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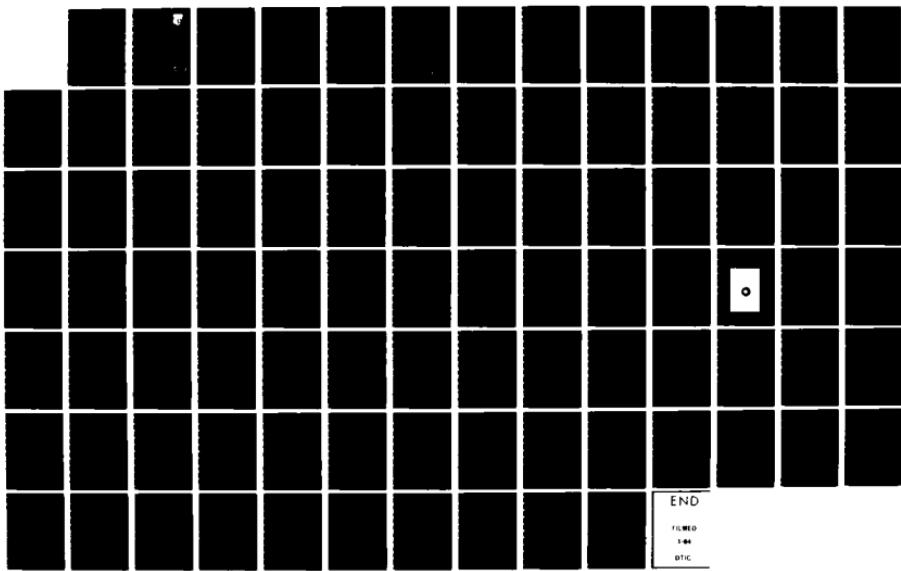
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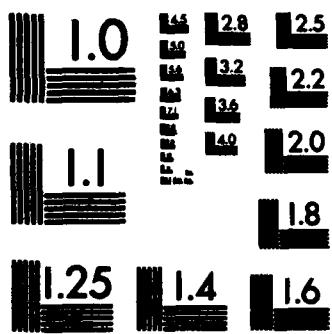
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**MODEL COMPOUND STUDIES OF RIGID ROD AROMATIC
HETEROCYCLIC POLYMER SYSTEMS, THE X-RAY
CRYSTAL STRUCTURE OF 2,6-DIPHENYLBENZO
(1,2-d; 5,4-d') DIIMIDAZOLE TETRAHYDRATE,
 $C_{20}H_{14}N_4 \cdot 4H_2O$, A MODEL SYSTEM FOR THE STUDY
OF POLYMER-WATER INTERACTION IN POLYBENZIMIDAZOLES**

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July 1983

Final Report for Period 1 August 1981 - 30 September 1982.

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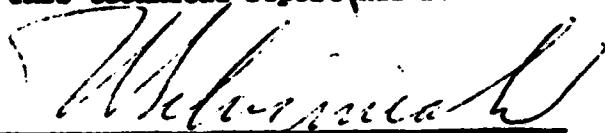
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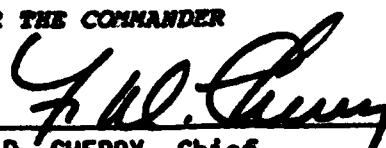


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20. Abstract

cell of volume $1925.8(1.3)\text{Å}^3$, and the measured density is 1.295 g/cc .

4850 unique reflections out to 56° in 2θ were collected with an automated diffractometer using niobium filtered MoK_α radiation. The 2θ scan technique was employed. Absorption corrections were made and approximately 11,000 reflections were averaged to give a hemisphere of independent observations. The direct method of phase determination was used to solve the structure, and full matrix least squares refinement gave a final R_{w} factor of 0.084 based on the 3570 reflections with $F_{\text{obs}} \geq 3\sigma(F)$.

The central benzodimidazole portion of the molecule is essentially planar, while the end phenyl rings are twisted in the same direction from the central plane by 6.0° and 7.9° . The carbon-nitrogen bonds on the imidazole rings are semi-localized, and the one lone electron pair nitrogen atom on each ring is positioned cis to that on the other ring. Molecules pack in herringbone fashion, held in the crystalline lattice by the strong hydrogen bonding provided by a three dimensional water structure. Four hydrogen bonded water molecules bridge the two lone electron pair nitrogen atoms on each molecule to form a ring. Each water molecule participates in hydrogen bonding with other molecules related by symmetry centers along the a and c axes so that two water molecules make use of all four possible coordination sites, while the other two make use of three. D-spacings in the polymer film are correlated with d-spacings of selected intense reflections in the single crystal. Powder diffraction patterns of the model compound are recorded for comparison with computer generated patterns and polymer film data. Implications of the model compound structure to the problem of water retention in polymer synthesis and processing are presented.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, and The University of Dayton Research Institute under contract F33615-81-C-5019 to the Materials Laboratory. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3 Work Unit Directive 2303Q307, "Structural Resins." Dr. Thaddeus E. Helminiak served as the AFWAL/ML Work Unit Scientist. Co-authors were Marilyn Hunsaker and W. W. Adams, Materials Laboratory (AFWAL/MLBP); and Dr. Albert V. Fratini, University of Dayton Research Institute.

This report covers research conducted from August 1981 to September 1982.

The authors express their appreciation to Douglas S. Dudis, who as an undergraduate student at the University of Dayton first prepared crystals of the model compound and recorded the initial x-ray photographs. Thanks are due to Mary Ryan for NMR Spectra and to Gary Griffin of the University of Dayton Research Institute for assistance in adapting computer programs to the PRIME 550. Thermogravimetric/mass spectral analysis and differential scanning calorimetry measurements were performed by E. G. Jones of Systems Research Laboratories and E. Soloski of the University of Dayton Research Institute.

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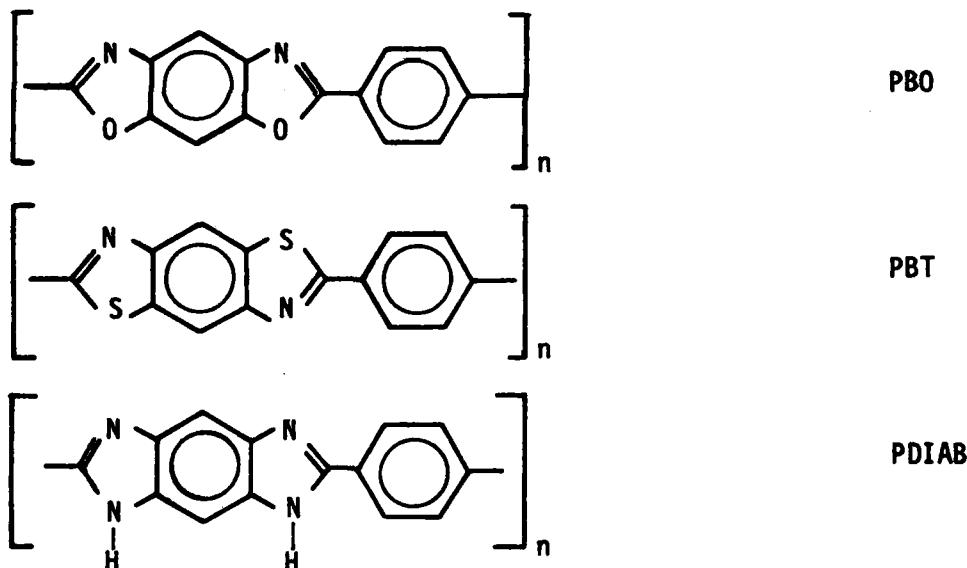
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SECTION I

BACKGROUND

Polymers are useful as structural materials due to their high strength-to-weight ratio, ease of processing, and availability of structural variations to control both mechanical and physical properties. In response to the need for high temperature adhesives and coatings, heat resistant fibers, and ablative systems, polymer scientists have been active in research in the area of thermally stable polymers for more than 20 years. Recently, particular emphasis has been placed on high temperature resistant, rodlike, aromatic heterocyclic polymers shown below. The para-configured poly (p-phenylenebenzobisoxazole) (PBO) and poly (p-phenylenebenzothiazole) (PBT), in particular, demonstrate high tensile strength, high modulus and good thermooxidative stability when solutions are spun into films and fibers (Reference 1).



As a class of polymers, the polybenzimidazoles are notable as heat-resistant polymers. Thermogravimetric analysis of wholly aromatic polybenzimidazoles showed weight losses starting around 600°C , reaching about 30% at 900°C (Reference 2). Unfortunately, these wholly aromatic polybenzimidazoles exhibit a high affinity for water, making these materials less attractive as structural materials when compared to the polybenzoxazoles and polybenzothiazoles. In (p-phenylenebenzodiimidazo)

polymer (PDIAB), the attraction for water is so pronounced that continued heating under vacuum does not completely eliminate the water. The nature of the polymer-water interaction in PDIAB is discussed more fully in Section V.

Polymer thermal stability is primarily dependent on the bond energy between atoms in a molecule. The strength of the chemical bond represents the upper limit of vibrational energy that the molecule may possess before bond dissociation occurs (about 100 kcal/mol for a single covalent bond). Intramolecular bond strength may be enhanced by resonance stabilization. The incorporation of aromatic or heterocyclic rings in the molecule may contribute 40 to 70 kcal/mol to the energy. Intermolecular attraction between neighboring atoms can add additional thermal stability. These interactions include van der Waals forces (about 0.5 kcal/mol, dipole-dipole interactions (about 6 kcal/mol), and hydrogen bonding (about 10 kcal/mol) (Reference 3).

The definition of thermal stability varies with the time and temperature requirements of the intended use. For example, Cassidy's definition of thermal stability (Reference 4) is the retention of physical properties at 250°C for extended periods; at 500°C for intermediate periods; and at 1000°C for short periods. A polymer may fail to reach the latter criteria and yet be satisfactory for the thermal requirements of its application.

Degree of crystallinity can influence thermal stability. Historically, polymer chemists sought to maximize the crystallinity of the system by designing molecules with a high degree of structural regularity, streamlined for optimum packing and exhibiting strong inter-chain bonding. Early in the 1960's, thermal stability to temperatures as high as 400-600°C in air by thermogravimetric analysis was realized for polyamides, polyimides, and polyoxazoles (Reference 3). Although stability up to 800°C in nitrogen was observed for polyquinoxalines and polyphenylenes, most high temperature polymers synthesized in the ensuing years had thermal stabilities in the 350-550° range.

Once polymer chemists felt that the upper limit of high temperature stability had been reached, attention turned to the problem of tractability.

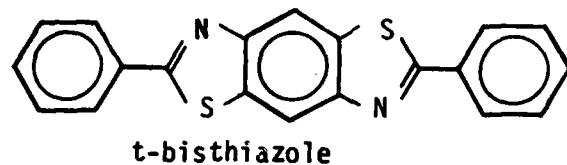
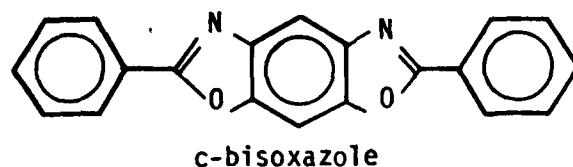
The problem of thermal stability versus tractability is exemplified in a class of materials known as semi-ladder polymers. These aromatic heterocyclic systems derive their thermal stability from the extension and stiffness of the chain. But structural characteristics which give these materials their superior thermal and mechanical properties also make them difficult to process (Reference 5). Strong mineral or organic acids are required as solvents, and the polymer morphology can be influenced only to a limited extent after processing.

The difficulty in processing these polymers led to the concept of using blends of paraconfigured and metaconfigured semi-ladder polymers. The flexibility in the backbone of the metaconfigured semi-ladder polymers would enhance ductility in the blend in the solid state. Reinforcing the flexible polymer with a rod-like polymer results in composites analogous to chopped fiber reinforced composites, combining the thermal stability of both polymers with the flexibility of the coil polymer. Various molecular composites have been studied recently for their mechanical and morphological properties as well as their tractability (Reference 6). In several of these blends reported to date, PDIAB functions as the reinforcing component.

Ideally, a molecular composite should be a homogeneous dispersion of rod polymers in the coil matrix. Electron microscopy can provide some information concerning the extent of dispersion, but for information on the atomic scale of the blends, x-ray or electron diffraction studies are required. Wide angle x-ray scattering patterns can reveal the orientation distributions as well as crystallite size and inter- and intra-molecular plane spacings. X-ray studies on the polymers are greatly facilitated by structure determination of model compounds (References 7 through 11). Detailed structure information on the individual polymer blend components can be extrapolated from the molecular geometry of the model compound.

