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THE STRUCTURE OF POLY-2,5-BENZOXAZOLE (ABPBO) AND POLY-2,6-BENZOTHIAZOLE (ABPBT) FIBERS BY X-RAY DIFFRACTION

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The determination of the crystalline structure of oriented fibers of poly-2,5-benzoxazole (ABPBO) and poly-2,6-benzothiazole (ABPBT) is described. Both unit cells are metrically orthorhombic, with the parameters: $\underline{a}$=6.06(17), $\underline{b}$=3.384(13), $\underline{c}$ (fiber axis)=11.575(6) A for ABPBO, and $\underline{a}$=6.044(6), $\underline{b}$-3.417(7), $\underline{c}$ (fiber axis)=12.194(18)A for ABPBT. The fiber repeat consists in each structure of two fused ring groups arranged in a planar, zigzag conformation. The conformational torsion angle and orientation of chains within the unit cells are derived from a linked-atom least squares refinement technique. Polymer chains pack laterally through van der Waals interations. A plausible disorder model which involves defects in chain direction is presented. Refinement of a static disorder model for ABPBO in which fifty percent of the chains have their chain directions reversed leads to a lower R residual and sum of constraints. The determination of the crystal structures of these two polymers is important for understanding of the processing, properties and morphology of high strength, high modulus fibers of these materials. These

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18. Polybenzothiazole ABPBT Polymer Crystal Structure

19. results provide a structural basis for further improvements in high performance organic polymeric materials.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division and the University of Dayton Chemistry Department under Grant AFOSR-84-0364 from the Air Force Office of Scientific Research. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Work Unit Directive 2303Q307, "Structural Resins." Dr. Thaddeus E. Helminiak served as the AFWAL/ML Work Unit Scientist. Co-authors were Lt Joseph O'Brien and W. W. Adams, Materials Laboratory (AFWAL/MLBP); and Dr. Albert V. Fratini and Elisa M. Cross, University of Dayton Department of Chemistry.

This report covers research conducted from April 1984 to December 1984.

INTRODUCTION

Success in achieving exceptional mechanical properties and high temperature stability in fibers produced from extended chain polymers such as poly(p-phenylene terephthalamide) (PPTA) has encouraged investigations of other stiff-chain and rigid rod polymers. The Materials Laboratory, through its Air Force Ordered Polymer Research Program [1], has sought to take advantage of the thermal and oxidative stability of the aromatic heterocyclic class of polymers, and to explore their engineering properties.

Recently, this effort has focused on the stiff-chain ABPBX (X=S, O, N) molecular structures. Two of the polymers synthesized as part of this program are illustrated in figures 1 and 2: poly-2,5-benzoxazole (ABPBO) and poly-2,6-benzothiazole (ABPBT).* They show improved thermal stability over the polyamides and poly(p-phenylene benzobisthiazoles), and do not have the moisture sensitivity of the benzimidazole structures. Because of their semiflexible nature, both polymers form lyotropic, nematic phases in which the chains are presumably well-aligned but are not in axial registry [2]. Spinning fibers from a liquid crystalline phase has distinct advantages. Besides enhancing the flow properties of the system, the polymer chains already have much of the ordering required in the crystalline fibrous state to exhibit the desired superior mechanical properties. This paper reports the crystalline structures of these two polymers.

*Figures and tables are located at end of report.

EXPERIMENTAL METHODS

MATERIALS

Oriented fibers of ABPBO and ABPBT were spun at elevated temperatures from liquid crystalline dopes containing polyphosphoric acid. Fibers were spun by W-F. Hwang of the University of Dayton Research Institute and M. Hunsaker of the AFWAL Materials Laboratory. Dopes were supplied by J. F. Wolfe of SRI International [3]. Monofilaments were heat treated under constant strain in a nitrogen atmosphere.

RECORDING OF X-RAY DIFFRACTION DATA

Diffraction intensities were collected using a conventional Weissenberg camera employing Ni-filtered CuK_{α} radiation. The entire range of intensities was recorded by the multiple-film method. Fiber rotation patterns are shown in figure 3. The fiber axis is perpendicular to the x-ray beam, and coaxial with the film.

Diffraction patterns were also recorded on a Buerger precession camera and are shown in figure 4. These photographs simplified the indexing of diffraction spots, in addition to providing accurate d-spacings for use in the determination of unit cell parameters. Integrated intensities were also measured from precession patterns. None of the intensities, however, were used in the structure refinement due to the uncertainty in the appropriate Lorentz factor of the meridional reflections [4].

DETERMINATION OF UNIT CELL PARAMETERS

The diffraction patterns for ABPBO and ABPBT were indexed in terms of orthogonal (metrically orthorhombic) unit cells. The unit cell parameters (see Table 1) were refined by minimizing the sum of the squares of the differences between observed and calculated d-spacings. Measured fiber densities were obtained by the flotation method.

DETERMINATION OF INTEGRATED INTENSITY OF DIFFRACTION MAXIMA

Fiber rotation patterns were scanned with an Optronics Photoscan P1000 microdensitometer. The PHOTO computer program [5] displayed the digitized pattern as iso-optical density contours on the screen of a graphics terminal. The "Peak Volume" option gave the volume of each spot, after correcting for background intensity. Because some spots were too weak to appear as a contour on the screen, their peak volumes were visually estimated. A calibration plot showed the optical density (OD) to be linear with exposure time to OD=1.4. However, to ensure that the measurements corresponded to a linear portion of the plot, only peak volume measurements on peaks with OD 1.0 were used. Because of the observed linearity, the peak volume was taken to be directly proportional to the integrated intensity of the diffraction spot. The intensity was apportioned between partly overlapping reflections. Reflections which could not be resolved were treated as an overlapping group. Finally, Lorentz and polarization corrections were applied directly to the peak volume data resulting in observed structure factors, F_o.

