylene sequences are also unrelated. Neither their conformations, nor their linkages

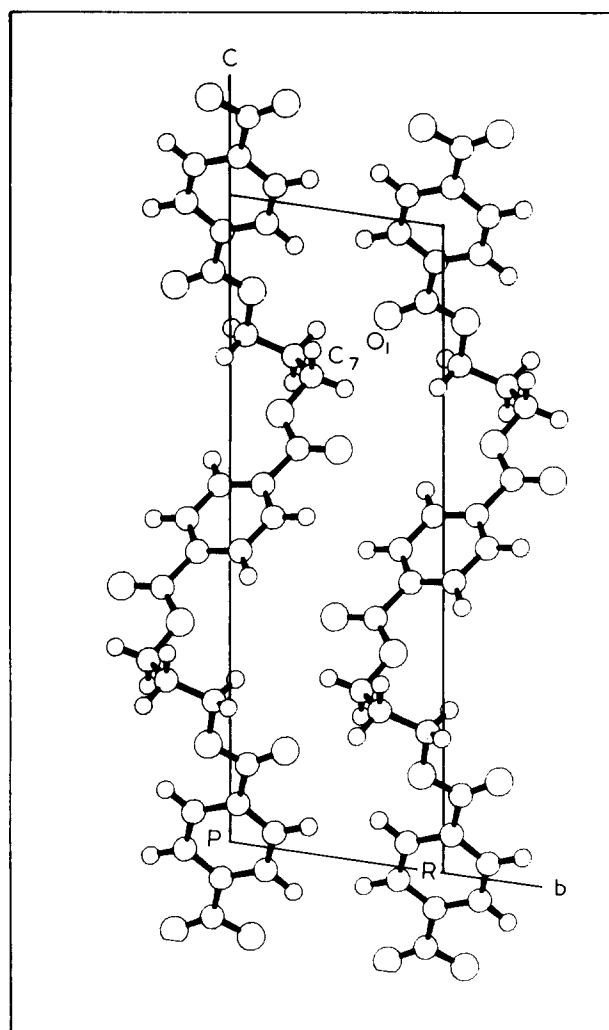


Figure 6 Projection on to *b*–*c* plane

Table 5 Fractional atomic coordinates

Atom	x	y	z
C ₁	0.111	0.240	0.024
C ₂	0.095	-0.143	0.038
C ₃	0.206	0.097	0.062
H ₁	0.196	0.425	0.042
H ₂	0.169	-0.254	0.067
C ₄	0.425	0.199	0.128
O ₁	0.503	0.399	0.159
O ₂	0.533	0.047	0.152
C ₅	0.703	0.121	0.222
H ₃	0.579	0.188	0.260
H ₄	0.920	0.248	0.218
C ₆	0.735	-0.093	0.245
H ₅	0.805	-0.181	0.200
H ₆	0.899	-0.045	0.288
C ₇	0.433	-0.261	0.268
H ₇	0.467	-0.407	0.281
H ₈	0.263	-0.311	0.226
O ₃	0.350	-0.136	0.332
O ₄	0.105	-0.478	0.372
C ₈	0.176	-0.268	0.380
C ₉	0.085	-0.130	0.442
C ₁₀	-0.146	-0.243	0.490
C ₁₁	0.2321	0.113	0.454
H ₉	-0.259	-0.429	0.478
H ₁₀	0.410	0.199	0.420

