A comparison of published crystalline structures of poly(tetramethylene terephthalate)

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Recently, various crystalline structures have been published for poly(tetramethylene terephthalate) in both the relaxed and strained forms. The differences between the experimental procedures which have been used to determine these structures are critically discussed in the present paper. It is shown that the unit cell parameters obtained by the various investigators for the relaxed (or α) form do not differ significantly. Improvements can be made in some of the procedures used in structure determination – in particular it is recommended that weighting schemes be used to prevent the stronger reflections unduly biasing the refinement procedure – and these lead to small changes in some of the published structures of the α-form. By using a diffractometer to plot profiles of equatorial reflections it is shown that one of the published cells of the strained (or β) form cannot be correct, and this leads to an incorrect structure. Small changes in the other published structure are also necessary.

INTRODUCTION

Several independent studies of the crystalline structure of oriented fibres of poly(tetramethylene terephthalate) (4GT) have recently been published. Jakeways *et al.*[1] have reported that two crystalline forms exist and that the material transforms reversibly from one to the other when it is subjected to mechanical stress. They also give unit cell parameters for each form and details of the transition between them. Yokouchi *et al.*[2] and Hall and Pass[3] have independently published the crystalline structure of each form.

While the structures of the relaxed forms are in fairly close agreement, larger differences exist between those of the stressed form. The purpose of the present communication is to provide a critical discussion of the experimental and computational procedures which led to these different results, to assess whether or not the differences are significant and, where they are, to propose a preferred structure.

Other structural investigations have been performed by Mencik[4], Joly *et al.*[5] and Boye and Overton[6]. These will be included in the discussion where appropriate.

The nomenclature of Yokouchi *et al.*[2], whereby the unstressed and stressed forms are called the α- and β-forms respectively, will be used.

THE α-FORM

Unit cell parameters

Four independent unit cells, all triclinic, have been published and the parameters of these are given in *Table 1*. A further independent determination has been made by Desborough[7] and the results are also included in the Table.

Any unit cell is acceptable provided the discrepancies between observed and calculated locations of all the reflections are less than the experimental error in their observed positions. This error will obviously depend upon the definition and diffuseness of the reflections, and the experimental arrangements for determining their position. In our experiments they were recorded photographically using CuKα radiation with a cylindrical camera of 30 mm radius and we estimate that the centre of a typical reflection can be located on the photograph (using polar coordinates) to an accuracy of about 0.2 mm in r and 2° in θ.

For each of the published cells the locations on film of members of two groups of reflections, ($hk0$) and ($00l$), have been calculated for our experimental conditions and compared with their measured positions in our experiments. (These two groups of reflections were chosen because they are insensitive to the tilt of the c-axis to the fibre axis which is observed in this material.)

Five ($hk0$) reflections were considered: (010), ($\bar{1}10$), (100), ($\bar{1}20$) and ($\bar{1}30$). For each of these, the range of the calculated equatorial film coordinates for the various unit cells was less than 0.2 mm, and the difference from our observed film coordinate less than 0.15 mm. Four ($00l$) reflections were considered [(001), (002), (003), (004)] and the range of calculated r and θ is less than 0.15 mm and 2.5° respectively. None of them differs from our observed coordinates by more than 0.25 mm in r or 2° in θ.

Table 1 Unit cell parameters of the α-form

	Joly[5]	Mencik[4]	Yokouchi et al.[2]	Hall and Pass[4]	Desborough[5]
a (Å)	4.87	4.83	4.83	4.89	4.87
b (Å)	5.96	5.96	5.94	5.95	5.99
c (Å)	11.71	11.62	11.59	11.67	11.67
α°	100.1	99.9	99.7	98.9	99.8
β°	116.6	115.2	115.2	116.6	116.2
γ°	110.3	111.3	110.8	110.9	110.9
Volume (Å^3)	261.9	260.0	260.4	262.8	262.9

a and b, α and β have been interchanged in the published cells of Joly and Mencik, to bring them all to a common convention

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Table 2 Values assumed for bond angles and lengths