DETERMINATION OF CHAIN CONFORMATION AND REFINEMENT

Planar zigzag chain structures in which two fused ring groups comprise the crystallographic (fiber) repeat were chosen for the initial models on the basis of the observed fiber periods. In support of this model were the systematic absences 00ℓ, $\ell = 2n+1$, indicative of a 2_1 screw axis along the chain axis. Values for bond lengths and angles (table 2) were assumed to be the same as those found in comparable model compounds (6,7,8). Thus, only the one conformational torsion angle (τ) between plans of the ring groups plus the three orientation parameters of the molecules within the unit cell were refined for each structure.

The Linked-Atom Least Squares (LALS) technique for the refinement of polymer structures has been described by Smith and Arnott [9]. The function minimized was $\theta = \sum_i w_i \Delta F_i^2 + \sum k_j \Delta D_j^2 + \sum \lambda_k G_k$, where ΔF_i is the difference between observed and calculated values of the i^{th} structure factor and w_i (taken to be unity) is the assigned weight. ΔD_j is the deviation of the calculated interatomic distance from the desired minimum value, and k_j is a weight. The third term imposes the coincidence constraints between pairs of atoms related by translational symmetry along the c-axis in order to ensure chain continuity. A scale factor, K, was also included as a variable in the refinement, and a constant overall isotropic temperature factor B of 6.0A^2 was used. Refinement was terminated when the crystallographic reliability index, $R = \Sigma|\Delta F| / \Sigma F_o$, did not change on successive cycles.

RESULTS

Parameters defining the chain conformation and orientation within the unit cell together with the R-factor (calculated with observed reflections only) are given in table 3. The orientation angles X, Y and Z refer to the rotation angle about the x, y and z axes, respectively, required to bring the chain into its correct orientation. Positive rotation is clockwise when viewed from positive infinity along each axis. The initial placement of the chain in the unit cell is accomplished by placing the root atom (C14 for ABPBO and C13 for ABPBT) on the c-axis with the bond to its precursor (C7 in each structure) pointing along the positive x-axis and its precursor (N1 for each structure) in turn lying in the (x,-y) plane.

The molecular conformation and packing within the unit cell are illustrated in figures 5 through 10 with space-filling drawings. The van der Waals radii are scaled down from their normal values in order to allow easier visualization of the structure. Fractional atomic coordinates are presented in tables 4 and 5. Calculated and observed d-spacings and structure factors are listed in tables 6 and 7.

DISCUSSION

The presence of a number of hkl Bragg maxima in the x-ray patterns of figures 3 and 4 is taken as evidence for three-dimensional order in fibers of ABPBO and ABPBT. It thus becomes possible for each polymer to solve the structure by conventional x-ray methods.

As is shown in table 1, the lattice dimensions of the two unit cells are very similar, except for the fiber identity period. Although the unit cells are observed to be metrically orthorhombic, the polymer chains lack the requisite Laue symmetry for the assignment of a primitive, orthorhombic space group. An orthogonal, monoclinic space group possessing a 2_1 screw axis would probably be a reasonable choice. The lack of knowledge of a unique space group did not thwart the attempt at a structure analysis in a primitive unit cell.

The packing arrangements of the planar zigzag chains are also quite similar (figures 5 thru 10). A layered or sheet structure of planar molecules is not strictly observed since the molecular planes are tilted out of the (100) face by 5.3° for ABPBO and 4.0° for ABPBT. The perpendicular separation between plans is roughly the same as the b-axis length, 3.4Å. Inspection of Table 8 shows that overly short intra-and interchain atomic distances are not found. The shortest interchain distance for ABPBO is 2.02Å for H2...H15, and the shortest value in ABPBT is 2.21Å for H12...H14.

CNDO/2 molecular orbital calculations recently reported by Welsh and Mark [10] corroborate the observed coplanar arrangement of atoms in ABPBO.

Conformational energy minima are observed at τ =0° and 180°, the τ =0° conformation being slightly preferred by about 0.1-0.20 kcal/mole. The barrier to free rotation about the single rotatable bond was found to be about 1.6 kcal/mole, so that rotation is facile at heat treatment temperatures of over 300C. Thus the observed enhancement in molecular ordering following heat treatment under tension presumably is associated with this type of motion.

The structures reported in this report are somewhat idealized since the assumed primitive lattice requires the chains to be in perfect registry, as would be the case in a highly crystalline material. The diffuseness of diffraction maxima, especially along the meridian, and the streaking visible along the hk1 and hk2 layer lines are clear indications of some axial translational disorder. A similar situation, but to a much greater extent, has been observed for the chemically related, rigid rod poly(p-phenylene benzobisthiazoles (PBT) (11,12,13). The molecular origin of this disorder can be understood, on one hand, by allowing the axial slippage of well-aligned chains past each other. For molecules stacked directly above one another (i.e., along the direction perpendicular to the molecular planes) the predictions of the minimum-energy arrangement are that the chains are out of register by 1.5Å for PBT and by as large as 3.0Å in the case of poly(p-phenylene benzobisoxazole) (PBO) [14].

Note that the polymer chain has directionality; that is, it has a distinct up and down sense and is not centrosymmetric. Thus an energetically feasible packing arrangement might be possible by mixing chains with opposite senses. Figure 11 illustrates a packing arrangement which includes a single defect chain. A 180° rotation of the defect chain about the chain axis does not introduce still another disorder mode since translation of the defect chain by half the fiber repeat returns it to the position shown in figure 11. If chain reversal were to occur on a large scale, then one would expect that the packing order of the fiber would be decreased. However, several polymers with irregular sequences such as atactic poly(vinyl alcohol) and poly(methylene) polysulfides are highly crystalline [15], so caution must be exercised in concluding that chain directionality is regular in ABPBO and ABPBT.