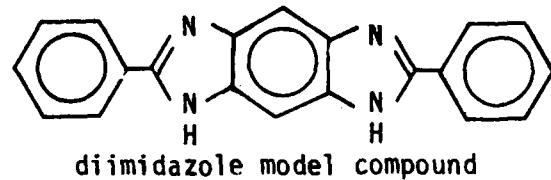
For example, recent interpretation of diffraction patterns of PBO and PBT have relied heavily on the detailed structure analysis of the

model compounds 2,6-diphenylbenzo-(1,2-d; 5,4-d')bisoxazole (c-bisoxazole) and 2,6-diphenylbenzo-(1,2-d; 4,5-d')bisthiazole (t-bisthiazole) (References 7 through 11). The diffraction



patterns of fibers of PBT exhibit strong Bragg-equatorial reflections at 3.4 and 5.9\AA , and many meridional layer lines with a fiber repeat distance of $12.41 (3)\text{\AA}$. These spacings have been interpreted, based upon comparison to the model compound crystal structures, as the lateral separation of adjacent molecules, packed as highly oriented rods of high chemical perfection.

This report presents the crystal structure analysis of 2,6-diphenylbenzo (1,2-d; 5,4-d') diimidazole, hereafter referred to as the diimidazole model compound, a model compound for the rigid rod poly (1,7-dihydrobenzo [1,2-d: 4,5-d'] diimidazole - 2,6-diyl-1,4-phenylene) (PDIAB).



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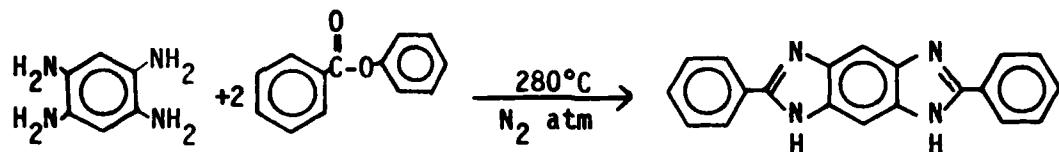
This structure serves to provide not only accurate molecular parameters for the monomer repeat unit for use in subsequent structural analysis of PDIAB fibers and blends, but also a glimpse into the nature of the polymer-water interaction in polybenzimidazoles.

Powder diffraction patterns have been recorded for the diimidazole model compound. The patterns of the ethanol grown and sublimed crystals are checked for structural similarities and compared with the computer generated pattern.

SECTION II
EXPERIMENTAL

1. SYNTHESIS

The diimidazole model compound was prepared in crude form by Dr. Fred Arnold, Polymer Branch, Materials Laboratory. The synthesis followed the original procedure of Vogel and Marvel (Reference 12), in which the stoichiometric combination of tetraamine and phenyl benzoate in melt condensation gave the desired product:



The product, 2,6-diphenylbenzo (1,2-d;4,5-d') diimidazole tetrahydrate, had a chemical formula of $C_{20}H_{14}N_4 \cdot 4H_2O$ and a molecular weight of 382.20 g/mol.

The proton nmr spectrum of the product in the nonprotonating solvent N,N' -dimethylacetamide (DMAC) has revealed the presence of two OH peaks at $\delta = 3.6$ and 8.0. All chemical shifts are relative to TMS. There are also two additional solvent NCH_3 peaks which are shifted upfield by 6 Hz from their position in the neat solvent, indicating the formation of one or more complexes between the model compound, water and DMAC.

Crystals suitable for diffraction studies were obtained both by vacuum sublimation at $360^{\circ}C$ and by slow evaporation from ethanol.

2. CRYSTAL MORPHOLOGY

The ethanol-grown crystals were well formed parallelepipeds with an ambient tint, while sublimation provided clusters of single crystals similar in morphology to the ethanol-grown crystals though smaller in size.

The ethanol-grown crystals were superior to the sublimed crystals in terms of diffraction characteristics. While polybenzimidazoles are known to be hygroscopic (Reference 13), microscopic inspection of the crystals after standing for several months at room temperature and humidity showed no deterioration apparently because the equilibrium water content was satisfied during crystal growth.

A translucent amber needle grown from ethanol was glued (Eastman 910 adhesive) onto a glass fiber with the needle parallel to the fiber direction. The fiber was mounted on the goniometer head with hard wax and visually oriented with the aid of a microscope. A second crystal, chipped from a large cluster, was mounted perpendicular to the wide face and used solely for precession and Weissenberg photography.

Another crystal, chosen from the batch of sublimed crystals was mounted in a similar manner and crystal structure analysis was attempted to examine possible retained solvent effects. This crystal, though beautifully formed, scattered weakly and as a result was unsuitable for an accurate crystallographic structure determination.

3. SPACE GROUP AND CELL CONSTANTS

The precession photographs of ethanol-grown crystals indicated the monoclinic space group $P2_1/c(C_2^5h)$, No. 14 in the International Tables for X-ray Crystallography, Vol. 1) (Reference 14). Even though the alternate space group, $P2_1/n$, actually corresponded to the reduced cell, we decided to proceed with the non-reduced $P2_1/c$ cell since it is the more conventional setting in the International Tables, Volume I. The transformation from the $P2_1/c$ to the reduced $P2_1/n$ cell is:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix} = [h' k' l']$$

where hkl are the Miller Indices for the $P2_1/c$ cell and $h'k'l'$, those of the $P2_1/n$ cell.

Accurate cell parameters were determined for ethanol-grown crystals by centering 14 reflections and their Friedel mates ($35^{\circ} < 2\theta < 38^{\circ}$) on the diffractometer using molybdenum $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$), followed by two cycles of least squares refinement (Table 1).

Precession photography on the sublimed crystal also revealed the same $P2_1/c$ space group. The cell parameters were determined in the same manner as the ethanol grown crystal; only 8 reflections and their Friedel mates were centered ($18^{\circ} < 2\theta < 24^{\circ}$).

4. DENSITY

Density measurements were made by the flotation in aqueous cesium chloride. A sample of the solution was then weighed in a pycnometer to determine the density at room temperature.

A density of 1.07 g/cc was calculated on the basis of four molecules per unit cell. A measured density of 1.295 g/cc for the ethanol grown crystal was the first indication that solvent had been incorporated into the structure. This seemed reasonable, given the characteristic absorption of water by benzimidazoles as previously mentioned.

Determination of the structure confirmed the presence of 16 water molecules per unit cell, corresponding to a calculated density of 1.319 g/cc. It is interesting to note that the sublimed material had a similar measured density of 1.304 g/cc suggesting that water was carried along in the sublimation process.

TABLE 1
SUMMARY OF CRYSTAL DATA FOR DIIMIDAZOLE MODEL COMPOUND

	Ethanol-Grown Crystals	Sublimed ⁺ Crystals
a	9.008(2) ⁰ Å	9.02(2) ⁰ Å
b	24.967(7) ⁰ Å	24.97(3) ⁰ Å
c	9.870(5) ⁰ Å	10.02(3) ⁰ Å
α	90.0 ⁰	90.0 ⁰
β	119.82(3) ⁰	119.12(4) ⁰
γ	90.0 ⁰	90.0 ⁰
Volume of unit cell	1925.8(1.3) Å ³	1960 Å ³
Measured density	1.295 g/cc	1.304 g/cc
Calculated density	1.319 g/cc	1.296 g/cc
F (0, 0, 0)	808	808
Linear absorption coefficient for MoK α radiation	0.877 cm ⁻¹	0.877 cm ⁻¹
Z	4	4
Water molecules per unit cell	16	16
Space group	P2 ₁ /C	P2 ₁ /C
Crystal system	Monoclinic	Monoclinic
Absorption factor min=	0.9883	
max=	0.9922	
ave=	0.9907	
Crystal volume	0.085 mm ³	< 0.08 mm ³

⁺A complete x-ray analysis was not performed on these crystals due to the lack of data at high 2 θ angles. Note the similarity in cell dimensions between the ethanol-grown and sublimed crystals indicating nearly equivalent structures.

SECTION III

DATA COLLECTION

1. DESCRIPTION OF THE INSTRUMENT

X-ray intensity data were collected on a computer-controlled Picker FACS-I diffractometer equipped with pulse height analyzer and NaI scintillation detector. Each reflection was recorded and stored on magnetic tape. The control programs used were written by Dr. P. Galen Lenhert of Vanderbilt University (Reference 15).

A standard focus molybdenum tube, operated at 50 kV (constant potential) and 12 mA, was used as the x-ray source for data collection. The K_B radiation was reduced by an incident beam niobium filter 0.005" in thickness. A symmetrically variable aperture (SVA) was placed near the counter (3.75 mm^2).

For data collection, the incident and diffracted beams were collimated by hollow cylinders tapered to 1.0 mm in diameter, approximately 23.5 cm from the crystal. The incident beam collimator was designed to hold the niobium filter, and the diffracted beam collimator contained independent pairs of top-bottom, left-right slit adjustments for use in crystal orientation. A calibrated microscope, attached at an angle to the chi circle, was used to center the crystal precisely. The optical centering was confirmed by comparison of positive and negative 2θ values for several reflections. The microscope was also calibrated for measurements of crystal size used later for absorption corrections.

2. DATA COLLECTION

The crystal was mounted on the diffractometer with the a axis coincident with ϕ . A stereoplot of the crystal morphology is shown in Figure 1. A total of 11,431 reflections were measured for the ethanol-grown crystal, using a θ - 2θ scan mode. Four equivalent octants of the sphere of reflection were measured (hkl , $\bar{h}k\ell$, $h\bar{k}\ell$, $\bar{h}\bar{k}\ell$). Intensities were recorded with a scan speed of 1° per minute for reflections of $2\theta < 56^\circ$. Scattering background counts were measured at equal angles above and below the respective values of the K_A peaks. Each background was

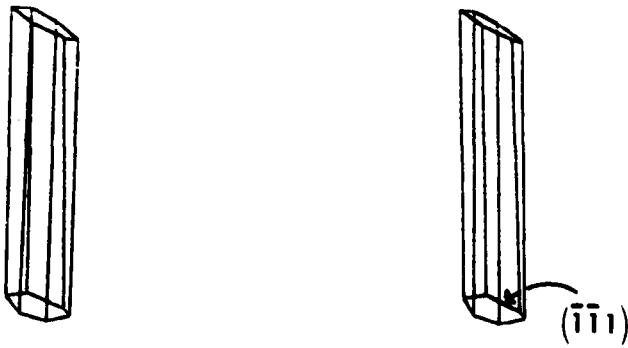


Figure 1. A Stereoplot of the Data Crystal Grown from Ethanol. Prominent side faces starting with the broad rear face and moving in a clockwise direction around the crystal are (111), (323), (010), (121), (323), and (010). The slanted top face is (100). The crystal was mounted with the vertical needle axis parallel to ϕ .

counted for about half the total peak scan time so that the scan time and total background times were approximately equal. Three standard reflections were recorded every 96 reflections with little observable decrease in intensity during the two months of data collection. In addition, four extra standards were checked periodically to monitor instrument stability. Table 2 contains summary of data collection.

3. DATA REDUCTION

Raw intensity data consisted of a scan count (C) and scan time (t_c), two background counts (b_1 and b_2) taken for a total time, t_b , on either side of the peak. Raw intensities were first processed to obtain the observed intensity (I_{obs}):

$$I_{obs} = C - \frac{(b_1 + b_2)t_c}{t_b}$$

The standard deviation, based on counting statistics alone, was:

$$\sigma(I_{obs}) = \left[C + (b_1 + b_2) \left(\frac{t_c}{t_b} \right)^2 \right]^{1/2}$$

TABLE 2
SUMMARY OF DATA COLLECTION

2θ range	0-56°
Reflection base width	1.3°
Dispersion factor	0.346°
No. of background counts per reflection	2
No. of peak scan per reflection	1
Background time per reflection	approximately twice the scan time
Scan speed	1°/min
Attenuation filter factors	2.163 for reflections 141, 151, 111 and 120 1.000 for all other reflections
Balanced filters	none
Take off angle	2.0°
Symmetrical variable aperture (SVA) dimensions	3.75 x 3.75 mm
Radiation for data collection	MoKα (Nb-filtered)

The data were collected in scale groups separated by successive measurements of standard reflections. Long term x-ray fluctuations were corrected by scaling each group to the current measurement of the standard intensities compared to the current average of standard intensities measured to that time:

$$K = \frac{k}{\sum I_{std}}$$

The arbitrary constant k was set equal to 200,000 for this determination.

The conventional Lorentz (L) and polarization (p) factors were applied and corrections for absorption of the beam by the crystal were calculated using crystal orientation, size and shape measured as described previously.

The value of 0.877 cm^{-1} for μ was calculated with the MURHO Fortran program of Lenhert (Reference 16) using the mass absorption coefficients tabulated in International Tables, Vol. III (Reference 14). The x-ray path distance was calculated for each reflection by considering crystal boundaries shown in Figure 1 and crystal orientation with respect to the incident beam. The absorption integral was numerically evaluated over the volume of the crystal for each reflection with the ORABS Fortran program of Wehe, Busing and Levy (Reference 17). Values of the transmission factor (A) ranged from 0.9883 to 0.9922, with an average of 0.9907.