	Length (Å)		
Bond	Mencik[4]	Yokouchi *et al.*[2]	Hall and Pass[3]
C_0–C_1	1.40	1.395	1.38
C_1–C_3	1.40	1.395	1.38
C_2–C_3	1.40	1.395	1.39
H_1–C_1	1.08		1.07
H_2–C_2	1.08		1.07
C_4–C_3	1.49	1.49	1.48
O_2–C_4	1.23	1.23	1.21
O_1–C_4	1.26	1.36	1.34
C_5–O_1	1.41	1.43	1.44
H_3–C_5	1.09		1.03
C_6–C_5	1.53	1.54	1.50
C_7–C_6	1.53	1.54	1.50
	Angle (degrees)		
α_1	119	120	119
α_2	119	120	121
α_3	121		120
α_4			120
α_5	121	123	125
α_6	119	114	113
α_7	120	123	122
α_8	119	111	119
α_9	104	110	105
α_{10}	105	110	113

All of these discrepancies are within experimental error and so it can be concluded that the differences between the various unit cells are within the range which might be expected, and that all are equally valid descriptions of the observed diffraction pattern. The following unit cell parameters are the averages of all the published cells together with an error spread to account for the variation in individual values. They probably represent the best estimate currently available of the unit cell of this form of the material: $a = 4.86 \pm 0.03$ Å; $b = 5.96 \pm 0.03$ Å; $c = 11.65 \pm 0.06$ Å; $\alpha = 99.7 \pm 0.6°$; $\beta = 116.0 \pm 0.7°$; $\gamma = 110.8 \pm 0.5°$; volume $= 261.5 \pm 1.5$ Å^3.

The diffraction pattern of 4GT shows more, and better defined, reflections than many oriented crystalline polymers, and so the uncertainties in its unit cell parameters should be towards the lower limit of what may be achieved with these materials. However, experience has suggested that by taking diffractometer scans of reflections, their peaks may be located with greater accuracy than by visual estimation from photographs. (For example, see *Figure 2*: on this the peaks of reflections of the β form, which were broader than those of the α-form, may be located to within ±0.1° which is equivalent to ±0.05 mm in film coordinates.) Thus, the use of such techniques might increase the accuracy of cell determination beyond the limits given.

Chain conformation

Experimental procedures. Three conformations have been published[2–4] and all have been determined in a similar way. Values have been assumed for bond angles and lengths, and angles determined which define the conformation of the chain and its orientation within the unit cell. This is done by a refinement process improving agreement between observed and calculated structure factors. Within this similarity of approach there are the following differences of detail.

(1) While all three investigations sought the set of conformation angles which minimized the sum of the squares of the differences between observed and calculated structure factors ($\Sigma(F_0 - F_c)^2$), Mencik and Yokouchi *et al.* treated all observed reflections as having equal weight whilst Hall and Pass used a weighting scheme. Since $F_0 - F_c$ is likely to be larger for a strong reflection than for a weak one, unless a weighting scheme is employed the strong reflections will make the dominant contribution to $\Sigma(F_0 - F_c)^2$ and so the minimization procedure will treat them preferentially. Hall and Pass used the weighting scheme proposed by Cruickshank[8] which weights each structure factor so that the contribution to $\Sigma(F_0 - F_c)^2$ from groups of reflections in different parts of the intensity range is equalized.

(2) Hall and Pass force the carbonyl unit to remain planar whereas Yokouchi *et al.* do not. Mencik lists bond angles implying that this part of the molecule is planar, but calculations from his atomic coordinates show that this is not so.

(3) The choices of bond length and angle differ between the three invesitgations (see *Table 2* and *Figure 1*).

(4) The measurement of the integrated intensity of a reflection involves subjective judgment of the level of background diffuse radiation. Also, Hall and Pass use a technique whereby the entire region of the reflection is integrated[9] whereas the other investigators applied corrections which avoided measuring its spread along the arc. Thus differences exist in the sets of intensity data used by the various authors.

The conformations which have been obtained from these independent investigations are similar, but differ in detail, and have been listed in columns 1–4 of *Table 3*. For ease of comparison the values given by individual authors have been transformed to the conventions used by Hall and Pass. θ is the clockwise rotation (looking in the negative c-direction) of the molecule about the c-axis which would bring the normal to the benzene ring into the (010) plane. ψ is the angle between the normal and the c-axis, ϕ is the angle between the bond C_3–C_4 (*Figure 1*) and the c-axis. Other symbols are defined in *Figure 1*.