To ascertain the effect of chain reversal on the structure of ABPBO, LALS refinement was carried out on a primitive unit cell in which fifty percent of the chains have their senses reversed. Chains were positioned in the lattice such that adjacent chains ran in opposite directions. Reversed chains were translated by one-half the $\underline{c}$-axis length to preserve the zigzag packing arrangement. Several cycles of refinement yielded a three percent lower R-index with a slight reduction in the sum of constraints. The conformational torsional angle remained about 0°. A lower value for the residual is to be expected, since refinement of this disorder model introduces additional parameters corresponding to the angular rotation about the $\underline{c}$-axis of each of four chains. Nevertheless, this type of disorder is considered reasonable based on the fact that there are no new short intermolecular contacts.

The structures presented here should aid in the understanding of the relationship between molecular order, morphology, and properties of these polymers. The high degree or order, which is comparable to that observed for PPTA, is undoubtedly associated with the high tensile modulus of these fibers. We plan further work to examine chain directional defects in non-primitive unit cells.

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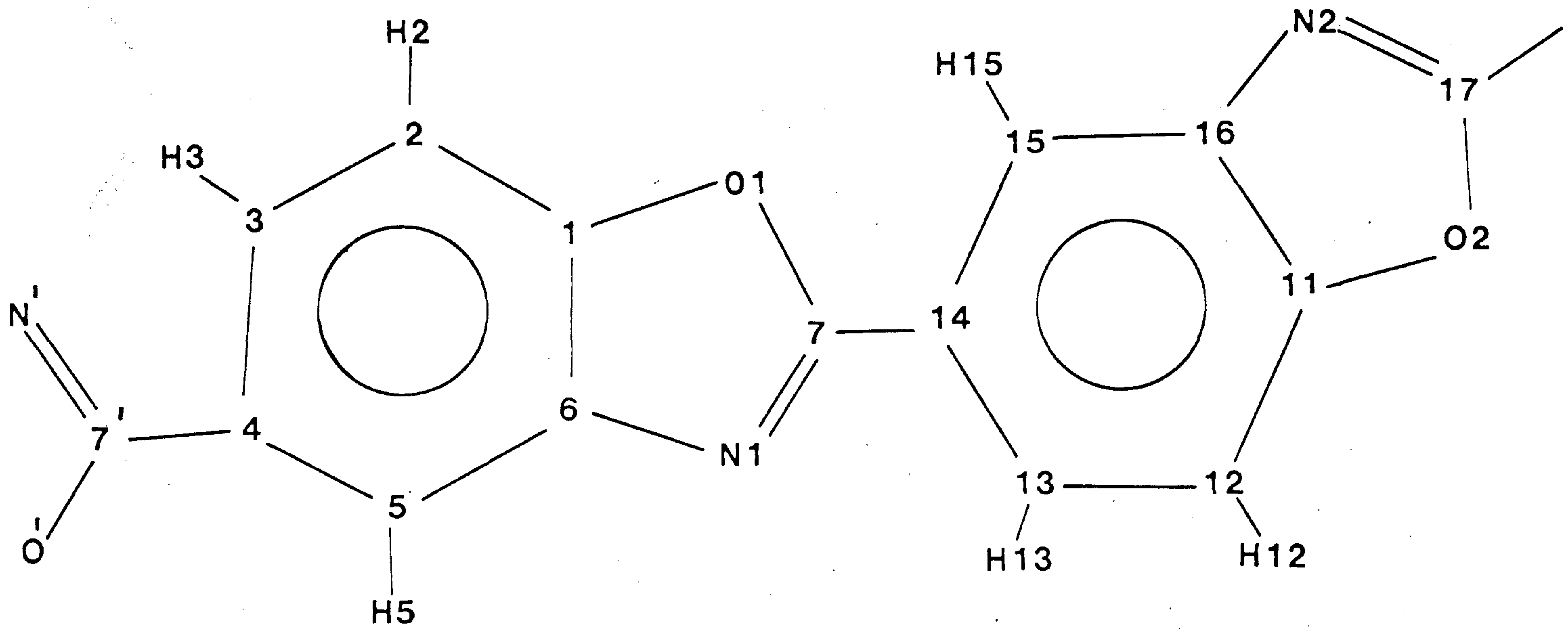

Figure 1. The chemical structure of poly-2,5-benzoxazole (ABPBO), showing the atom numbering scheme. The three primed atoms N^1, 7^1 and O^1 were constrained to coincide with atoms N2, 17, and O2 establishing chain continuity in the linked-atom least squares refinement.