These corrections were applied to the observed intensity to give the experimental magnitude of the structure factor:

$$|F_{\text{obs}}|^2 = \frac{I_{\text{obs}}^K}{LpA}$$

The standard deviation of F^2 based on counting statistics alone was

$$\sigma(F_{\text{obs}}) = \frac{\sigma(I_{\text{obs}})^K}{LpA}$$

and the variance of F^2 was

$$\sigma^2(|F_{\text{obs}}|)^2 = \frac{\sigma^2(I_{\text{obs}})^K^2}{L^2 p^2 A^2}$$

Data reduction was accomplished using the ORABS Fortran program (Reference 17). Input for data reduction included raw intensity data with data collection conditions specified, a list of attenuation filter factors, crystal shape data and linear absorption coefficient, and unit cell parameters. Before actual structure determination was begun, equivalent and multiply measured reflections were sorted and averaged.

SECTION IV

STRUCTURE DETERMINATION

The structure was solved by application of the Fortran program MULTAN 80 (Reference 18), which assigned the phases of 296 reflections with normalized structure factors (E 's) ≥ 1.9 from a starting set comprised of three origin-defining reflections [129, 0; 215, 0; 727, π], where 0 refers to a positive phase and π refers to a negative phase, and four additional reflections [4 24 $\bar{4}$, 0; 2 5 0, π ; 8 3 $\bar{3}$, 0; 2 15 $\bar{6}$, 0]. The corresponding E-map gave plausible positions for 24 non-hydrogen atoms in the structure.

The four solvent molecules, later shown to be water molecules, were located in a difference Fourier map, which followed two cycles of isotropic least squares refinement carried out by CRYLSQ, a subroutine of the Fortran program XRAY 72 (Reference 19).

Subsequent difference Fourier syntheses located all 14 hydrogen atoms of the benzodimidazole molecule and 7 of the 8 hydrogen atoms associated with the water structure. A thermal ellipsoid plot of the molecule, including the numbering system, is shown in Figure 2.

Refinement of the water structure was carried out by an iterative process in which atomic positions were adjusted slightly according to the location of positive or negative electron density ("peaks" or "holes") in the difference map. In the case of O4 and its bonded hydrogen atoms, H07 and H08, residual peaks and holes remained near these hydrogen atoms. When the two hydrogen atoms were removed and a difference Fourier map was recalculated, a smeared region of electron density resulted. A representative difference density map of this region is included in Figure 3. H08 could not be accurately pinpointed, which indicates some disorder in the water structure, and was omitted from the final cycles of refinement.

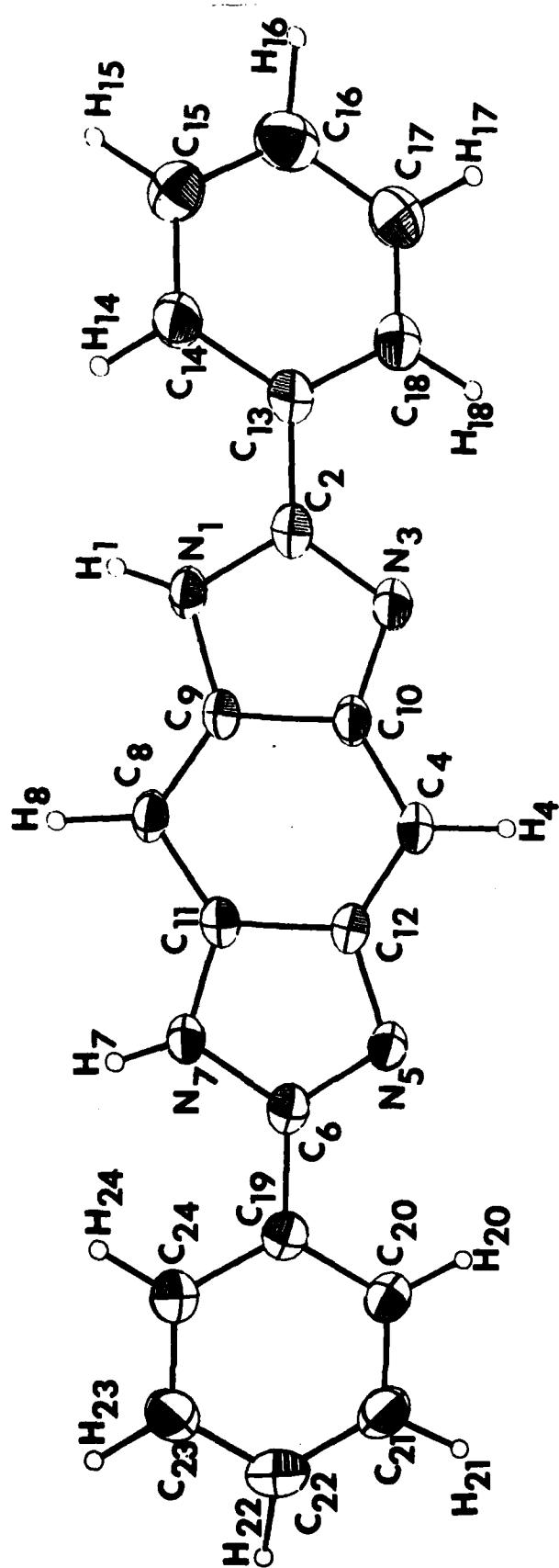


Figure 2. Thermal Ellipsoid Plot of the Diimidazole Model Compound Showing the Numbering System.

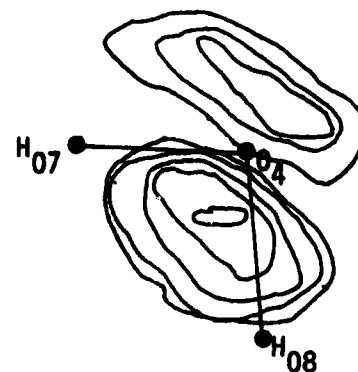


Figure 3. Residual Difference Density in the Vicinity of Water Molecule 4. Atoms H08 and H07 are included in the Map. Contours are at intervals of $5 \times 10^{-2} \text{ e}/\text{\AA}^3$. The lowest contour is at $30 \times 10^{-2} \text{ e}/\text{\AA}^3$.

For the final refinement of all 49 atoms in the asymmetric unit, anisotropic temperature factors were used for all non-hydrogen atoms, expressed in the general form:

$$T = \exp [-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}kla^{*}c^{*})]$$

where a^* , b^* and c^* are the reciprocal cell constants, and U_{ij} , the components of a symmetric matrix describing the orientation and three major axes of an equiprobability ellipsoid of thermal vibration.

An additional variable, S , was included to place the observed structure factors $|F_O|$ and the calculated structure factors $|F_C|$ on a common scale. The parameters were varied to minimize the function

$$L = \sum_{hkl} w(hkl) (|F_O(hkl)| - s|F_C(hkl)|)^2$$

where the reliability of each term in the sum was weighted by a factor $w(hk\ell)$, estimated as $w(hk\ell) = 1/\sigma^2 |F_0(hk\ell)|$ and calculated from counting statistics as described by Miller, Joesten and Lenhart (Reference 20). The final refinement used only F 's $\geq 3\sigma$.

The final residual index for all measured reflections $R_w = (\sum w|F_o| - |F_c|)/\sum w|F_o|$ was 0.084, based on 3570 reflections. The magnitude of $[\sum w|F_o| - |F_c||^2/(m - n)]^{1/2}$, where m is the number of reflections and n , the number of parameters defined, was 1.822. The average shift/error was 0.029 and 0.030 for nonhydrogen and hydrogen atom refinements respectively. The maximum shift/error was 0.301 and 0.191. A final difference synthesis showed no peaks above 0.36 eA^{-3} , with the exception of a peak in the vicinity of the disordered water ($O4$, $H07$, and $H08$), where the electron density was 0.61 eA^{-3} . Table 3 (see Appendix) lists the observed and calculated structure factors. Tables 4, 5, and 6 list the fractional coordinates for nonhydrogen and hydrogen atoms, with their thermal parameters. Atomic scattering factors for nonhydrogen atoms were those of Cromer and Mann (Reference 21) and for hydrogen atoms, those of Stewart, Davidson, and Simpson (Reference 22). Calculations for MULTAN 80 were performed on the Prime 550; for XRAY 72, on the CDC 6600, both at Wright-Patterson Air Force Base, Ohio.

TABLE 4

FRACTIONAL ATOMIC COORDINATES FOR NON-HYDROGEN ATOMS
WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
O1	0.17974 (25)	0.45513 (9)	0.66875 (23)
O2	0.19769 (32)	0.62610 (10)	0.83752 (29)
O3	0.14868 (27)	0.56144 (8)	0.58426 (24)
O4	0.52865 (32)	0.63848 (11)	1.07177 (31)
N1	0.35231 (30)	0.55994 (9)	1.43324 (27)
C2	0.48124 (39)	0.58762 (12)	1.43252 (35)
N3	0.51130 (31)	0.57032 (10)	1.32069 (29)
C4	0.36788 (40)	0.49772 (12)	1.11888 (37)
N5	0.18440 (33)	0.42266 (10)	0.94658 (28)
C6	0.05893 (40)	0.39541 (12)	0.94874 (35)
N7	0.02811 (31)	0.41293 (10)	1.06298 (28)
C8	0.16171 (39)	0.48492 (12)	1.26643 (36)
C9	0.29073 (35)	0.52239 (12)	1.31520 (32)
C10	0.39337 (37)	0.52935 (12)	1.24364 (34)
C11	0.24056 (36)	0.45995 (12)	1.06811 (33)
C12	0.14001 (35)	0.45405 (12)	1.14256 (33)
C13	0.57338 (40)	0.63083 (12)	1.54275 (36)
C14	0.54190 (43)	0.64287 (13)	1.66351 (39)
C15	0.62653 (48)	0.68443 (15)	1.76545 (42)
C16	0.74292 (51)	0.71466 (15)	1.74637 (45)
C17	0.77927 (52)	0.70245 (17)	1.62950 (49)
C18	0.69150 (48)	0.66129 (15)	1.52606 (42)
C19	-0.04070 (39)	0.35251 (12)	0.84046 (35)
C20	-0.02020 (42)	0.34051 (13)	0.71344 (39)
C21	-0.11988 (46)	0.30166 (14)	0.60639 (40)
C22	-0.23836 (45)	0.27288 (14)	0.62612 (41)
C23	-0.25837 (46)	0.28423 (15)	0.75261 (44)
C24	-0.15977 (44)	0.32325 (13)	0.86026 (39)

TABLE 5

ANISOTROPIC THERMAL PARAMETERS OF NON-HYDROGEN ATOMS ($\times 10^3$) WITH STANDARD DEVIATIONS IN PARENTHESES. THE THERMAL PARAMETERS ARE OF THE FORM

$$T = \exp [-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} \ell^2 c^{*2} + 2U_{12} hka^{*b^{*}} + 2U_{13} h\ell a^{*c^{*}} + 2U_{23} k\ell b^{*c^{*}})]$$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	50(1)	64(2)	52(1)	8(1)	33(1)	13(1)
O2	92(2)	87(2)	89(2)	-25(2)	71(2)	-31(2)
O3	60(2)	55(2)	57(1)	-2(1)	38(1)	1(1)
O4	77(2)	104(2)	98(2)	10(2)	55(2)	15(2)
N1	44(2)	47(2)	47(2)	1(1)	34(1)	-1(1)
C2	44(2)	45(2)	47(2)	2(2)	31(2)	4(2)
N3	50(2)	51(2)	55(1)	-8(1)	39(1)	-8(1)
C4	54(2)	58(2)	57(2)	-10(2)	45(2)	-7(2)
N5	58(2)	45(2)	50(2)	-4(1)	40(1)	-3(1)
C6	48(2)	43(2)	46(2)	7(2)	31(2)	7(2)
N7	47(2)	45(2)	52(2)	-3(1)	37(1)	-2(1)
C8	50(2)	44(2)	50(2)	3(2)	39(2)	1(2)
C9	33(2)	43(2)	40(2)	3(1)	24(1)	0(2)
C10	44(2)	47(2)	46(2)	-1(2)	32(2)	0(2)
C11	43(2)	47(2)	42(2)	2(2)	29(2)	0(2)
C12	37(2)	39(2)	43(2)	2(1)	26(2)	4(2)
C13	48(2)	42(2)	47(2)	2(2)	29(2)	2(2)
C14	54(2)	50(2)	52(2)	0(2)	33(2)	-2(2)
C15	72(3)	54(2)	58(2)	4(2)	39(2)	-1(2)
C16	83(3)	57(3)	64(3)	-15(2)	32(2)	-14(2)
C17	91(3)	82(3)	82(3)	-39(3)	57(3)	-20(3)
C18	72(3)	70(3)	67(3)	-20(2)	49(2)	-16(2)
C19	46(2)	39(2)	42(2)	5(2)	24(2)	3(2)
C20	61(2)	52(2)	60(2)	-3(2)	41(2)	-5(2)
C21	72(3)	59(2)	58(2)	2(2)	40(2)	-9(2)
C22	63(3)	49(2)	55(2)	1(2)	22(2)	-2(2)
C23	65(3)	66(3)	60(2)	-18(2)	35(2)	-5(2)
C24	69(2)	58(2)	55(2)	-10(2)	40(2)	-5(2)