As well as the differences already mentioned, the different investigators each used different computer programs for the refinement. That this had an effect on their published models is shown by the following computation. The model of Yokouchi *et al.* was refined against their unweighted intensity data with the refinement program used by Hall and Pass (the Linked Atom Least-Squares Refinement System – LALS) but otherwise reproducing their conditions as exactly as possible. The model refined to the conformation given in column 5 of *Table 3* which more closely resembles the conformations published by Hall and Pass, and which has a lower R-factor than that given by Yokouchi *et al.*

The LALS program will be used in the computations described below, which assess the effects of the differences in

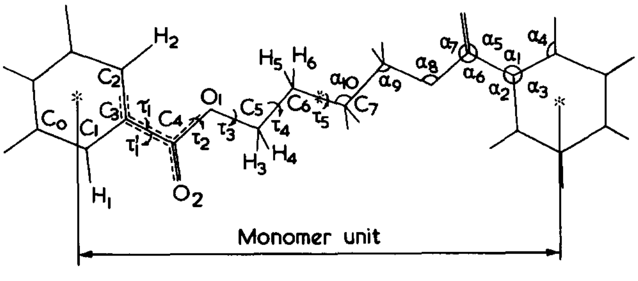

Figure 1 Monomer of 4GT.
* Centre of symmetry

Table 3 Conformation of the α-form

	1	2	3	4	5	6	7	8
τ_1 (degrees)	174.8	173.8	179.(4)	179.(7)	−179.7	178.4	179.2	±2.5
τ'_1 (degrees)	−3.5	1.8	−0.(6)	−0.(3)	3.8	−1.6	−0.8	
τ_2 (degrees)	177.5	178	−177.(9)	−177.(1)	−179.0	−176.2	−177.1	±1.7
τ_3 (degrees)	−90.6	−88	−94.(3)	−94.(3)	−95.2	−88.8	−92.5	±4.2
τ_4 (degrees)	−88.4	−68	−79.(3)	−77.(7)	−56.6	−71.7	−76.2	±6.8
θ (degrees)	7.3	3.4	4.(4)	4.(1)	0.7	3.5	4.0	±0.5
ϕ (degrees)	26.2	26.0	28.(4)	28.(4)	25.9	27.0	27.9	±0.7
ψ (degrees)	74.1	73.4	73.(7)	73.(6)	72.4	73.2	73.5	±0.4
R (%)	14.8	14.4	16.8	17.0	13.4	13.5		

(1) Mencik[4]. (2) Yokouchi *et al.*[2]. (3) and (4) Alternative models published by Hall and Pass[3]. In (3), C_6–C_7 = 1.50 Å, in (4) C_6–C_7 = 1.54 Å. (5) Model and intensity data of Yokouchi *et al.* refined by present authors. No weighting scheme. (6) Modified model of Yokouchi *et al.* refined against their data. Weighting scheme used. (7) 'Best' estimate of model parameters. (8) Probable errors

procedure, and so the effects of the programme itself must be borne in mind when making comparisons.

Effect of weighting structure factors. Refinements differing only in whether or not structure factors were weighted, produced structures in which no parameter differed by more than 5°. The *R*-factors (%) obtained without weighting were between 0.5 and 1.0 smaller than those obtained when a weighting scheme was used, which would be expected, since under such conditions the discrepancies in the stronger reflections would be minimized preferentially and these make the dominant contribution to *R*. However, it is advisable to use a weighting scheme because this enables weaker reflections to contribute to the refinement procedure and in the subsequent investigations reported in this paper weighted structure factors will be used.

Effect of planarity of carbonyl unit. The differences between the parameters of refined models in which the carbonyl unit was either forced to remain planar, or allowed to become non-planar, were less than 2°. The extra degree of freedom in the molecule only produced a reduction in the %*R*-factor of about 0.1.

The most recently published crystallographic data on low molecular-weight analogues of glycol–terephthalate polymers[10–12] all reveal a maximum deviation in the planarity of the carbonyl unit of less than 0.1° and so it is unjustifiable to allow them to become non-planar. Hence it will be forced to remain planar in the subsequent investigations reported here.