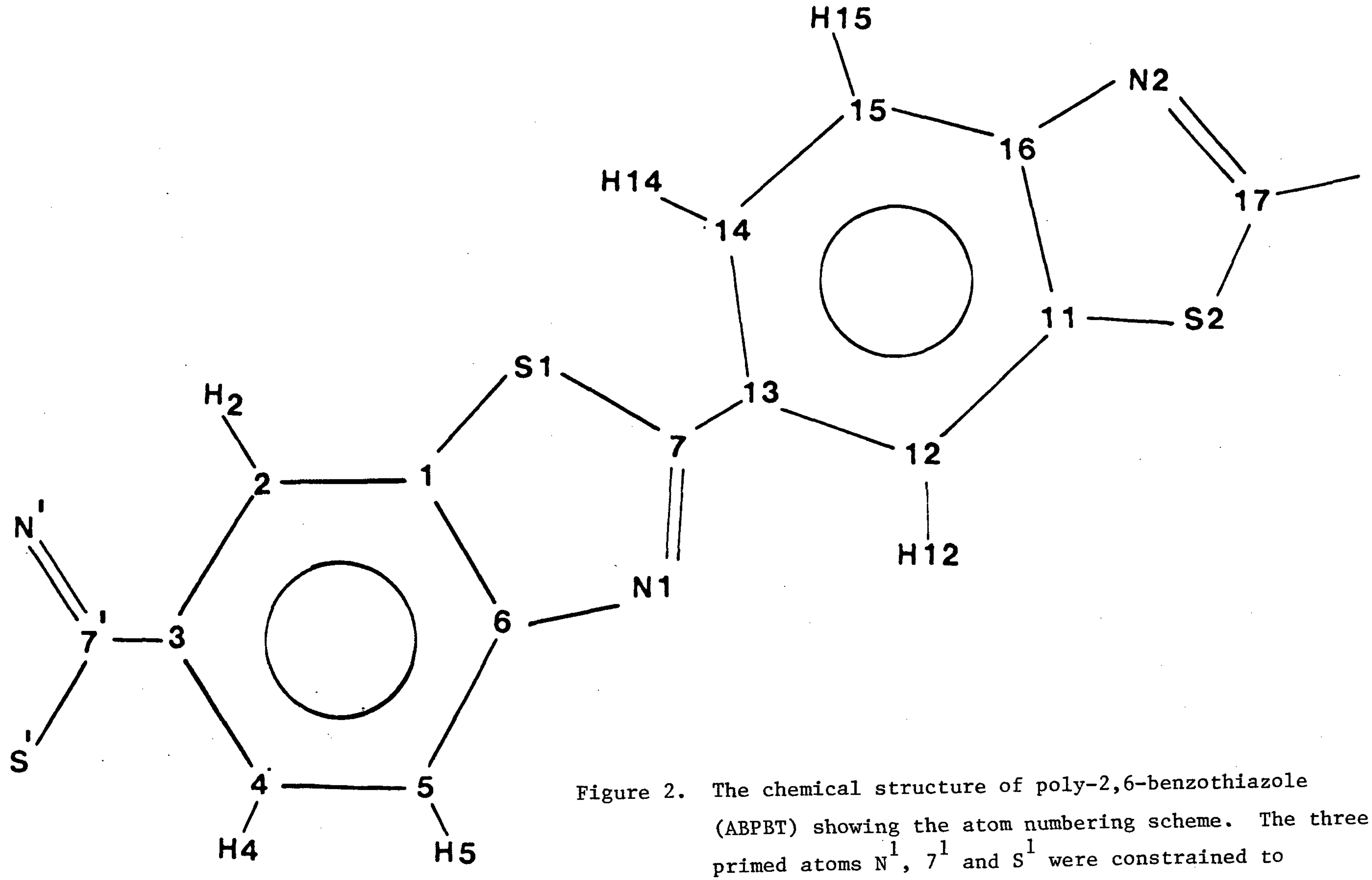

Figure 2. The chemical structure of poly-2,6-benzothiazole (ABPBT) showing the atom numbering scheme. The three primed atoms N^1, 7^1 and S^1 were constrained to coincide with atoms N2, 17 and S2 establishing chain continuity in the linked-atom least squares refinement.

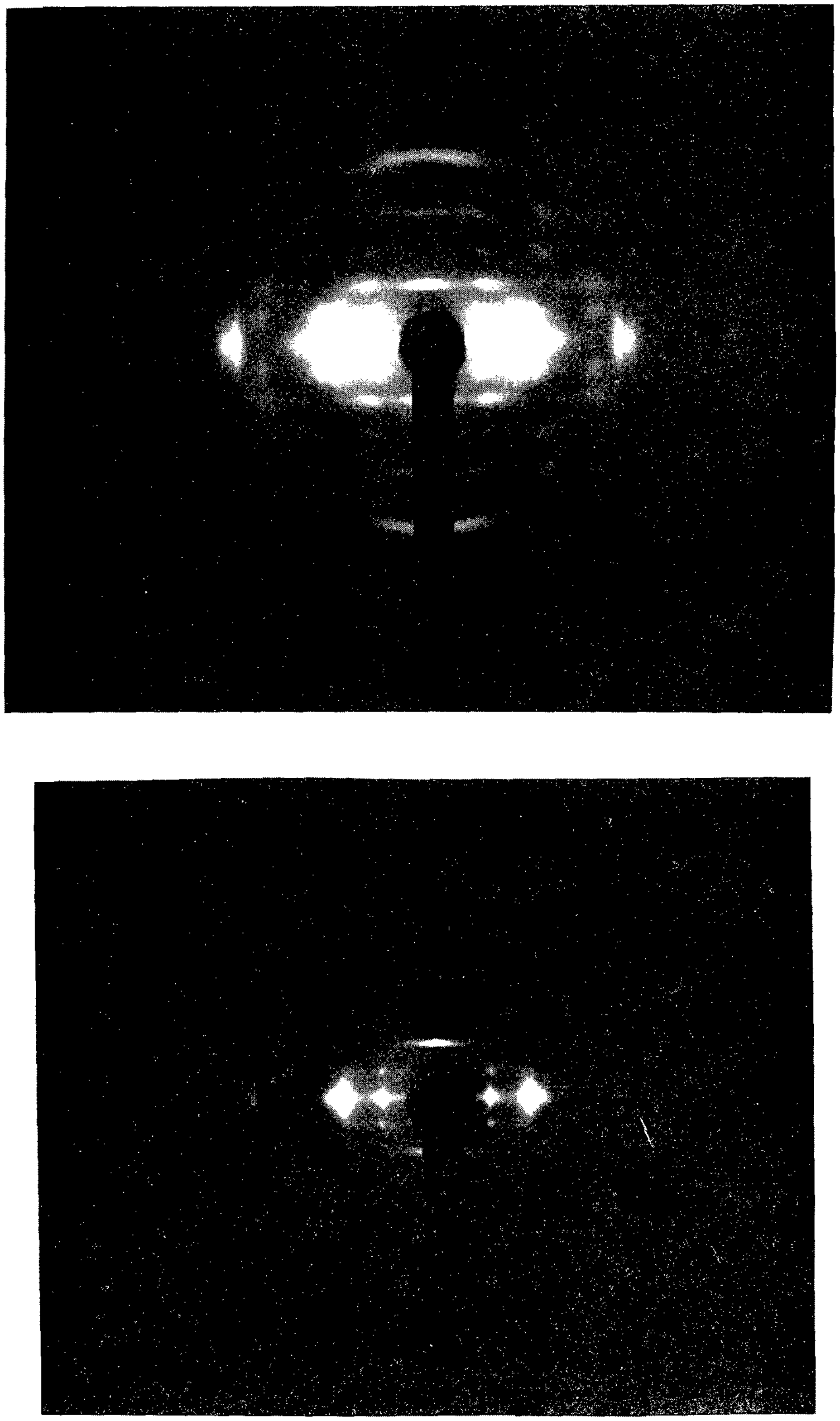

Figure 3. Fiber rotation photograph (fiber direction vertical) of ABPBO (top) and ABPBT (bottom) CuK$_\alpha$ radiation, camera radius 28.648.