TABLE 6
FRACTIONAL HYDROGEN ATOM COORDINATES WITH STANDARD DEVIATIONS IN
PARENTHESES AND ISOTROPIC THERMAL PARAMETERS ($\times 10^2$)

Atom	X	Y	Z	U
H1	0.3046(30)	0.5647(10)	1.4869(28)	5.0
H4	0.4407(30)	0.5009(9)	1.0750(28)	5.0
H7	-.0487(31)	0.4011(9)	1.0794(28)	5.0
H8	0.0832(30)	0.4803(10)	1.3042(27)	5.0
H14	0.4537(30)	0.6246(9)	1.6705(28)	6.0
H15	0.5989(32)	0.6915(10)	1.8529(29)	6.0
H16	0.8198(30)	0.7415(11)	1.8291(29)	6.0
H17	0.8706(31)	0.7213(10)	1.6221(29)	6.0
H18	0.7190(32)	0.6504(10)	1.4459(30)	6.0
H20	0.0689(31)	0.3565(10)	0.7043(28)	5.0
H21	-.0995(32)	0.2958(10)	0.5211(30)	6.0
H22	-.3448(30)	0.2474(11)	0.5304(29)	6.0
H23	-.3538(31)	0.2677(10)	0.7611(30)	6.0
H24	-.1707(33)	0.3324(10)	0.9532(29)	6.0
HO1	0.3020(35)	0.4414(11)	0.6882(31)	7.0
HO2	0.1987(33)	0.4484(10)	0.7515(31)	6.0
HO3	0.1739(32)	0.6114(10)	0.7647(30)	6.0
HO4	0.3622(30)	0.6234(10)	0.9403(28)	5.0
HO5	0.0250(31)	0.5580(10)	0.4921(29)	5.0
HO6	0.1727(31)	0.5366(10)	0.6256(28)	5.0
HO7	0.5972(34)	0.6274(11)	1.0694(31)	7.0

SECTION V
RESULTS AND DISCUSSION

Determination of the structure reveals a nearly planar diphenylbenzodiimidazole molecule with semilocalized carbon-nitrogen double bonds. The nitrogen atoms with lone electron pairs are positioned cis to each other. The monomer repeat distance, as measured by the C16-C19 separation, is $12.197(6)\text{\AA}$, which would correspond to the polymer repeat in rodlike PBI. Molecules pack in herringbone fashion, held in the crystalline lattice by a network of solvent water molecules. Features of the structure discussed in this section include:

- Atomic Coordinates, Bond Lengths and Angles
- Least Squares Planes
- The Molecule: Central Benzene Ring, Substituent Phenyls, Imidazole Rings
- Water Structure
- Packing
- Relationship to Polymer Film and Fiber Data
- X-Ray Powder Diffraction Patterns
- Simulated Powder Patterns Computed with POWD7

1. ATOMIC COORDINATES, BOND LENGTHS AND ANGLES

The final fractional coordinates and anisotropic temperature factors for non-hydrogen atoms are listed in Tables 4 and 5. Estimated standard deviations, obtained from the last cycle of least squares refinement, average 0.0002\AA for atom coordinates in the central benzodiimidazole moiety. The substituent phenyl groups, exhibiting greater thermal motion, show a slightly higher average standard deviation of 0.0003\AA in their atomic positions.

Hydrogen atom fractional coordinates and isotropic temperature factors are listed in Table 6. The average standard deviation for hydrogen atoms is 0.002\AA , one order of magnitude higher than the average for non-hydrogen atomic positions.

Bond lengths and angles with estimated standard deviations are summarized in Tables 7 and 8. The average standard deviation for distances in the central ring system is 0.004\AA , and in the phenyl substituents, 0.006\AA . Bond distances to hydrogen atoms as expected, have much higher average standard deviations of 0.03\AA .

Bond angles show a similar trend in the standard deviations of fused ring bond angles (0.3°) versus end phenyl bond angles (0.5°). Standard deviations for bond angles involving hydrogen atoms average 1.5° .

A more detailed discussion of bond lengths and angles for each component of the molecule is presented in a later section.

2. LEAST SQUARES PLANES

Table 9 presents the least squares planes calculated for the individual ring components of the molecule: the central benzene ring, the two imidazole rings, and the two phenyl substituents. In addition, the plane of the entire benzodimidazole moiety (Plane 1) has been calculated and has revealed an essentially planar fused ring system. The standard deviation of this plane is 0.0048\AA . Atomic displacements range from -0.008\AA to $.008\text{\AA}$, while displacement of hydrogen atoms bonded to atoms in the central ring system range from -0.05\AA to 0.06\AA .

The atoms in the substituent phenyl rings show greater deviation from the plane, with atomic displacements ranging from -0.008 to 0.008\AA for plane 3; and from -0.015 to 0.013\AA for the plane 2. Hydrogen atom displacements range from -0.11\AA to 0.24\AA . The standard deviation for the C19-C24 plane is 0.007; for the C13-C18 plane, 0.010.

The acute dihedral angles between the plane of the central benzene ring and those of the fused imidazole are 0.10 and 0.4° , respectively.

The phenyl ring planes are twisted in the same direction from coplanarity with the central benzodimidazole moiety by 6.0 and 7.9° , respectively. The slight torsion angles are probably attributable to crystal packing forces rather than steric hindrance, as the intramolecular contacts between the nitrogen atoms and adjacent ortho hydrogen atoms average 2.62\AA , which is close to the normal van der Waals separation of 2.7\AA .

TABLE 7

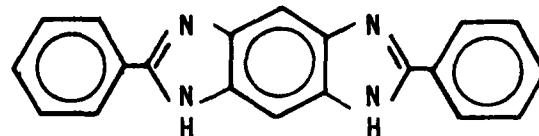
BOND DISTANCES (\AA) AND STANDARD DEVIATIONS
IN BENZODIIMIDAZOLE MODEL COMPOUND

N ₁ -C ₂	1.356(4)	C ₁₉ -C ₂₀	1.386(5)
C ₂ -N ₃	1.333(5)	C ₂₀ -C ₂₁	1.382(4)
N ₃ -C ₁₀	1.399(3)	C ₂₁ -C ₂₂	1.375(6)
C ₄ -C ₁₀	1.383(5)	C ₂₂ -C ₂₃	1.379(6)
C ₄ -C ₁₁	1.369(4)	C ₂₃ -C ₂₄	1.390(4)
C ₁₁ -C ₁₂	1.428(5)	C ₁₉ -C ₂₄	1.385(5)
N ₅ -C ₁₁	1.401(4)	N ₁ -H ₁	0.89(3)
N ₅ -C ₆	1.333(4)	C ₄ -H ₄	0.94(3)
C ₆ -N ₇	1.359(5)	N ₇ -H ₇	0.87(3)
N ₇ -C ₁₂	1.381(3)	C ₈ -H ₈	0.95(3)
C ₈ -C ₁₂	1.374(4)	C ₁₄ -H ₁₄	0.92(3)
C ₈ -C ₉	1.376(4)	C ₁₅ -H ₁₅	1.00(3)
C ₉ -C ₁₀	1.425(5)	C ₁₆ -H ₁₆	0.98(2)
N ₁ -C ₉	1.379(3)	C ₁₇ -H ₁₇	0.96(3)
C ₂ -C ₁₃	1.468(4)	C ₁₈ -H ₁₈	0.93(3)
C ₁₃ -C ₁₄	1.387(6)	C ₂₀ -H ₂₀	0.87(3)
C ₁₄ -C ₁₅	1.376(4)	C ₂₁ -H ₂₁	0.96(3)
C ₁₅ -C ₁₆	1.374(6)	C ₂₂ -H ₂₂	1.09(2)
C ₁₆ -C ₁₇	1.375(7)	C ₂₃ -H ₂₃	0.97(3)
C ₁₇ -C ₁₈	1.387(5)	C ₂₄ -H ₂₄	0.99(3)
C ₁₃ -C ₁₈	1.378(6)		

TABLE 8
BOND ANGLES ($^{\circ}$) IN BENZODIIMIDAZOLE MODEL COMPOUND

C ₂ -N ₁ -C ₉	109.1(3)	C ₁₉ -C ₂₄ -C ₂₃	120.3(4)
N ₁ -C ₂ -N ₃	111.6(2)	H ₁ -N ₁ -C ₂	131(1)
C ₂ -N ₃ -C ₁₀	105.9(3)	H ₁ -N ₁ -C ₉	120(1)
C ₄ -C ₁₀ -N ₃	130.3(3)	H ₄ -C ₄ -C ₁₀	121(1)
C ₄ -C ₁₀ -C ₉	120.7(3)	H ₄ -C ₄ -C ₁₁	122(1)
N ₃ -C ₁₀ -C ₉	109.0(3)	H ₇ -N ₇ -C ₆	125(2)
C ₁₀ -C ₄ -C ₁₁	117.0(4)	H ₇ -N ₇ -C ₁₂	126(2)
C ₄ -C ₁₁ -N ₅	130.5(3)	H ₈ -C ₈ -C ₉	127(1)
N ₅ -C ₁₁ -C ₁₂	108.6(2)	H ₈ -C ₈ -C ₁₂	119(1)
C ₄ -C ₁₁ -C ₁₂	120.9(3)	H ₁₄ -C ₁₄ -C ₁₃	119(2)
C ₆ -N ₅ -C ₁₁	106.0(3)	H ₁₄ -C ₁₄ -C ₁₅	119(2)
N ₅ -C ₆ -N ₇	111.9(2)	H ₁₅ -C ₁₅ -C ₁₄	120(1)
C ₆ -N ₇ -C ₁₂	108.6(3)	H ₁₅ -C ₁₅ -C ₁₆	121(1)
N ₇ -C ₁₂ -C ₈	131.7(3)	H ₁₆ -C ₁₆ -C ₁₅	121(2)
N ₇ -C ₁₂ -C ₁₁	104.9(3)	H ₁₆ -C ₁₆ -C ₁₇	118(2)
C ₈ -C ₁₂ -C ₁₁	123.5(3)	H ₁₇ -C ₁₇ -C ₁₆	121(2)
C ₉ -C ₈ -C ₁₂	114.5(3)	H ₁₇ -C ₁₇ -C ₁₈	119(2)
N ₁ -C ₉ -C ₈	132.1(3)	H ₁₈ -C ₁₈ -C ₁₃	118(1)
C ₈ -C ₉ -C ₁₀	123.4(3)	H ₁₈ -C ₁₈ -C ₁₇	121(1)
N ₁ -C ₉ -C ₁₀	104.5(2)	C ₁₉ -C ₂₀ -H ₂₀	120(2)
N ₁ -C ₂ -C ₁₃	123.0(3)	H ₂₀ -C ₂₀ -C ₂₁	119(2)
N ₃ -C ₂ -C ₁₃	125.4(3)	C ₂₀ -C ₂₁ -H ₂₁	117(1)
C ₂ -C ₁₃ -C ₁₄	121.1(3)	H ₂₁ -C ₂₁ -C ₂₂	123(1)
C ₂ -C ₁₃ -C ₁₈	120.3(3)	C ₂₁ -C ₂₂ -H ₂₂	123(2)
C ₁₃ -C ₁₄ -C ₁₅	121.0(4)	H ₂₂ -C ₂₂ -C ₂₃	117(2)
C ₁₄ -C ₁₅ -C ₁₆	119.7(4)	C ₂₂ -C ₂₃ -H ₂₃	121(1)
C ₁₅ -C ₁₆ -C ₁₇	120.2(3)	H ₂₃ -C ₂₃ -C ₂₄	118(2)
C ₁₆ -C ₁₇ -C ₁₈	119.8(4)	C ₂₃ -C ₂₄ -H ₂₄	124(1)
C ₁₃ -C ₁₈ -C ₁₇	120.6(4)	H ₂₄ -C ₂₄ -C ₁₉	115(1)
C ₁₄ -C ₁₃ -C ₁₈	118.6(3)		
N ₅ -C ₆ -C ₁₉	125.4(3)		
N ₇ -C ₆ -C ₁₉	122.7(3)		
C ₆ -C ₁₉ -C ₂₀	120.8(3)		
C ₆ -C ₁₉ -C ₂₄	121.0(3)		
C ₁₉ -C ₂₀ -C ₂₁	121.2(4)		
C ₂₀ -C ₂₁ -C ₂₂	120.5(4)		
C ₂₁ -C ₂₂ -C ₂₃	118.8(3)		
C ₂₂ -C ₂₃ -C ₂₄	121.0(4)		
C ₂₀ -C ₁₉ -C ₂₄	118.2(3)		

TABLE 9
LEAST SQUARES PLANES AND TWIST ANGLES



Plane 3

Plane 1

Plane 2

Equation of the Plane*		
Plane 1	$-3.5572x + 16.6240y - 3.4823z = 3.0684$	
Plane 2	$-4.3989x + 15.7519y - 2.7658z = 3.1459$	
Plane 3	$-4.4395x + 17.0610y - 2.1935z = 4.3429$	

Plane 1: Deviations x 10^{+3}			
$\sigma = 0.0048$			
N1	-4.1	N7	-5.3
C2	-0.2	C8	7.7
N3	-5.1	C9	1.7
C4	0.8	C10	1.6
N5	5.7	C11	2.6
C6	-8.5	C12	3.1

Plane 2: Deviations x 10^{+3}			
$\sigma = 0.0103$			
C13	1.7		
C14	-4.0		
C15	-3.5		
C16	13.3		
C17	-15.6		
C18	8.1		

Plane 3: Deviations x 10^{+3}			
$\sigma = 0.0067$			
C19	8.4		
C20	-8.6		
C21	5.8		
C22	-2.7		
C23	2.7		
C24	-5.6		

Twist Angles	
Plane 1 - Plane 2:	6.0°
Plane 1 - Plane 3:	7.9°

*x, y and z are fractional coordinates in direct space.
The deviations and coefficients of each coordinate are
in Angstroms.