Effect of choice of bond angle and length. Yokouchi *et al.* differ significantly from both other investigations in their choice of α_8 and α_9 (see *Table 2*), and their chosen values lie outside the range of those determined in single crystal studies. (See Table 1 of reference 3.) Mencik differs significantly from the other investigators and from single crystal values in the choice of the length of C_4O_1 and the magnitude of α_6 and α_{10}. The smallest changes that could be made in these parameters to bring them within the range of single-crystal values were to alter Yokouchi *et al.*'s values of α_8 and α_9 to 119° and 105° respectively, and Mencik's values of C_4O_1, α_6 and α_{10} to 1.33 Å, 114°, and 110° respectively.

The only other choices which differ appreciably amongst the three investigations are those of Hall and Pass for the methylene bond lengths, and the reasons for this choice have been argued[3].

When the above alterations have been made, the remaining differences represent a genuine range of uncertainty in the choice of values for bond length and angle, and the effects of these were investigated by refining models incorporating each of the sets of values against the intensity data of Hall and Pass. The resulting variations in conformation parameters, which were less than 1° in θ, ϕ, ψ, 2° in τ_1, τ_2, τ_3 and 8° in τ_4 represent the uncertainty in the final model due to this effect.

Bond angles and lengths revised as above were used in the remainder of this investigation.

Effect of errors in intensity data. To assess the effects of errors in intensity data the models obtained in the preceding section incorporating the choices of bond angle and length of Yokouchi *et al.* and of Hall and Pass were refined against the intensity data of each group of investigators. (The data of Mencik was not available, and so his model was excluded from the comparison at this stage.) The differences in a given model, when refined against each set of data, were less than 1° in θ, ϕ and ψ, and less than 4°, 2°, 8° and 6° in τ_1, τ_2, τ_3 and τ_4 respectively. The parameters defining the model which incorporated the bond lengths and angles chosen by Yokouchi *et al.* (modified as described above), and which was refined against their data are listed in column 6 of *Table 3.*

Choice of 'best' model. The models listed in columns 3, 4 and 6 of *Table 3* were obtained following the procedures recommended in this paper; the differences between them result from genuine uncertainties in bond angles and lengths and in intensity data. Thus the best available estimate of the parameters defining the structure may be obtained by averaging the values in these columns. These averages are listed in column 7. The uncertainties in the average parameters are the sums of the uncertainties due to choice of bond length and angle, and due to errors in intensity data estimated as described above. These are listed in column 8.

Conclusions

(1) In structure refinement of polymers, intensity data should be weighted so that stronger reflections do not unduly bias the refinement procedure.

(2) In all low molecular weight compounds of similar chemical constitution where structure has been determined, the carbonyl unit is closely planar. It should therefore be constrained to remain planar in this polymer and related compounds. However, provided the other recommendations of this paper are followed non-planarity is small when this constraint is removed.

(3) Certain choices of bond length and angle made by Yokouchi *et al.* and by Mencik lie outside the permissible

Table 4 Unit cell parameters of the β-form

	Yokouchi *et al.*[2]	Hall and Pass[3]	Desborough[7]
a (Å)	4.95	4.69	4.73
b (Å)	5.67	5.80	5.83
c (Å)	12.95	13.00	12.90
α°	101.7	101.9	101.9
β°	121.8	120.5	119.4
γ°	99.9	105.0	105.1
Volume (Å^3)	285.0	268.9	274.6

range indicated by structural determinations on low molecular weight compounds.

(4) Differences in the refined model parameters which arise because of permissible variations in choice of bond lengths and angles, and because of errors inherent in intensity measurement have been estimated and are listed in column 8 of *Table 3.* The largest is 7°, and they are generally about 2°.

(5) Because of the points made above the structures of Yokouchi *et al.* and Mencik are likely to contain small errors. When the model of Yokouchi *et al.* has been modified as in (3) above and refined following the procedure laid down in (1) and (2) above a structure is obtained which differs from that of Hall and Pass by amounts less than the permissible variations already given. Thus the parameters of these structures are averaged to estimate a 'best' model for the α-form given in column 7 of *Table 3.*

THE β-FORM

Unit cell parameters

Three independent unit cells, all triclinic, have been published, and the parameters of these are given in *Table 4.* Because there are fewer reflections than in the α-form, and they are not so sharply defined, these cells would not be expected to be in as close agreement as those given in *Table 1.* However, the parameters given by Yokouchi *et al.*, particularly the values of a, b and γ, differ from those of other investigators by amounts which we will show to be significant.