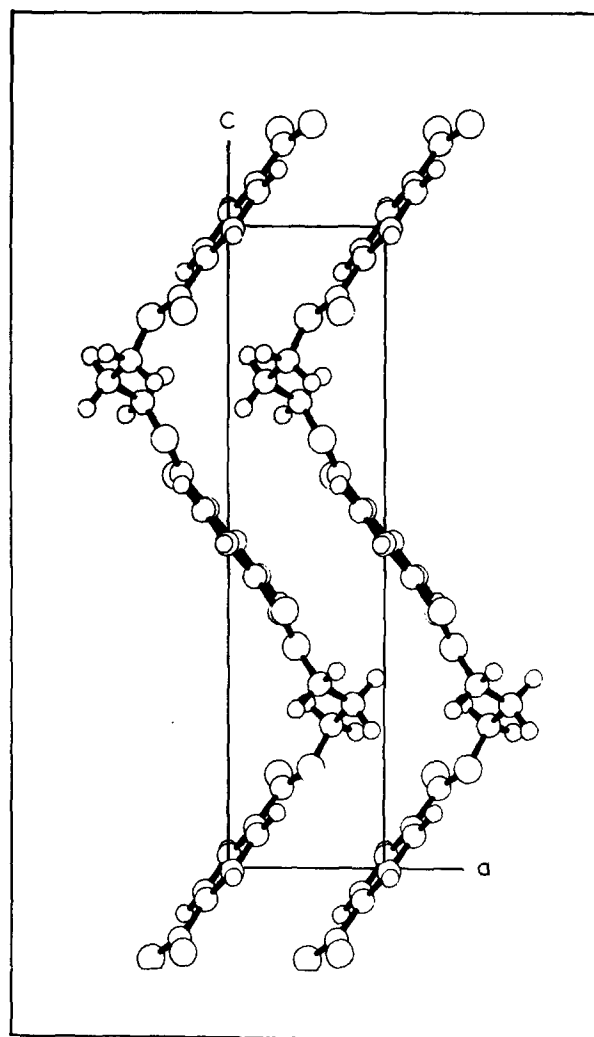


Figure 7 Projection on to a-c plane

Table 6 Observed and calculated *d*-spacings and structure factors

Indices	<i>d</i> (calc) Å	<i>d</i> (obs) Å	<i>F_c</i>	<i>F_o</i>
010	5.71	5.69	62	82
110	4.26	4.27	19	10
100	4.26			
120	2.93	—	6	(7)
110	2.93			
020	2.85	—	15	(12)
210	2.30	—	7	(7)
220	2.13	—	16	(11)
200	2.13			
130	2.04	—	19	(17)
120	2.04			
030	1.90	1.91	33	32
230	1.79	—	25	(22)
210	1.79			
040	1.43	1.43	37	34
330	1.42			
300	1.42			
011	5.69	—	2	(6)
012*	5.20	5.21	56	67
011	5.23			
111	4.20	—	17	(22)
101	4.20			
111	4.10	4.11	38	51
101	4.10			
121	2.95	—	17	(16)
111	2.95			
021	2.89	—	2	(6)
121	2.84	—	26	(22)
111	2.84			

Indices	<i>d</i> (calc) Å	<i>d</i> (obs) Å	<i>F_c</i>	<i>F_o</i>
021	2.76	—	5	(7)
211	2.28	2.29	16	11
211	2.28			
221	2.13	2.12	29	11
201	2.13			
221	2.10	—	11	(9)
201	2.10			
131	2.06	—	16	(14)
121	2.06			
131	2.00	—	6	(11)
121	2.00			
012	4.53	4.54	46	67
112	3.94	—	37	(27)
102	3.94			
112	3.77	3.79	89	125
102	3.77			
122	2.89	2.86	24	22
112	2.89			
022	2.85			
122	2.70	—	6	(7)
112	2.70			
022	2.61	2.60	18	18
212	2.22	—	14	(12)
212	2.22			
222	2.10	—	14	(12)
202	2.10			
132	2.05	2.05	35	31
122	2.05			
222	2.05			
202	2.05			