3. THE MOLECULE

A mean carbon-carbon bond distance of 1.395\AA , with a root mean square deviation of 0.002\AA is found in the central benzene ring whereas the corresponding value for the end phenyl groups is 1.381\AA , with an rms deviation of 0.006\AA .

Table 10 lists ring dimensions for several imidazoles taken from the literature. Comparison of the four carbon-nitrogen lengths in this investigation with values in Table 10 shows that all bonds are within the expected range for a delocalized imidazole system.

The imidazole moieties in the model compound, however, can be seen to be slightly asymmetrical about a line passing through the apical carbon, C2 or C6, and bisecting the opposite bond. The difference between the N1-C2 and N3-C2 bond is 0.023\AA (roughly four times the estimated standard deviation); between the N5-C6 and N7-C6 bonds, 0.026\AA . There is also an associated difference of 3.2° between the C2-N3-C10 and C2-N1-C9 bond angles, and of 2.6° between the C6-N5-C11 and C6-N7-C12 bond angles. Though moderate, these differences point to a semi-localization of the carbon-nitrogen double bond on the pair with the shorter bond distance, which is consistent with the observation that hydrogens H1 and H7 are bonded to N1 and N7, respectively.

Semi-localization of the carbon-nitrogen double bond is characteristic of some benzimidazoles. Selected bond lengths and angles for these benzimidazoles are compared in Table 11. Table 11 also lists benzimidazoles in which π electron density is delocalized over the imidazole ring, as is apparently the case with 2-mercaptobenzimidazole. The compound exists as one of two tautomers, a thiol (I) or a thione (II). The resonance structures are drawn for each tautomer, excluding resonance structures contributed from the benzene ring. The negative charge on nitrogen in resonance structure (b) makes it an unlikely contributor to resonance stabilization of structure I. The number of favorable resonance contributors to structure II, however, predicts this structure to be thermodynamically favored over structure I.

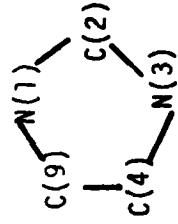


TABLE 10
SELECTED IMIDAZOLE RING DIMENSIONS (\AA)

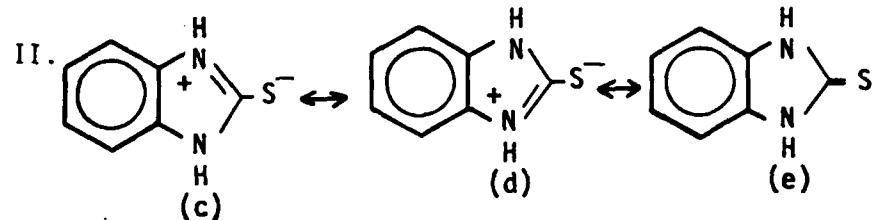
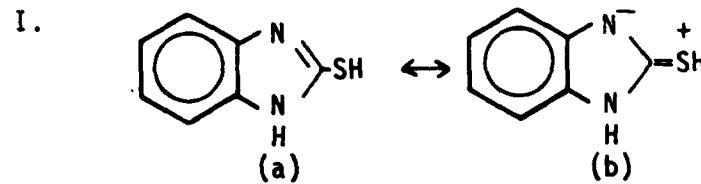
	<u>N(1)-C(2)</u>	<u>C(2)-N(3)</u>	<u>N(3)-C(4)</u>	<u>C(4)-C(9)</u>	<u>C(9)-N(1)</u>	<u>Reference</u>
Imidazole at -150°C	1.326	1.349	1.369	1.358	1.378	(23)
Imidazole at 24°C	1.311	1.337	1.372	1.311	1.381	(24)
6-mercaptopurine monohydrate	1.352	1.333	1.368	1.394	1.373	(25)
Hypoxanthine hydrochloride	1.333	1.318	1.376	1.368	1.375	(26)
1,3-dimethyl-2(3H)-imidazolethione	1.35	1.35	1.41	1.31	1.41	(27)
2-mercaptopbenzimidazole	1.362	1.362	1.383	1.400	1.383	(28)
2,6-diphenyl(1,2-d';5,4-d')benzodimidazole	1.356	1.333	1.399 ^a	1.425 ^a	1.379	(this work)

^aThese distances refer to the N(3)-C(10) and C(9)-C(10) bonds in the model compound.

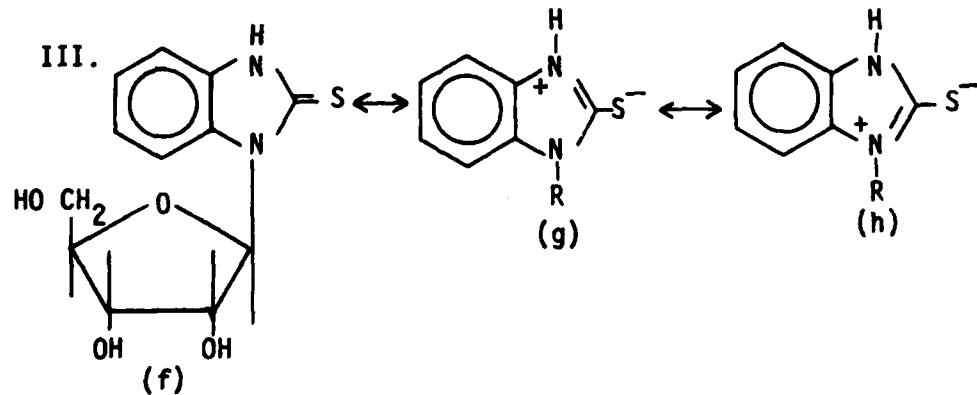
TABLE 11
COMPARISON OF SELECTED BOND LENGTHS AND ANGLES OF SEVERAL BENZIMIDAZOLES

Compound	(Ref.)	Bond Length (Å)	Bond Angle (°)		
		N ₁ -C ₂	N ₃ -C ₂	C-N ₁ -C	C-N ₃ -C
2-mercaptopbenzimidazole (I, II)*	(28)	1.362(6)	1.362(6)	110.4(4)	110.4(4)
2-thio-1-(β-D-ribofuranosyl)-3-H-benzimidazole (III)**	(29)	1.344(5)	1.377(5)	110.9(3)	109.4(3)
2-chloro-1-(β-D-ribofuranosyl)-benzimidazole (IV)***	(30)	1.293(7)	1.367(8)	104.4(4)	104.1(4)
Benzimidazole-benzimidazolium fluoroborate salt (protonated) (V)	(32)	1.320(3)	1.338(4)	109.1(2)	109.8(2)
Benzimidazole-benzimidazolium fluoroborate salt (non-protonated)	(32)	1.306(3)	1.364(3)	105.5(2)	106.9(2)
Benzimidazole	(31)	1.311(4)	1.346(5)	106.6(3)	104.2(2)
Imidazole 5,5-diethyl barbituric acid complex	(33)	1.300(3)	1.324(4)	105.2(2)	107.0(2)
2,6-diphenyl (1,2-d; 5,4-d')benzodimidazole	(this work)	1.356(5)	1.333(5)	109.2(3)	106.0(3)

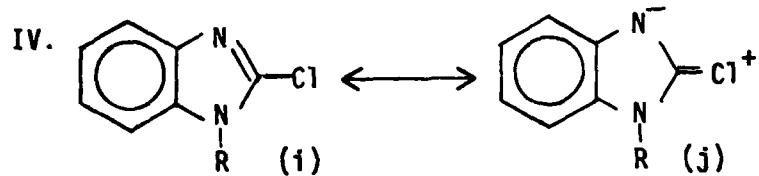
*C=S bond length, 1.671(8) Å
**C=S bond length, 1.693(4) Å
***C=S bond length, 1.768(8) Å



The crystal structure determination of 2-mercaptopbenzimidazole (Reference 28) shows hydrogen atoms covalently bonded to both nitrogen atoms, equivalent C-N and C-N bond lengths intermediate between single and double bonds, and a carbon-sulfur double bond, which confirms structure II as the preferred tautomer. 2-thio-1-(β -D-ribofuranosyl) 3-H-benzimidazole (III) is similar to mercaptobenzimidazole in that the apical carbon is double bonded to sulfur (Reference 29). The presence of an electron donating group, ribofuranosyl, increases the thermodynamic favorability of (g) and makes it a stronger contributor to resonance. Hence, though the imidazole ring is still delocalized, one C-N bond will be slightly shorter than the other. There is an 0.033\AA difference between the C2-N1 and C2-N3 bond lengths.



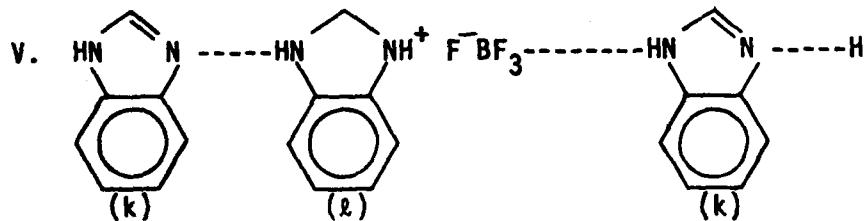
In contrast, the chloro analog of 2-thio-1-(β -D-ribofuranosyl) benzimidazole (IV) shows semi-localization of the carbon-nitrogen double bond, with a 0.074\AA difference between the C2-N1 and C2-N3 bond lengths (Reference 30).



The positive charge on chlorine in resonance structure (j) makes it a very weak contributor to resonance stabilization.

Benzimidazole has a tendency to form intermolecular hydrogen bonds. The involvement of the electron lone pair on nitrogen in hydrogen bonding lessens its contribution to the π system in the ring. This would explain in part the apparent semi-localization of electron density on the C2-N1 bond in benzimidazole (Reference 31). The difference in C-N bond lengths is 0.035 \AA .

An interesting example of the effect of environment on the delocalization of the imidazole ring is the benzimidazole-benzimidazolium fluoroborate salt (Reference 32), in which the fluoroborate anion forms a salt with one benzimidazole cation.



Thus (κ) is in an environment similar to intermolecular hydrogen bonded benzimidazoles, with a marked difference in C-N bond lengths (0.058 \AA). The protonated form (ι), on the other hand, has hydrogen atoms covalently bonded to each nitrogen, delocalizing the ring and minimizing differences in bond lengths (0.018 \AA).

The extent of semi-localization in the diimidazole model compound may now be qualitatively evaluated in terms of the correlation between the extent of semi-localization and the difference in C-N bond lengths. Compared to other benzimidazoles cited, one concludes that the imidazole ring in the model compound exhibits only a slight degree of semi-localization of the C-N double bond, due to extensive hydrogen bonding of all four nitrogen atoms with solvent water molecules. This is similar to that observed for 5,5-diethylbarbituric acid - imidazole complex, which experiences hydrogen bonding between NH---N on the imidazole (Reference 33). The bond length difference between C2-N1 and C2-N3 is slight at 0.024\AA .

It would be shortsighted to use bond length differences alone to determine whether a system is semi-localized or not. Such factors as the contributions to resonance, environment of the molecule, and opportunity for hydrogen bonding must be taken into account.