The differences between the locations of reflections calculated from the various unit cells will be particularly apparent on the equator of the diffraction pattern, and so in *Figure 2* the calculated locations of the (010), $(\bar{1}10)$ and (100) reflections from each unit cell are compared with an equatorial diffractometer scan of a 4GT fibre extended by 10%. This reveals the extent and location of the diffraction peaks more precisely than is possible from photographs and shows clearly that the locations of the (100) and $(\bar{1}10)$ reflections calculated from the cell of Yokouchi *et al.* lie outside the bounds of the observed peaks. This cell is, therefore, unsatisfactory.

This investigation has differed from the other two in that it treats the $(\bar{1}10)$ and (100) reflections as an unresolvable overlapping pair. From *Figure 2*, there is only a slight shoulder on the low 2θ side of the (100) peak which can be attributed to the $(\bar{1}10)$ reflection (we use the indices given by the cells of Hall and Pass and of Desborough; *Figure 2* shows that Yokouchi *et al.*'s cell leads to different indices), but diffraction photographs taken at different strains and exposures show clearly that as the strain increases the $(\bar{1}10)$ reflection moves progressively towards the (100) and at 10% strain is still identifiable from the assymetry of the diffraction spot. Hence, although it cannot be located accurately, it clearly has a lower 2θ value than the (100) reflection and should be treated as such in the construction of trial lattices.

This apparently continuous movement of reflections in the equatorial direction with increasing strain is in contrast to the behaviour along the meridian where at intermediate strains two distinct reflections can be seen in positions corresponding to the α- and β-forms. For the equatorial reflections considered, the two positions would not be resolved, and the apparently continuous movement could arise because one component of the two unresolved peaks grows while the other decays. The profile of the peak does not, however, favour this interpretation. It thus appears that whereas the chain conformation changes discontinuously with strain their lateral repacking is a more gradual process.

These lateral changes continue at strains greater than 10%, at which the transformation of chain conformations is complete. Since Yokouchi *et al.* determined their cell from data obtained at a fibre strain of 12% whereas the diffractometer scan in *Figure 2* was recorded at a strain of 10%, this might account for the discrepancy revealed above. Experiments at different strains have shown that as strain increases in this range the (010) reflection moves towards lower 2θ and the $(\bar{1}10)$ moves towards the (100). This would improve agreement between the observed and calculated positions of the (010) peak, and increase the justification for treating (100) and $(\bar{1}10)$ as an overlapping pair. However, the (100) peak moves towards higher 2θ, and so disagreement between the observed and calculated location of this reflection, which is already unacceptably large, would be worsened. Thus their different cell parameters cannot be explained in this way.

Although the above discussion has concentrated on the equatorial reflections, there are also a few others for which the locations calculated from the cell of Yokouchi *et al.* lie outside the bounds of reflections observed by us.

On the basis of this evidence it is concluded that the unit cell published by Yokouchi *et al.* does not provide a satisfactory description of the experimentally observed diffraction pattern. The cells of Hall and Pass and of Desborough differ by less than the range of uncertainty established for the α-form, and must be considered equally good. *Figure 2* suggests a preference for that of Hall and Pass, but the discrepancies between the locations of the observed reflections

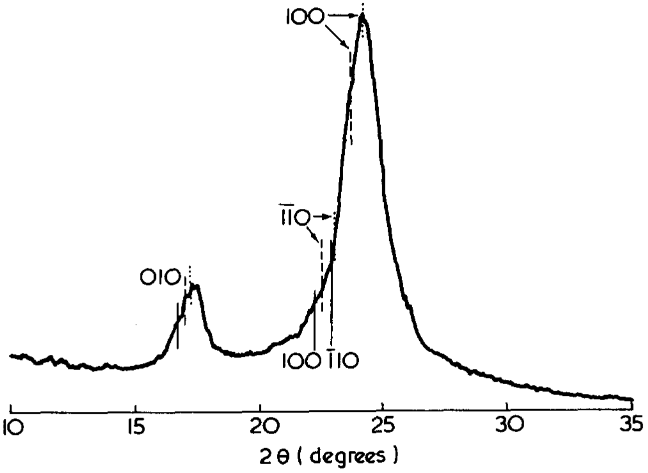

Figure 2 Comparison of calculated locations of equatorial reflections against diffractometer scan: ———, Yokouchi *et al.*; – – –, Desborough; . . . . , Hall and Pass