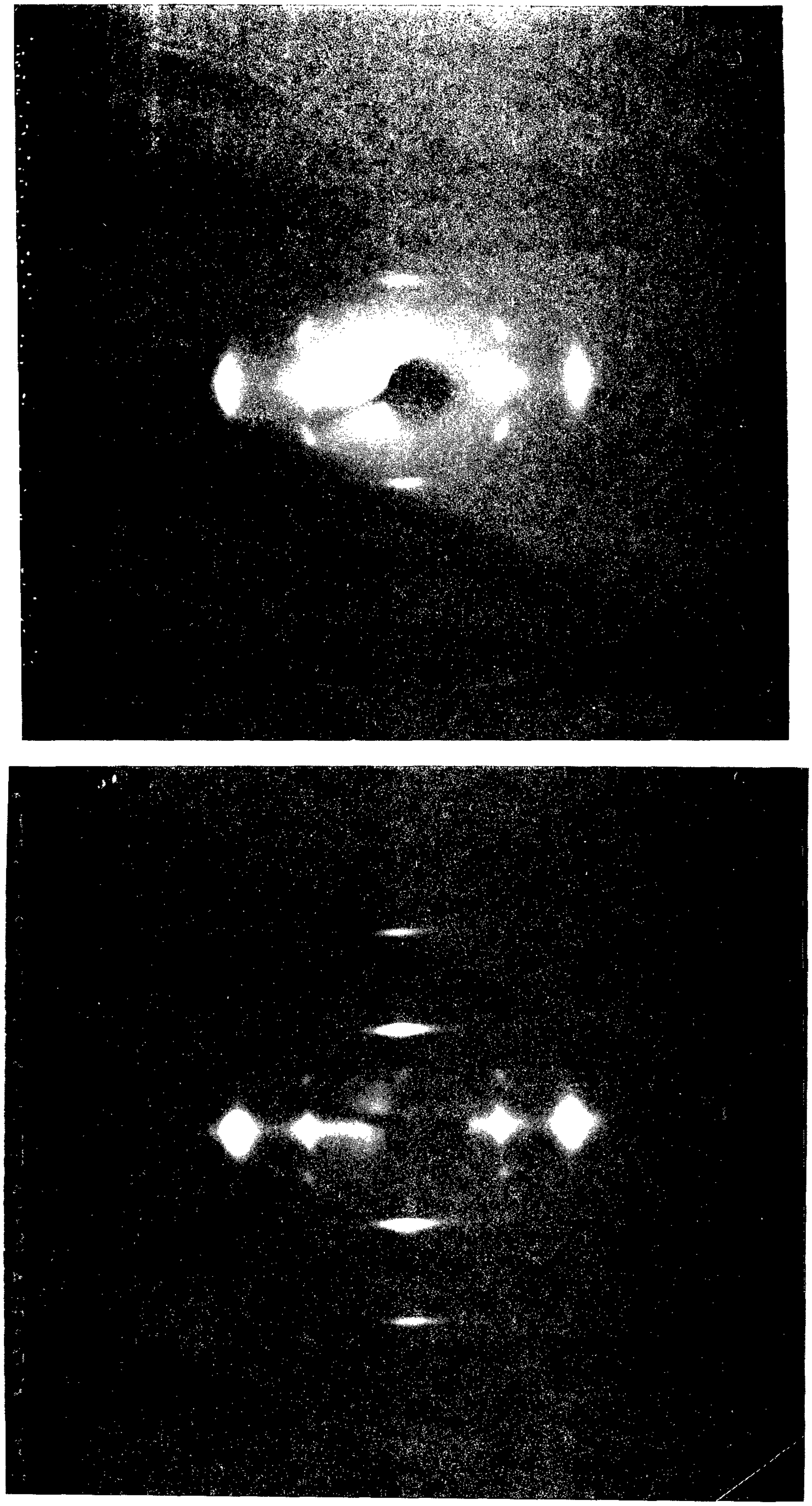

Figure 4. Buerger precession patterns of ABPBO (top) and ABPBT (bottom), fiber direction vertical, zero layer screen, $\mu = 25^{o}$, CuK_{α} radiation, sample to film distance 6.0cm.

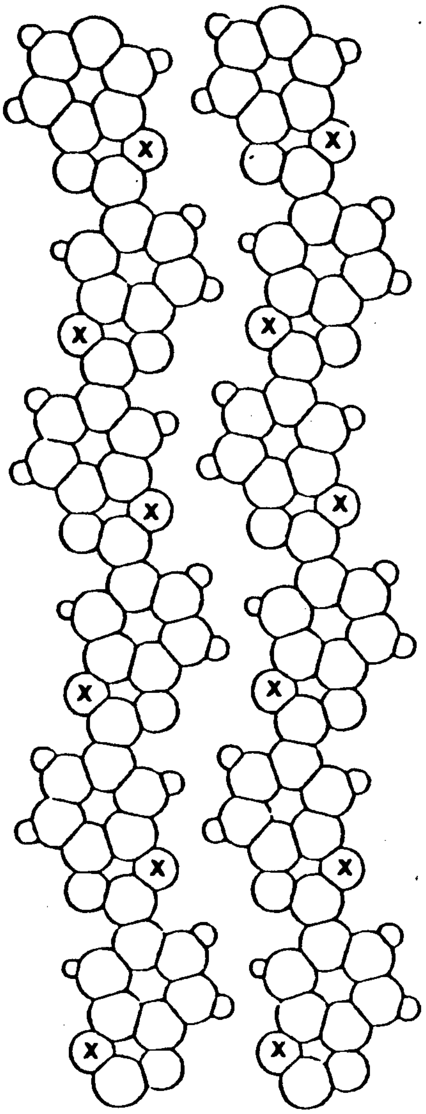

Figure 5. Ring normal view of two chains of ABPBO separated by one translation along the a-axis. x denotes the nitrogen atom.