The quantitative determination of delocalization in a system depends on calculation of bond orders. In an analysis of imidazo-[1,2-b]-as-triazine (Reference 34), simple LCAO calculations were used to correlate bond orders with bond lengths to evaluate the extent of semi-localization in a system where comparison of bond lengths was not a sufficient determinant. Least squares fit of the reported bond lengths vs bond orders in Figure 2 of Reference 34 produces a linear function with the equation $y = -4.57x + 6.808$, where y is the bond order and x is the bond length, with a standard deviation 0.168 and a correlation coefficient -.517. A comparison of the results of the imidazo-[1,2-b]-as-triazine study with carbon-nitrogen bonds reported in this investigation calculates a bond order of 0.718 for the N3-C2 bond and of 0.613 for the N1-C2 bond, on a scale where .500 is the bond order of a single bond, 1.000 is the bond order of a double bond. The calculated bond orders indicate that both carbon-nitrogen bonds are higher than single bond order, with the N3-C2 bond possessing more double bond character than the N1-C2 bond.

The difference in the C9-N1-C2 and C10-N3-C2 bond angles is reflected in larger N3-C10-C9 and N5-C11-C12 bond angles (109.0° , 108.6° , respectively) and smaller N1-C9-C10 and N7-C12-C11 angles (104.5° and

104.9° respectively). The other C-N bonds, N1-C9, N3-C10, N5-C11 and N7-C12, appear roughly equivalent at about 1.379 Å to 1.401 Å.

Another significant feature of the diimidazole structure is the cis orientation of the lone pair nitrogen atoms. The nonstereo-specific synthesis should result in a crystalline product that contains both isomers. A mixture of isomers most probably would lead to disorder in the structure; fortunately, disorder was not a serious problem in this investigation. An explanation for the preferential isolation and crystallization of one isomer over another is discussed in the next section.

4. WATER STRUCTURE

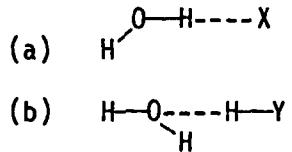
An early indication of the presence of solvent in the crystal was the difference between the calculated and measured densities (1.07 g/cc and 1.31 g/cc respectively). Both the ethanol-grown and sublimed crystals appeared to contain solvent since their measured densities were comparable to each other. Difficulties experienced by synthetic polymer chemists in drying polybenzimidazoles (Reference 13) suggested that these compounds strongly attract water. The strength of this attraction was demonstrated by the fact that in the crystallization of the model compound water was carried over with the material in the sublimation process. Thermogravimetric/Mass Spectrometric (TGA) analysis showed a substantial weight loss (\approx 30%) at 375° attributed mainly to water. The stability of the crystals in air at room temperature and normal humidity indicated that the water present was incorporated into the crystal lattice rather than merely absorbed through the surface.

Refinement of the structure confirmed the presence of 16 water molecules per unit cell. Elucidation of the water network gave a possible explanation for the preferential crystallization of the cis isomer over the trans isomer. Perhaps the hydrogen bonded network of the cis isomer provides a crystalline structure that is more efficiently packed and hence favored over a possible structure involving the trans isomer. Additionally, the preference of water for the cis isomer could affect the solubility of both isomers, leading to an unexpected separation of the two isomers during purification and recrystallization of the crude product.

It is probable that the sublimed crystal also involves the cis isomer exclusively. Density measurements indicate that the sublimed crystals are also hydrated. It is possible that any water present in the crude material was carried over in the sublimation process to form the hydrate of the cis isomer, while the starting material left in the bottom of the sublimation apparatus may have been a mixture of the trans isomer and impurities.

Survey Weissenberg and precession photographs show that the sublimed crystal belongs to the same space group ($P2_1/c$) as the ethanol grown crystal. A cursory comparison of a limited diffractometer data set collected on the sublimed crystal with data collected on the ethanol-grown crystal shows little difference in the relative magnitude of intensities for selected reflections. This indicates that the cis isomer and accompanying water structure persist in crystals grown by sublimation, although a more detailed comparison of the two structures would require a full, three-dimensional structure determination of the sublimed material.

Solvent water molecules in the ethanol grown crystal form hydrogen bonds bridging molecules related by an inversion center. Surprisingly, hydrogen bonding between molecules related by a glide plane is not observed. The network makes maximal use of the four coordination sites on each water molecule. At least three sites are engaged on each water molecule; in the case of O1 and O3, all four coordination sites are occupied. Each water acts as both a hydrogen bond donor (illustrated in (a)) and a hydrogen bond acceptor (illustrated in (b)).



Donor-acceptor relationships for each water are detailed in Table 12.

Four water molecules in the asymmetric unit link N3 and N5 to form a large ring (Figure 4). The ring bends over the molecule, with the best plane containing atoms N3-04-01-N5 inclined 37° to the benzodimidazole plane. The best plane through 04-02-03-01 makes roughly a 53° angle with

TABLE 12

DONOR-ACCEPTOR RELATIONSHIPS AND CONTACT
DISTANCES (Å) FOR WATER MOLECULES

Atom	Donor	Acceptor	Symmetry Operation	Contact Distance
O_1	O_1	N_5^*	2	2.837(4)
	O_3^*	O_1	2	2.755(3)
	O_1	N_3^*	4	2.808(4)
	O_3^*	O_1	6	2.796(3)
O_2	O_2	O_3^*	2	2.819(4)
	O_2	O_4^*	2	2.734(3)
	N_7^*	O_2	5	2.835(5)
O_3	O_3	O_1^*	2	2.755(3)
	O_3	O_1^*	6	2.796(3)
	N_1^*	O_3	1	2.881(4)
	O_2^*	O_3	2	2.819(4)
O_4	O_4	N_3^*	2	3.081(4)
	O_4	N_5^*	4	3.084(5)
	O_2^*	O_4	2	2.743(3)

Symmetry Operations: If the atom has fractional coordinates of x, y, z , then atom is located at the coordinates indicated by each symmetry operation:

<u>Sym Op</u>	<u>Fract Coord</u>	<u>Sym Op</u>	<u>Fract Coord</u>
1	$x \quad y \quad 1+z$	5	$-x \quad 1-y \quad 2-z$
2	$x \quad y \quad z$	6	$-x \quad 1-y \quad 1-z$
4	$1-x \quad 1-y \quad 2-z$		

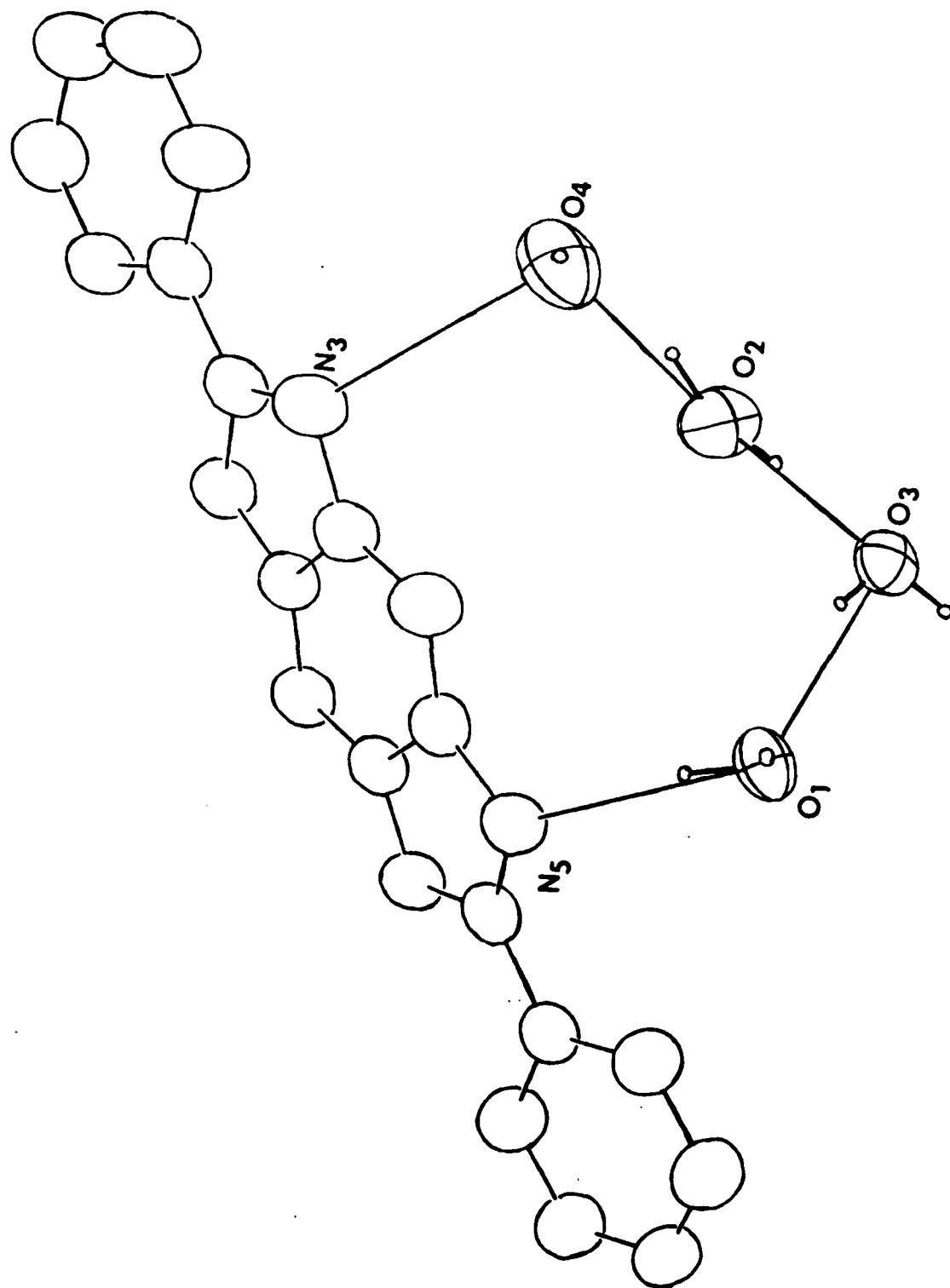


Figure 4. The Four Hydrogen Bonded Water Molecules in the Asymmetric Unit Bridging N_3 and N_5 of the Benzodiazole Segment, Viewed Approximately Down \underline{c} .

the N3-04-01-N5 plane. Table 13 lists bond lengths and angles for water molecules. The average O-H bond is 0.83 \AA ; the average H-O-H bond angle is 108°. The O3-H06 bond length is especially short at 0.72 \AA , while the H-01-H bond angle of 98° is somewhat smaller than the normal value. Contact distances range from 2.734 \AA to 3.084 \AA , within the expected range for hydrogen bonds.

TABLE 13

BOND DISTANCES (\AA) AND BOND ANGLES (°) AND STANDARD DEVIATIONS IN BRIDGING WATER STRUCTURE

O1-H01	1.01(3)	H01-01-H02	98(2)
O1-H02	0.81(2)	H03-02-H04	116(2)
O2-H03	0.82(2)	H05-03-H06	112(2)
O2-H04	1.22(2)		
O3-H05	1.00(2)		
O3-H06	0.72(2)		
O4-H07	0.86(3)		

When viewed along a, molecules related by a center of symmetry at (1/2, 0) are stacked such that O1 and O4 of one molecule hydrogen bonds with N3⁺ and N5⁺, respectively, of the other molecule. (+ denotes atoms related by an inversion center to those in the asymmetric unit.) Thus, two four-membered rings are formed whose contact distances are comparable to those in the asymmetric unit. Figures 5 and 6 show the water structure of a pair of molecules related by an inversion center. O1 is a hydrogen bond donor to N5 and N3⁺, and O4 is a hydrogen bond donor to N3 and N5⁺. In addition, hydrogen bonds along a link O2 with N7⁺ of another molecule related by another inversion center at (0, 1/2, 0), with N7 acting as a hydrogen bond donor.

When viewed along c, molecules related by a center of symmetry at (0, 1/2, 0) are bridged by hydrogen bonds between O1 and O3 to O3⁺ and O1⁺, forming still another four-membered ring composed solely of water molecules. Contact distances in the ring are 2.755 and 2.796 \AA . Absent in Figures 5 and 6 are the additional hydrogen bonds between O3 and N1⁺, and O2 and N7⁺ mentioned above.