Table 6 continued

Indices	$d(\text{calc})\text{\AA}$	$d(\text{obs})\text{\AA}$	F_c	F_o	Indices	$d(\text{calc})\text{\AA}$	$d(\text{obs})\text{\AA}$	F_c	F_o
$\bar{1}32$	1.94	—	10	(9)	$\bar{1}15$	2.69	2.69	24	18
122	1.94	—	—	—	105	2.69	—	—	—
032	1.81	1.81	17	16	025	2.43	2.42	37	31
$0\bar{1}3$	4.50	—	0	(5)	$\bar{1}25$	2.42	—	—	—
013	3.87	—	18	(22)	$\bar{1}15$	2.42	—	—	—
$\bar{1}13$	3.57	3.59	109	133	$\bar{1}25$	2.16	—	10	(7)
$\bar{1}03$	3.57	—	—	—	115	2.16	—	—	—
$\bar{1}13$	3.39	3.41	26	12	025	2.09	—	1	(6)
103	3.39	—	—	—	215	1.94	1.94	52	66
$\bar{1}23$	2.76	—	10	(9)	215	1.94	—	—	—
$\bar{1}13$	2.76	—	—	—	$0\bar{1}6$	2.85	2.87	13	13
023	2.74	—	2	(6)	116	2.53	—	15	(13)
$\bar{1}23$	2.52	—	16	(14)	$\bar{1}06$	2.53	—	—	—
113	2.52	—	—	—	016	2.52	—	3	(5)
023	2.44	—	11	(9)	116	2.40	2.41	30	44
$\bar{2}13$	2.14	—	5	(6)	106	2.40	—	—	—
213	2.14	—	—	—	026	2.25	2.23	28	24
$\bar{2}23$	2.04	—	12	(10)	$\bar{1}26$	2.23	—	—	—
203	2.04	—	25	(22)	$\bar{1}16$	2.23	—	—	—
$\bar{1}33$	2.02	—	—	—	017*	2.23	—	—	—
$\bar{1}23$	2.02	—	—	—	$\bar{1}26$	1.99	2.00	29	27
$\bar{2}23$	1.97	—	31	(25)	116	1.99	—	—	—
203	1.97	—	—	—	026	1.93	—	2	(6)
033	1.90	—	9	(7)	$\bar{2}16$	1.83	1.80	52	67
$0\bar{1}4$	3.84	3.83	5	7	216	1.83	—	—	—
014	3.31	3.30	35	18	$\bar{1}36$	1.81	—	—	—
$\bar{1}14$	3.19	3.20	64	91	$\bar{1}26$	1.81	—	—	—
$\bar{1}04$	3.19	—	—	—	$\bar{2}26$	1.79	—	—	—
$\bar{1}14$	3.02	3.02	20	14	206	1.79	—	—	—
104	3.02	—	—	—	$0\bar{1}7$	2.50	—	10	(7)
$\bar{1}24$	2.60	2.60	42	41	$\bar{1}17$	2.27	—	15	(22)
$\bar{1}14$	2.60	—	—	—	$\bar{1}07$	2.27	—	—	—
024	2.60	—	—	—	$\bar{1}17$	2.16	2.16	49	64
$\bar{1}24$	2.34	2.35	23	44	$\bar{1}07$	2.16	—	—	—
114	2.34	—	—	—	027	2.08	—	14	(9)
024	2.27	—	12	(9)	$\bar{1}27$	2.06	2.03	21	25
$\bar{2}14$	2.05	—	15	(11)	$\bar{1}17$	2.06	—	—	—
214	2.05	—	—	—	$\bar{1}27$	1.84	—	13	(11)
$\bar{2}24$	1.97	1.97	29	44	117	1.84	—	—	—
204	1.97	—	—	—	027	1.79	—	11	(11)
$\bar{1}34$	1.96	—	—	—	$\bar{1}37$	1.72	1.70	11	44
$\bar{1}24$	1.96	—	—	—	$\bar{1}27$	1.72	—	—	—
$\bar{2}24$	1.89	1.87	34	38	$\bar{2}17$	1.72	—	—	—
204	1.89	—	—	—	$\bar{2}17$	1.72	—	—	—
034	1.86	—	—	—	217	1.69	1.69	28	44
$\bar{1}34$	1.78	—	11	(11)	227	1.69	—	—	—
124	1.78	—	—	—	207	1.69	—	—	—
$\bar{2}34$	1.72	1.71	31	40					
214	1.72	—	—	—					
$0\bar{1}5$	3.29	—	19	(13)					
015	2.87	—	0	(5)					
$\bar{1}15$	2.84	2.87	17	16					
105	2.84	—	—	—					

An asterisk indicates that the unit cell tilt has caused overlapping between layer lines.

Where a structure factor is given in brackets, the reflection was not observed. The value given is an estimate of the value of the structure factor of a reflection which would be just visible at that location on the photograph

to the terephthaloyl residues satisfy the requirements of 2/1 symmetry.

This type of molecular arrangement, in which successive terephthaloyl residues are inclined to a crystal axis by opposite inclinations, giving a Z-shaped arrangement, is also seen in low-molecular-weight oligomers^{11,13,15}. If the oligomer contains *gauche* conformations^{11,13}, one molecule forms two arms of the Z, and a neighbouring molecule is packed so that adjacent terephthaloyl residues on the two molecules are stacked parallel, thereby completing the Z. If it contains *trans* conformations¹⁵, the terephthaloyl residues on a given molecule are parallel to each other, but successive molecules form the arms of the Z. These observations suggest

that this 'herring-bone' arrangement of the terephthaloyl residues is a preferred packing mode of this chemical system.

In 2GT and both phases of 4GT the molecular chains pack in a mode whereby the planes of the benzene rings are stacked one behind the other in the direction of the *a* (or shorter)^{1,9} axis. The α -phase of 5GT has also been shown to approximate to this mode of packing⁶. From Figures 5 and 7 it will be seen that 3GT also packs in this way. Because the normals to the planes of the two benzene rings of the molecular chain differ in direction by a rotation of nearly 180° about the chain axis (see values of θ_1 and θ_2 in Table 3), both rings may pack in this manner.