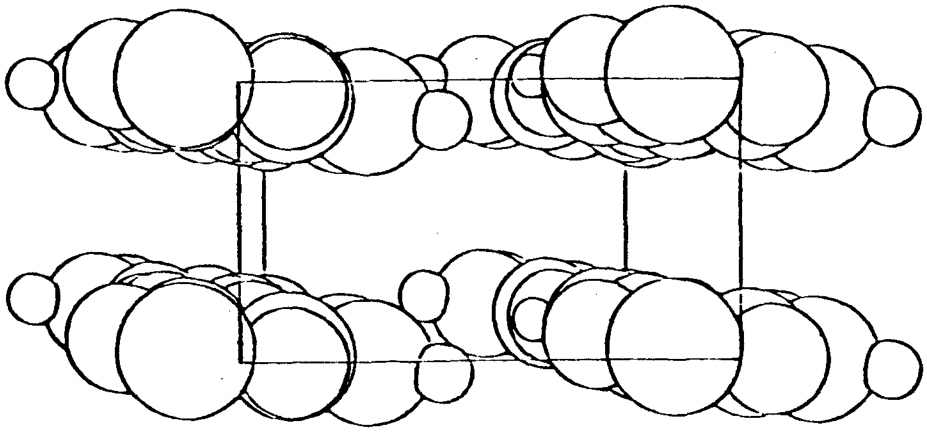

Figure 6. C-axis (fiber axis) view of unit cell of ABPBO. The a-axis is horizontal.

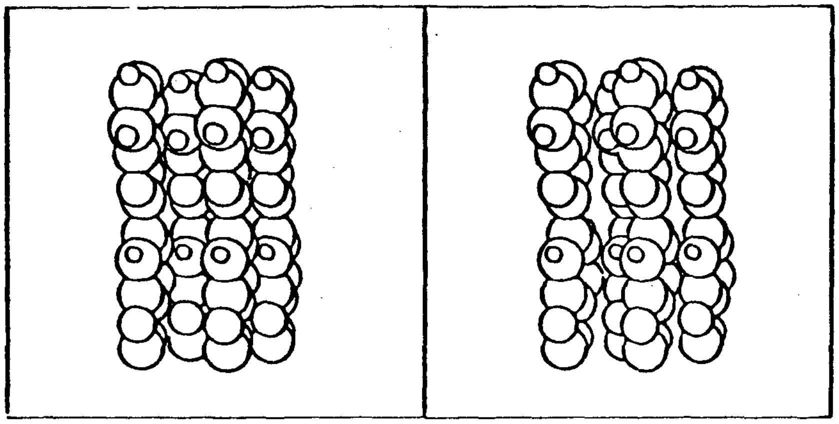

Figure 7. Stereoview along the b-axis of unit cell of ABPBO.

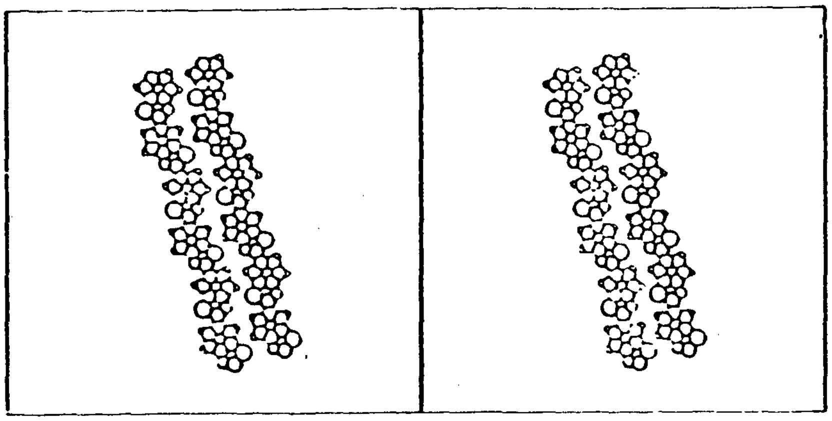

Figure 8. Ring normal view of two chains of ABPBT separated by one translation along the a-axis. The largest sphere signifies the sulfur atom.

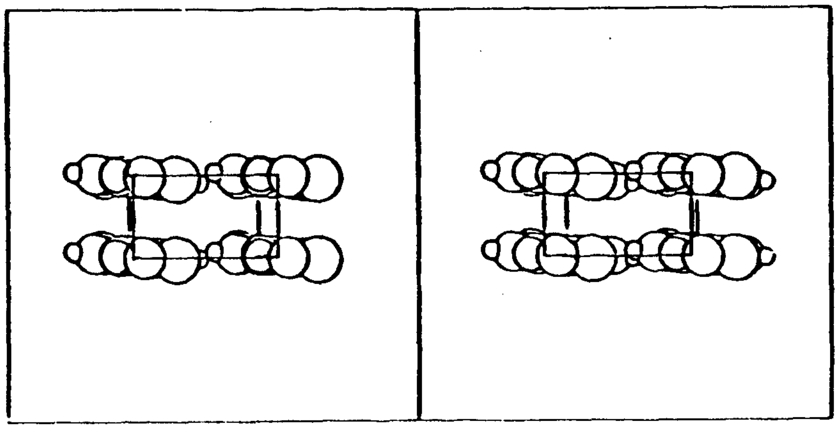

Figure 9. Stereoview along the c-axis (fiber axis) of unit cell of ABPBT. The a-axis is horizontal.