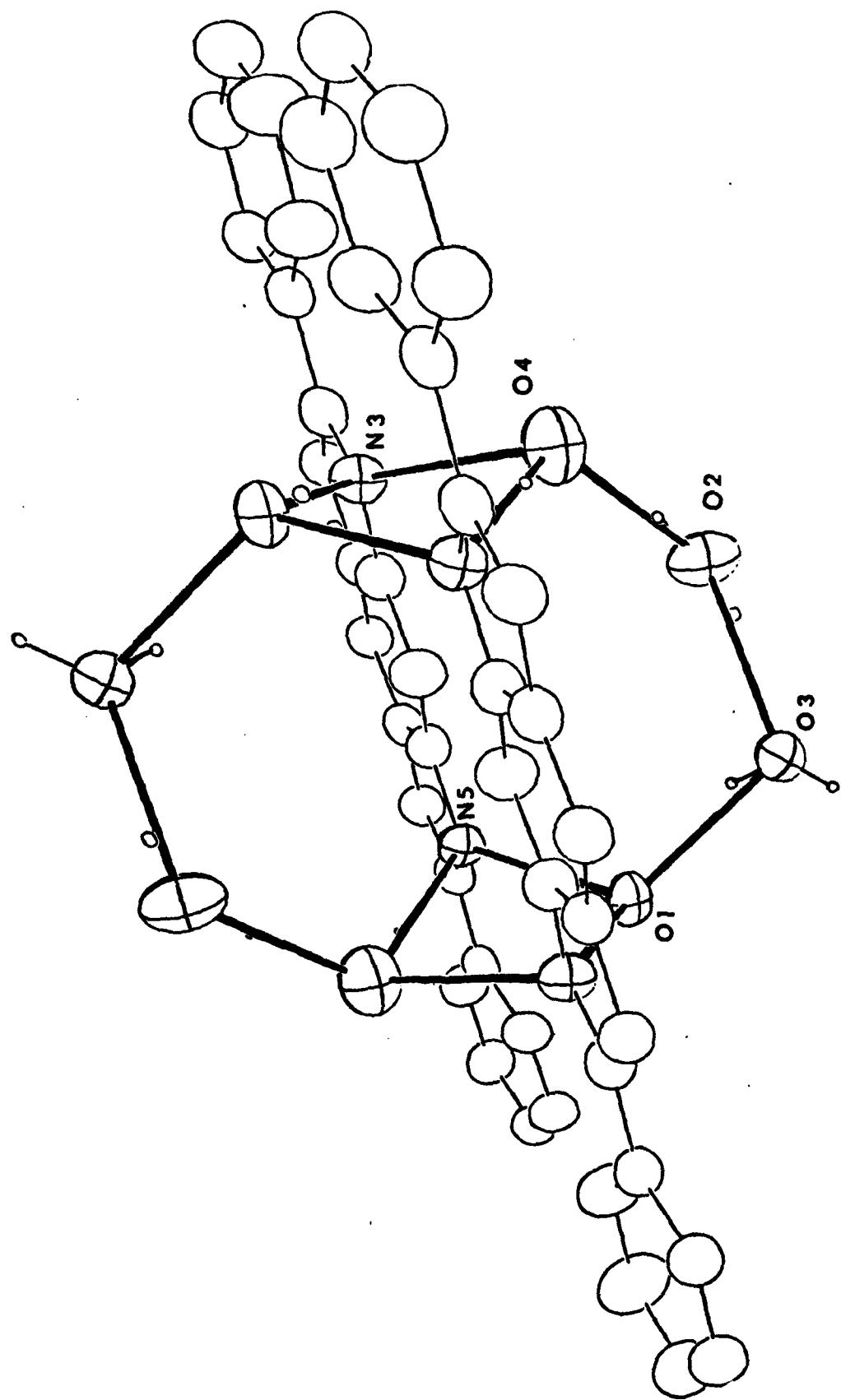


Figure 5. Water Structure of a Pair of Molecules Related by an Inversion Center Viewed Approximately Down z.

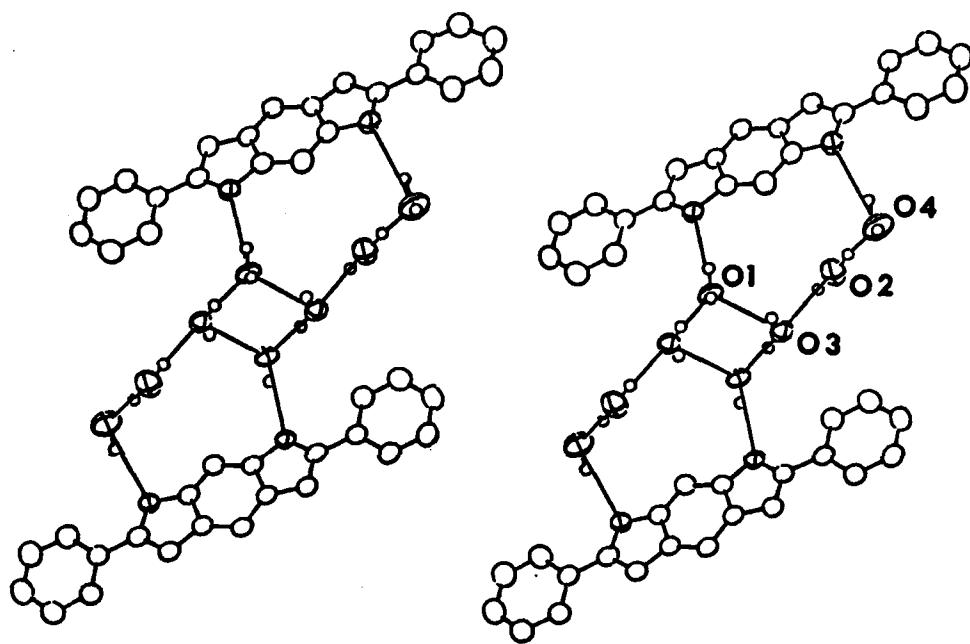


Figure 6. Stereoview of Water Structure of a Pair of Molecules Related by an Inversion Center, Viewed Approximately Down c.

5. PACKING

The c glide plane perpendicular to b generates two vertical columns of molecules of different orientation, characteristic of a herringbone pattern. The molecules are inclined at an angle of 48.2° to the b axis. The perpendicular distance between adjacent molecules in a stack is 3.93A. A stereoview of one unit cell is shown in Figure 7.

Thus, molecules within a particular stack are intricately connected through hydrogen bonds, while weaker van der Waals interactions relate molecules of adjacent stacks. Since no hydrogen bonding occurs between molecules along b, crystals would be expected to cleave most readily perpendicular to b, or parallel to the ac plane. Experience in cleaving ethanol-grown crystals of the model compound confirms these predictions.

Comparison of Figure 7 with the packing plots of c-bisoxazole (Figure 8) and t-bisthiazole (Figure 9) shows similarities between the three structures. Delocalization of the fused ring system accounts for the high degree of planarity in the c-bisoxazole model compound, but in bisthiazole planarity is precluded by the steric clash between nitrogen and sulfur atoms on the thiazole ring with ortho hydrogen atoms on the phenyl substituents, resulting in a torsion angle of 23.2° between the benzobisthiazole moiety and the phenyl groups.

No hydrogen bonding occurs in c-bisoxazole and t-bisthiazole; packing forces are of the van der Waals type. The low heat of sublimation in c-bisoxazole reflects the absence of significant intermolecular interaction in the crystal.

6. WATER UPTAKE EXPERIMENTS

It has already been noted that the polybenzimidazoles have a high affinity for water. In the case of PDIAB, 379 hours of atmospheric exposure produces an uptake of water of 20.1%, or a pickup of 2.6 moles of water per mole of repeat unit. In a related set of experiments, exposure of a dry sample of PDIAB to a humidity chamber for forty eight hours resulted in a pickup of 30.2%, or 3.9 moles of water per mole of repeat unit. These experiments are in good agreement with the four water molecules per asymmetric unit found in the structure of the diimidazole model compound. Thus, it appears that saturation of available binding sites for water is achieved with four water molecules per polymer repeat unit.

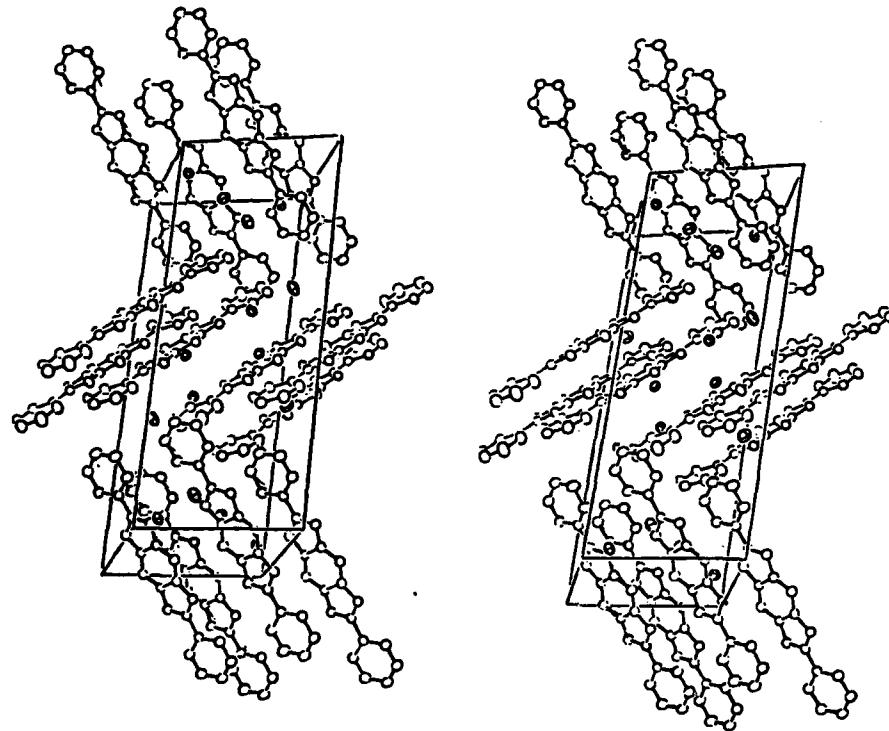


Figure 7. Stereoview Down the Negative a-axis of the Molecular Packing in the Unit Cell. Water molecules are contoured for clarity. The b-axis is vertical.

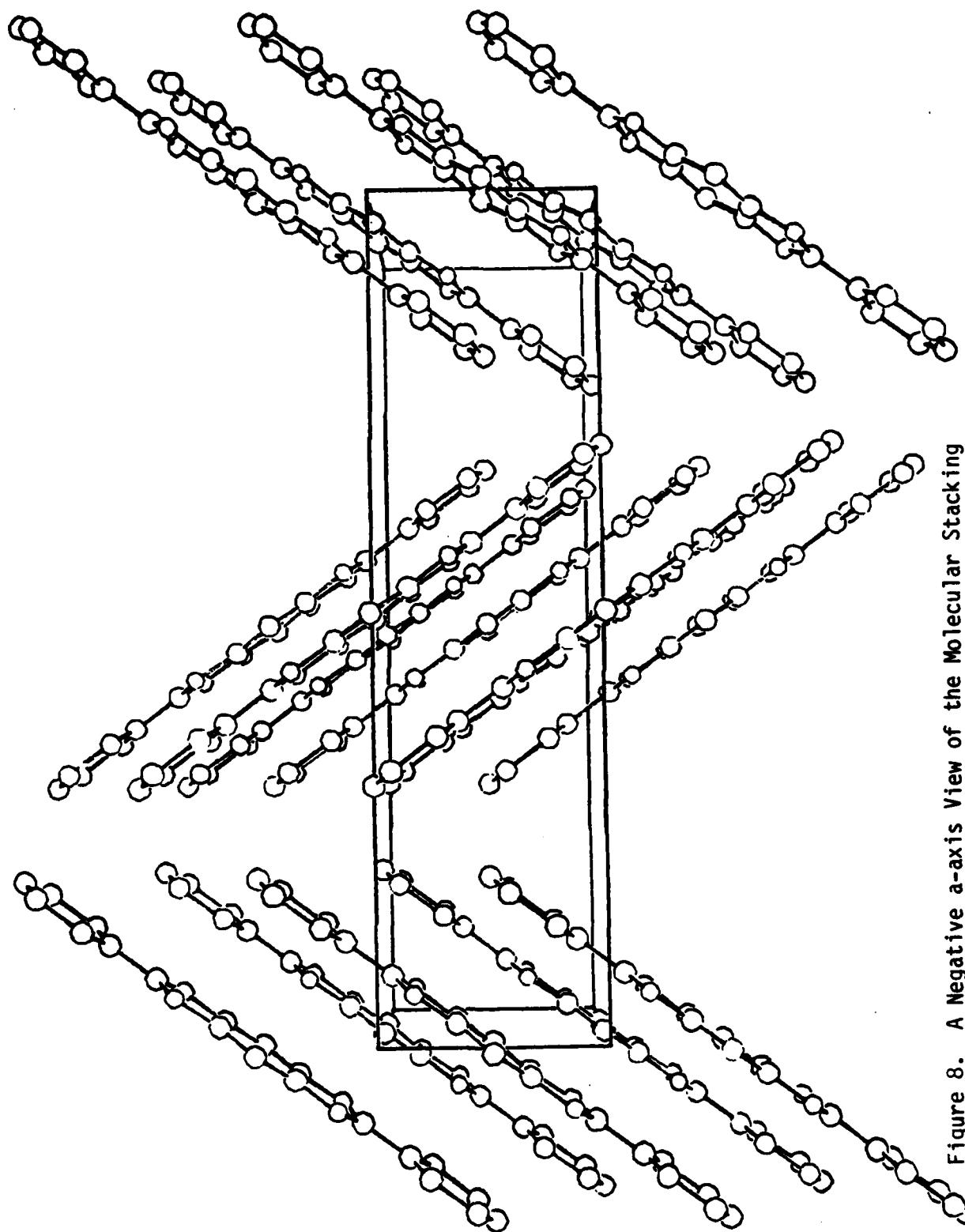


Figure 8. A Negative \bar{a} -axis View of the Molecular Stacking in the Benzobisoxazole Unit Cell. The \bar{b} -axis is vertical and the \bar{c} -axis is horizontal. Taken from Figure 2 of Reference 11.