Table 5 Conformation of the β-form

	1	2	3	4	5	6	7
τ_1°	179.3	172.9	174.1	172.5	170.2	172.3	±2.7
τ_1'°	−2.7	−7.1	−5.9	−7.5	−9.8	−7.7	
τ_2°	179	−178.6	−177.2	−179.0	−176.8	−177.7	±1.7
τ_3°	−179	−159.1	−156.7	−157.4	−151.5	−155.2	±10.6
τ_4°	113	162.2	160.2	157.6	146.3	154.7	±12.1
θ°	−6.2	19.5	14.8	15.1	11.9	13.9	±2.3
ϕ°	25.7	26.4	26.8	27.2	25.7	26.6	±1.5
ψ°	83.7	86.9	85.9	86.1	85.1	85.7	±0.8
R (%)	19.1	22.3	17.8	17.8	19.9		

(1) Yokouchi *et al.*[2]. (2) Hall and Pass[3]. (3) and (4) Model and modified intensity data of Hall and Pass. In (3) C_6–C_7 = 1.50 Å, in (4) C_6–C_7 = 1.54 Å. (5) Model and intensity data of Yokouchi *et al.* re-indexed to unit cell of Hall and Pass. (6) 'Best' estimate of model parameters. (7) Probable errors.

on this Figure and those calculated from Desborough's cell are acceptable and a choice between them cannot be made without more extensive diffractometer data.

Chain conformation

Experimental procedures. Two independent structures have been published[2,3] and the differences in experimental procedure which have already been discussed for the α-form also apply to these determinations. However there are three further differences which need consideration.

(1) Unobserved reflections (i.e. reciprocal lattice points where the observed intensity was not significantly above background) were omitted in the refinements of Yokouchi *et al*, whereas Hall and Pass adopted a procedure which enabled them to be included[3].

(2) Yokouchi *et al.* treat the (100) and ($\bar{1}$10) reflections as an unresolved overlapping pair, whereas Hall and Pass assigned individual intensities to them.

(3) Unit cell parameters differ sufficiently to cause some of the observed reflections to be indexed differently in the two investigations.

The structures which have been obtained are listed in columns 1 and 2 of *Table 5* and these differ significantly, both in conformation and in the orientation of the molecule within the unit cell.

Treatment of unobserved reflections. The number of observed reflections was small, and if unobserved reflections are omitted from the refinement, no use is made of the information that their calculated intensities should be less than that of the background in their vicinity. Hall and Pass adopted a procedure which enabled this information to be included[3]. It is important to make use of all the information which is available and so this procedure has been followed here.

(100) and ($\bar{1}$10) reflections. Reconsideration of diffraction photographs has led to the conclusion that the degree of overlap between the ($\bar{1}$10) and (100) reflections is such that it is not possible to apportion the intensity between them, although the innermost reflection is certainly very much the weaker member of the pair. The model of Hall and Pass has, therefore, been refined treating them as an overlapping pair and the results are given in columns 3 and 4 of *Table 5*. (They set the bond C_6–C_7 equal to 1.50 Å for the β-form, because in the α-form this value had given a slightly lower *R*-factor than 1.54 Å. As a result of the considerations described earlier it has been decided that this evidence is not conclusive, and that both values should be considered as possibilities for the β-form.)

The *R*-factors are appreciably lower than when both reflections were assigned individual intensities, and this is still true if they are omitted from the *R*-factor calculations. Therefore it seems that in the original refinement the intensities of these reflections were apportioned wrongly, and this prevented the model adjusting itself into the best agreement with the other reflections. The calculated intensity of the innermost reflection of the pair ($\bar{1}$10) was about 1/6th of that of the outer, which is in accord with experimental observation.