From Figure 8, the diagonal of the *a*-*b* face of the unit

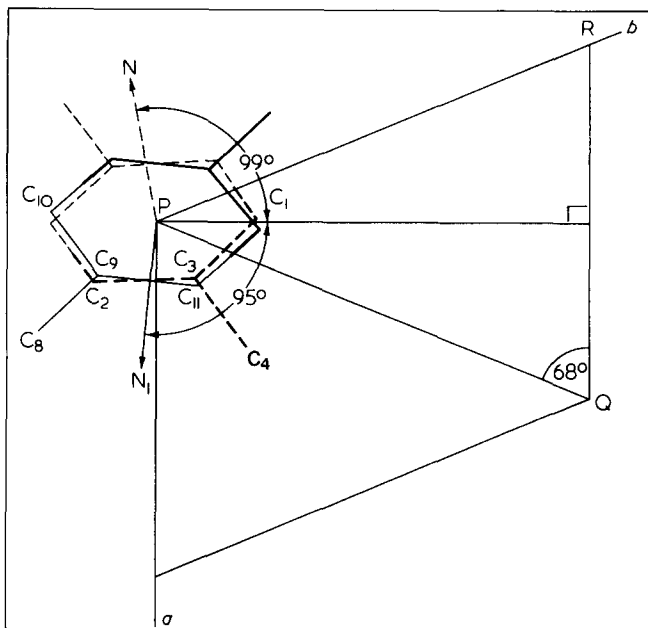


Figure 8 Projection down *c*-axis showing 'distorted hexagonal' packing. - - - - Atoms C₁-C₄; — Atoms C₈-C₁₁. N Normal to group of atoms C₁-C₄; N₁ Normal to group of atoms C₈-C₁₁

cell projected normal to the *c*-axis divides the face into two isosceles triangles with a base angle of 68°*. The packing of the chains thus approaches hexagonal. The orientation of the benzene ring planes is such that the projections of their normals on the plane normal to the *c*-axis are at 95° (clockwise) and 99° (anticlockwise) to the bisector of the vertex angle of the triangles. Thus the planes of both rings are very close to this bisector, being displaced from it by small rotations which are opposite in sense and almost equal in magnitude (Figure 8). The vertical height of the triangles is greater than it would be for hexagonal packing, i.e. the packing is distorted from hexagonal by an increase in chain separation in the direction of the planes of the benzene rings. The orientation of these planes is such that the one on any corner of the unit cell (e.g. P in Figure 5) passes almost midway between those on an opposite edge (e.g. Q and R in Figure 5).

Another feature of the chain packing which is common to 2, 4 and 5GT is that hydrogen atoms on adjacent benzene rings tend to interleave. From Figure 6 it will be seen that this is true for the two adjacent molecules along the *b*-axis. Because, (i) $\beta = 90^\circ$, (ii) the triangle PQR is isosceles, and (iii) the plane of the benzene ring at P almost bisects QR (Figure 8), the ring at P is in almost the same spatial relationship with that at Q as with that at R. Thus the hydrogen atoms on the benzene rings of the molecules at P and Q would also interleave.

* It follows from this that a monoclinic unit cell could have been chosen, *a* and *c*-axes would have been as in the present cell, but *b* would be along the perpendicular bisector of the isosceles triangle. *a* would be the unique axis, and there would be two chains in the cell with space group C2. The triclinic cell was chosen as it facilitated comparison with other members of the series.

The only short atomic separation between molecules (Table 4) occurs between O₁ of the molecule at R and C₇ of the one at P (Figures 5 and 6). The similar spatial relationships which have just been described between molecules P and R and between P and Q hold only for the benzene rings, and thus the short separation does not also occur between P and Q.

The terephthaloyl residues are more sharply inclined to the *c*-axis than in the other members of this series ($\psi \approx 52^\circ$ for both residues of 3GT, compared with 74° for α -4GT and 65° and 72° for the two residues of α -5GT). The lattice compliance in the *c*-direction of these materials is in the order 3GT > 5GT > 4GT (see Figures 4 and 5 of ref 7 and Figure 5 of ref 5). It would therefore appear that the inclination of the terephthaloyl residue to the fibre axis might be related to the lattice compliance in this direction.

From the preceding discussion it is clear that features of chain packing common to other members of this series are also shown by the present material, and that packing is dominated by the terephthaloyl parts of the molecule.

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