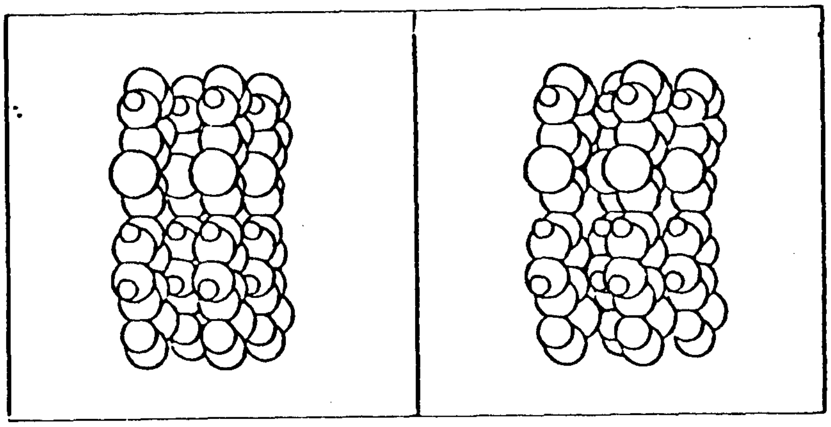

Figure 10. Stereoview along the b-axis of unit cell of ABPBT.

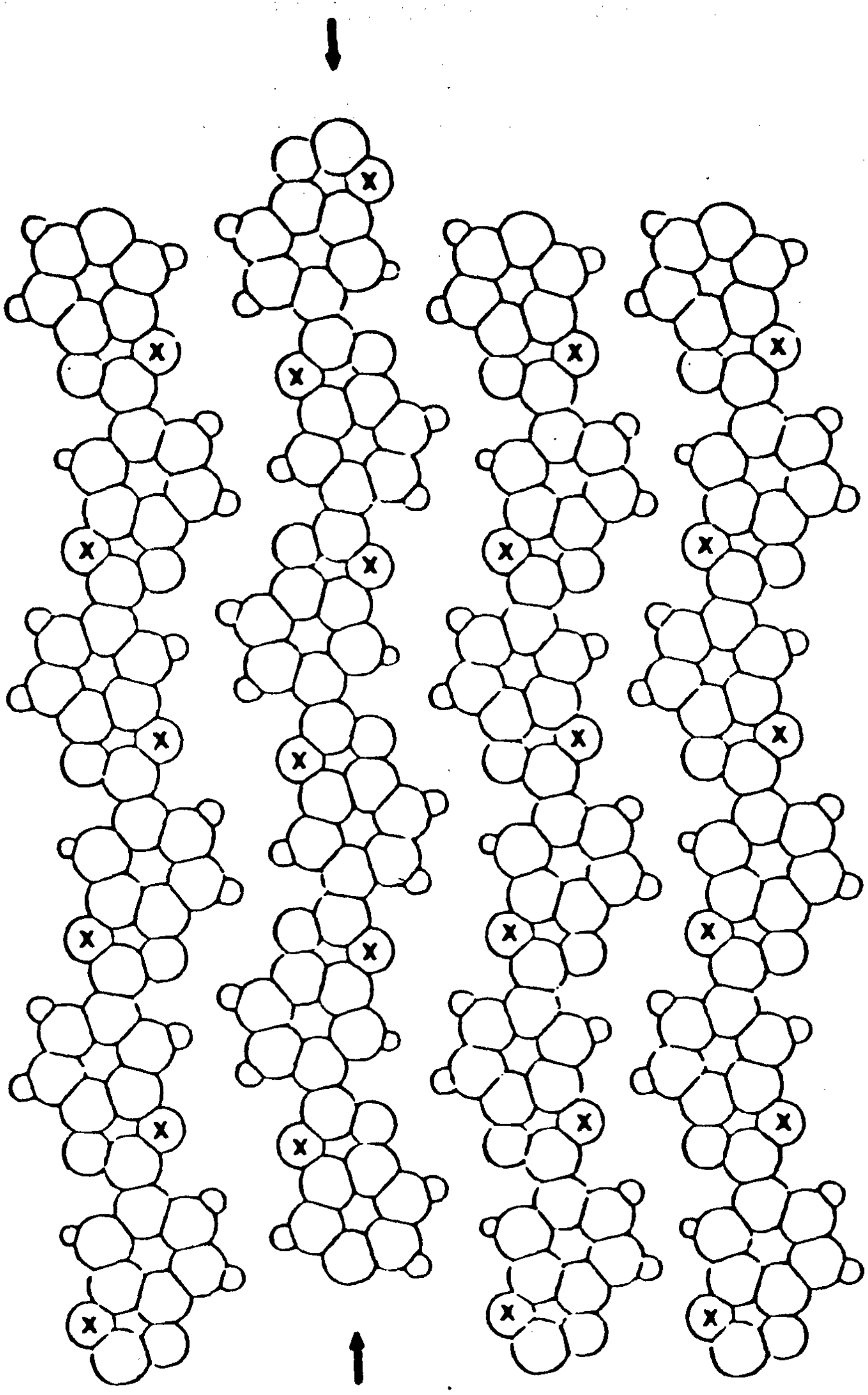

Figure 11. Representation of a possible disorder mode in ABPBO viewed normal to molecular planes. The arrow denotes the chain in the opposite direction. x indicates the nitrogen atom.