The main change from the original structure is that the molecule has rotated about 5° around the *c*-axis towards the orientation reported by Yokouchi *et al.*; its conformation is only slightly altered.

Differences in unit cell. Because the unit cell of Yokouchi *et al.* is unsatisfactory, their data have been re-indexed, using their published *d*-spacings, to accord with the unit cell of Hall and Pass. Their published model was then refined against these revised data.

The orientation of the molecule within the unit cell was only slightly altered, but the conformation was closer to that published by Hall and Pass than the original. However, the calculated intensity of the ($\bar{1}$10) reflection was greater than that of the (100) which was contrary to experimental observation. (It should be noted that the unit cell of Yokouchi *et al.* indexes the (100) reflection as the innermost member of the pair. Thus if they found this distribution of intensity, they would regard it as being in accord with experimental observation.) This model was, therefore, rejected.

All refinements using the published model of Yokouchi *et al.* as starting point led to structures giving an unacceptable distribution of intensity between this pair of reflections, and so an initial model was chosen which had their values of bond lengths and angles, but with other structural parameters taken from column 4 of *Table 5*. This refined to the parameters given in column 5; the calculated intensity of the ($\bar{1}$10) reflection was about 1/5th of that of the (100) which was considered satisfactory.

It will be seen that this structure is now similar to those derived from the data of Hall and Pass. Thus the incorrect unit cell chosen by Yokouchi *et al.* has led them to publish an incorrect structure. Estimates of the correct structural parameters are given in columns 3–5 of *Table 5*, and except for a small change in the orientation of the molecule within the unit cell these are close to those published by Hall and Pass.

Revised structure. Estimates have been made of the uncertainty in the structural parameters caused by the different choices of bond length and angle, and by errors in intensity measurement. This was done by performing two additional refinements on each of the structures given in columns 3, 4 and 5 of *Table 5*. In one the choices of bond angle and length were changed to those used by the other investigating team; in the other the intensity data were changed. The spread of values caused by each of these changes was added to give the uncertainties listed in column 7 of *Table 5*. These are, in general, about double the uncertainties in the parameters of the α-form, and this probably arises from the smaller number and more diffuse nature of the observed reflections.

The uncertainty in θ is particularly large relative to the α-form, and this arises because it is not possible to assign accurate intensities to the $(\bar{1}10)$ and (100) reflections. Refinements resulting in different ratios of the calculated intensities of these reflections differed particularly in the value of θ.

The parameters in columns 3, 4 and 5 of *Table 5* were averaged to give the 'best model' in column 6.

The diagrams and discussion in reference 3 are based on the structural parameters given in column 2 of *Table 5*. Of these only θ is changed significantly. Thus the only diagram in reference 3 to be altered appreciably will be *Figure 6b*, in which the terephthaloyl residues must be turned through an angle of about 6° in a clockwise direction. This rotation will increase the intermolecular distance between H_1 and C_2 (these are in close contact) by about 0.1 Å. That between O_2 and H_5 is shortened so that each of these separations are now shorter than the sum of the Van der Waals radii of the atoms concerned by similar amounts.

Conclusions

(1) The locations of some diffraction spots calculated from the unit cell of the β-form determined by Yokouchi *et al.* lie outside the possible bounds of experimental error on diffraction photographs taken by us.

(2) The discrepancies cannot be explained by the fact that their experiments were performed at different strains from those of Hall and Pass.

(3) Using Yokouchi *et al.*'s published values for lattice plane spacings of the β-form, their observed reflections may be satisfactorily indexed on the unit cell of Hall and Pass.

(4) Hall and Pass were unjustified in resolving the intensities of the $(\bar{1}10)$ and (100) reflections in the diffraction pattern of the β-form, although the former is certainly very much the weaker of the pair.

(5) If the structures of the β-form are refined after making these corrections, the resulting models only differ significantly from that published by Hall and Pass in that the plane of the molecule is rotated by about 5° around the *c*-axis. Thus the unit cell and structure published by Yokouchi *et al.* are incorrect. There is independent confirmation of this conclusion; infra-red and Raman spectroscopy are strongly indicative of an all-*trans* methylene sequence in the β-form[13,14], showing no indication of the near-eclipsed conformation proposed by Yokouchi *et al.*

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