TABLE 1

DIFFRACTION DATA FOR ABPBO AND ABPBT

	ABPBO	ABPBT
$\underline{a}$ (Å)	6.061(17)	6.044(6)
$\underline{b}$ (Å)	3.384(13)	3.417(7)
$\underline{c}$ (Å)	11.575(6)	12.194(18)
Unit Cell Symmetry	Orthogonal (pseudo orthorhombic)	Orthogonal (pseudo orthorhombic)
Chain Symmetry	2_1	2_1
Molecules per cell (Z)	1	1
Formula Unit	$[C_{14}H_6N_2O_2]_n$	$[C_{14}H_6N_2S_2]_n$
Formula units per fiber repeat (n)	2	2
Calculated density (g cm^{-3})	1.638	1.756
Measured density (g cm^{-3})	1.4	1.5

TABLE 2

SELECTED FIXED BOND LENGTHS AND BOND ANGLES INCORPORATED IN STARTING MODELS

ABPBO		ABPBT	
	Lengths (Å)		
C7-C14	1.467	C7-C13	1.468
C7-N1	1.300	C7-N1	1.300
C7-O1	1.370	C7-S1	1.762
	Angles (degrees)		
N1-C7-01	115.6	N1-C7-S1	115.5
N1-C7-C14	127.3	N1-C7-C13	124.0

TABLE 3

PARAMETERS DEFINING CHAIN CONFORMATION AND CHAIN ORIENTATION WITHIN UNIT CELL

	ABPBO	ABPBT
torsion angle (τ)(degrees)	0.0	0.0
X (degrees)	90.0	90.0
Y (degrees)	-120.4	-82.5
Z (degrees)	5.3	4.0
R-factor (%)	20.8 (based on 14 Bragg maxima)	9.5 (based on 10 Bragg maxima)

TABLE 4

FRACTIONAL ATOMIC COORDINATES FOR ABPBO

Atom	X	Y	Z
H2	-0.579	0.096	0.228
C2	-0.422	0.070	0.202
C3	-0.373	0.062	0.085
H3	-0.494	0.082	0.027
C4	-0.158	0.026	0.047
C5	0.013	-0.002	0.127
H5	0.169	-0.028	0.099
C6	-0.046	0.008	0.242
N1	0.087	-0.014	0.341
C7	-0.052	0.009	0.426
O1	-0.269	0.045	0.396
C1	-0.267	0.044	0.277
C14	0.000	0.000	0.550
C13	0.216	-0.036	0.586
H13	0.337	-0.056	0.528
C12	0.268	-0.045	0.703
H12	0.426	-0.071	0.728
C11	0.095	-0.016	0.778
O2	0.104	-0.017	0.897
C17	-0.112	0.019	0.931
N2	-0.255	0.042	0.847
C16	-0.128	0.021	0.747
C15	-0.194	0.032	0.632
H15	-0.353	0.059	0.613

TABLE 5

FRACTIONAL ATOMIC COORDINATES FOR ABPBT

Atom	X	Y	Z
H2	-0.209	0.026	0.097
C2	-0.064	0.008	0.125
C3	0.114	-0.014	0.050
C4	0.330	-0.040	0.087
H4	0.445	-0.054	0.035
C5	0.377	-0.046	0.198
H5	0.523	-0.064	0.224
C6	0.202	-0.025	0.270
N1	0.223	-0.027	0.383
C7	0.031	-0.004	0.431
S1	-0.198	0.024	0.342
C1	-0.017	0.002	0.231
C13	0.000	0.000	0.550
C12	0.179	-0.022	0.624
H12	0.324	-0.040	0.596
C11	0.130	-0.016	0.735
S2	0.310	-0.038	0.846
C17	0.081	-0.010	0.935
N2	-0.111	0.014	0.887
C16	-0.090	0.011	0.774
C15	-0.265	0.032	0.702
H15	-0.411	0.050	0.727
C14	-0.218	0.027	0.591
H14	-0.333	0.041	0.539

TABLE 6

OBSERVED AND CALCULATED SPACINGS AND STRUCTURE AMPLITUDES (x10) FOR ABPBO

h k l	d_o^* (Å)	d_c (Å)	F_o	F_c
1 0 1	5.36	5.37	116	154
1 0 0	6.08	6.06	375	417
1 1 0	3.38	2.95	897	860
0 1 0		3.38		
1 1 1	2.93	2.86	126	176
2 0 1		2.93		
1 0 3	3.29	3.25	33	48
1 1 4	2.15	2.07	81	139
0 1 4		2.20		
2 0 4		2.09		
1 0 2	4.20	4.19	71	108
0 2 0	-	1.69	271	253
3 0 1	-	1.99	50	76
3 0 2	-	1.91	78	122
3 0 4	-	1.66	102	82
1 2 0	-	1.63	173	234
1 1 3	-	2.35	41	88
2 0 3		2.38		
1 1 2	-	2.63	16	90
2 0 2		2.68		

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*Accurate d_o values could not be measured for the more diffuse reflections.

TABLE 7

OBSERVED AND CALCULATED SPACINGS AND STRUCTURE AMPLITUDES (x10) FOR ABPBT

h k l	d_o (Å)	d_c (Å)	F_o	F_c
1 0 1	5.39	5.42	111	165
1 0 0	6.06	6.04	379	388
0 1 0	3.42	3.42	868	878
2 0 2	2.71	2.71	152	178
2 0 0	3.03	3.02	271	213
2 0 4	2.15	2.15	226	230
1 2 0	1.65	1.64	211	198
0 2 0	1.75	1.71	398	355
2 0 1	2.93	2.93	68	112
1 0 3	-	3.37	144	135

TABLE 8

Intra- and Interchain Atomic Distances (Å)*

ABPBO		ABPBT	
H2 · · H15(I)	2.02	H12 · · H14(I)	2.21
H13 · · H15(I)	2.20	S2 · · H15(I)	2.24
H5 · · H2(I)	2.24	H4 · · H2(I)	2.24
H5 · · H3(I)	2.31	H5 · · S1(I)	2.24
O2 · · H5(II)	2.38	H5 · · H2(I)	2.26
H12 · · N2(I)	2.45	H12 · · H15(I)	2.28
N1 · · H2(I)	2.51	S2 · · H4(II)	2.45
N2 · · H3(II)	2.52	C17 · · H4(II)	2.52
C17 · · H3(II)	2.55	N2 · · H2(II)	2.63
H15 · · O1(III)	2.56		
C12 · · H15(I)	2.60		
C17 · · H5(II)	2.62		
H12 · · C15(I)	2.63		
H13 · · N1(III)	2.65		

*The left hand member of each pair of atoms has parameters (xyz) corresponding to those listed in Tables 4 and 5. The parameters for the atom on the right are indicated as follows: (I) x+1,y,z; (II) x,y,z+1; (III) x,y,z.

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