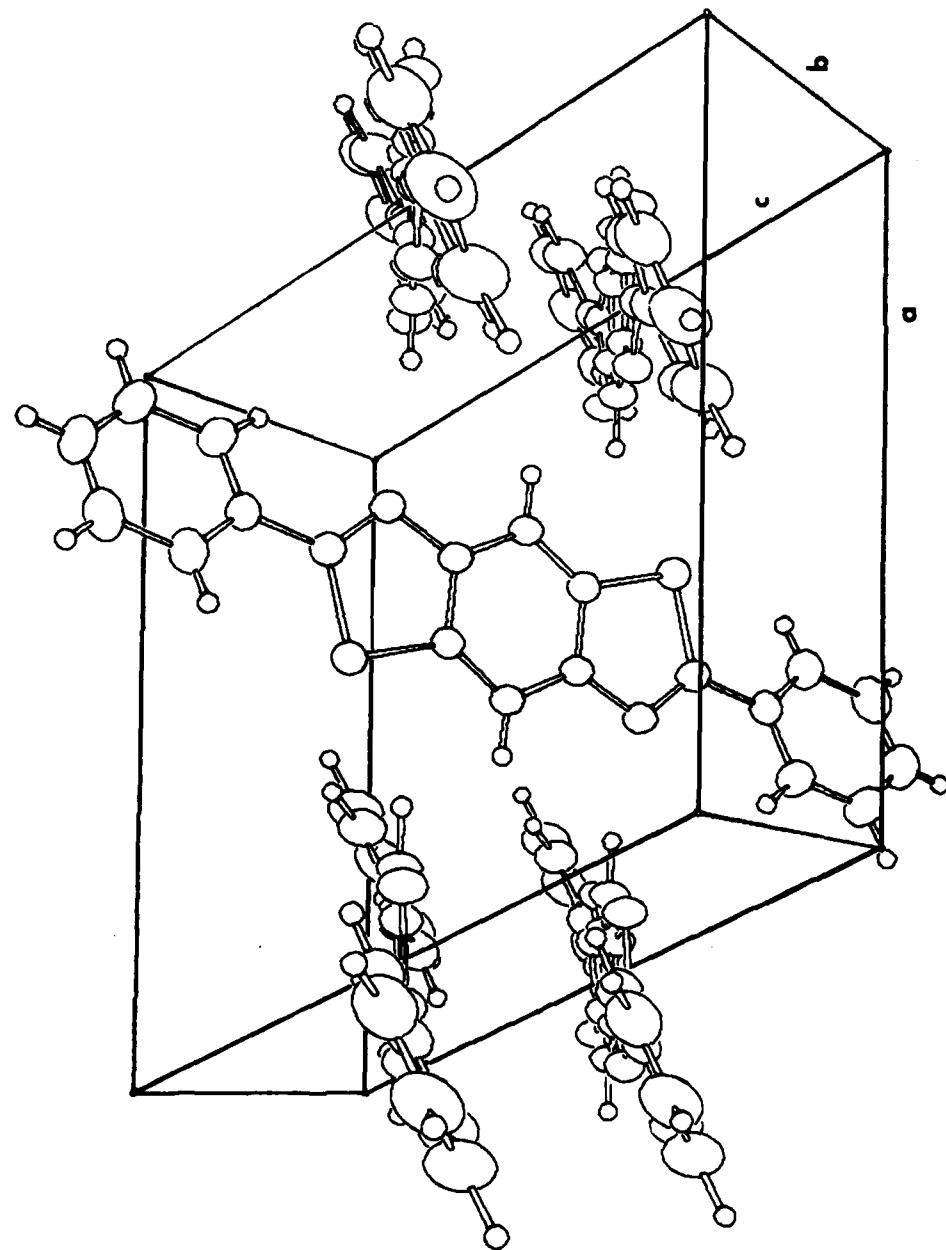


Figure 9. Molecular Stacking in the Benzobisthiazole Unit Cell. The a-axis is horizontal and the c-axis is approximately vertical.

Although repeated heating of PDIAB under vacuum can drive off this water, there is good evidence that much of the chemically bound water remains intact in the solid material.

The retention of water by the diimidazole model compound was examined by thermogravimetric/mass spectral analysis and differential scanning calorimetry. TGA/MS of the impure model compound shows a 30% weight loss at 375°C , 61% at 480°C , and 84% at 915°C . The fairly low ion intensities for this amount of weight loss points to extensive sublimation of the sample. At least three volatile products are detected below 480°C , with water as the principal product.

DSC data indicates higher lattice energies in the diimidazole model compound compared to the PBO and PBT model compounds. Whereas melting endotherms are observed at approximately 300°C for the PBO and PBT model compounds (the T_m of c-bisoxazole is obscured by the onset of sublimation), the diimidazole model compound exhibits two broad endotherms at 300° and 480°C , which are not characteristic of melting transitions but indications of the possible loss of water.

7. RELATIONSHIP TO POLYMER FILM AND FIBER DATA

Figure 10 depicts a wide angle x-ray diffraction photograph of poly(p-phenylenebenzodiimidazole) solution cast film. The pattern is interpreted in terms of a sample consisting of randomly ordered crystallites. A very faint outermost ring (visible on the photographic negative only) corresponds to an interplanar spacing of 2.4\AA . The d-spacing of the prominent broad ring measures 3.97\AA , which correlates well with the interplanar spacing calculated for the model compound (3.93\AA).

A few d-spacings for some of the more intense reflections in the single crystal study may be calculated for a hypothetical polymer powder pattern. The intense 141 and 210 reflections, with calculated d-spacings of 3.77\AA and 3.86\AA , respectively, correlate with the measured d-spacing in the solution cast film (3.97\AA).

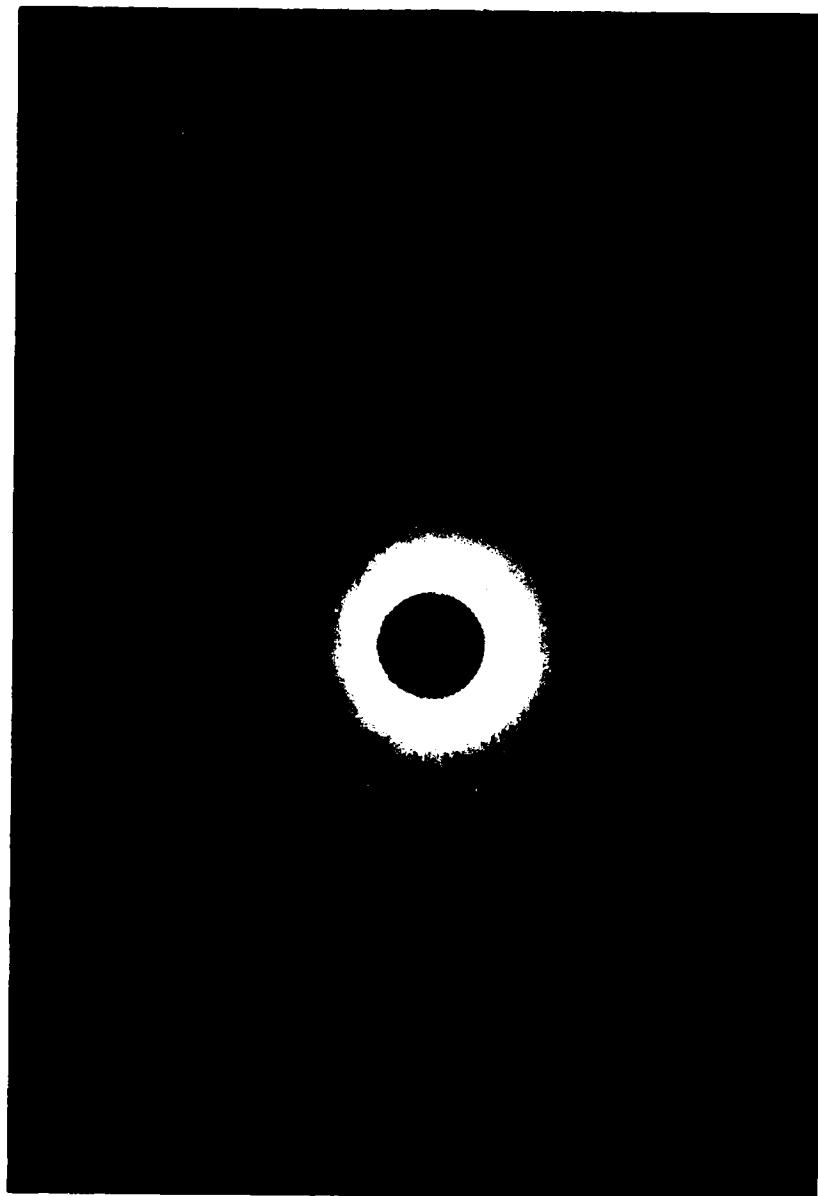


Figure 10. Wide Angle X-Ray Diffraction Pattern of Solution Spun Poly (p-phenylenebenzodiimidazole) Film.

In the absence of any fiber diffraction data for PDIAB, a plausible model for the packing in oriented fibers would involve chains of polymer extending in the direction of elongation, in the manner found for PBT (References 8 and 9). It now seems likely that a hydrogen bonded water structure, which plays such an important role in the crystal packing of the model compound, might serve as lateral connections between polymer chains. Given the increased lattice strength due to these intermolecular forces, it is expected that PDIAB would have a higher T_m than either PBO or PBT, as these polymers would be held in a crystalline lattice solely by van der Waals forces.

8. X-RAY POWDER DIFFRACTION PATTERNS

It was mentioned previously that crystals grown from ethanol and sublimation had similar structures. This conclusion was based on a comparison of unit cell dimensions and uncorrected intensities of a few reflections (Table 1). As a result, powder patterns of both materials should exhibit obvious similarities. It was decided at this point to record Debye-Scherrer photographs of the two materials in order to check for polymorphism. Specimens of both crystals were prepared by grinding prior to being loaded into 0.5 mm glass capillary tubes. The tubes were mounted in a 57.3 mm radius powder camera and irradiated with filtered CuK_{α} radiation for 48 hours. The crystals grown from ethanol produced a much richer pattern of lines visible out to $2\theta=53^{\circ}$. The sublimed sample, on the other hand, did not diffract beyond about $2\theta=38^{\circ}$, and lines observed below this angle were sparse and fairly diffuse. The experimental powder patterns are presented in Table 14 and Figure 11. Taking into account the low resolution and overall poor quality of the sublimed pattern compared to the ethanol-grown one, a line-for-line comparison of the two patterns shows them to be in only fair agreement. Unexplained is the discrepancy in the location and intensity of the 7.8\AA^0 line (7.38\AA^0 in the sublimed pattern), as well as the apparent mismatch in the d-spacing of the 3.76\AA^0 line (4.04\AA^0 in the pattern of sublimed crystals). In view of the rather convincing evidence presented in Table 1, it would be premature at this point to cite these observed differences in the powder patterns as evidence of polymorphism.

TABLE 14
MEASURED POWDER PATTERNS FOR THE ETHANOL-GROWN
AND SUBLIMED SAMPLES

$2\theta(^{\circ})$	<u>Ethanol-Grown</u>			<u>Sublimed</u>		
	d(meas) (\AA)	$^{\circ}$	Intensity ^a	2θ	d(meas)	Intensity ^a
7.8	12.31		43	7.37	12.00	66
11.38	7.78		100	11.99 ⁰	7.38	25
12.95	7.84		17	too weak		
14.23	6.72		16	14.74	6.01	22
15.31	5.79		16	too weak		
17.85	4.96		19	18.24	4.86	60
19.26	4.61		22			
21.16	4.19		43	20.99	4.23	48
23.68	3.76		52	21.94	4.04	100
25.08	3.55		31	25.56	3.48	37
26.06	3.42		62			
27.21	3.28		32	27.19	3.28	42
29.03	3.07		23	too weak		
30.10	2.97		12	31.74	2.82	5
33.96	2.64		6			
35.77	2.51		6	36.27	2.48	5
40.88	2.20		6	37.87	2.37	6

^aIntensities (peak heights) are derived from microdensitometer scans of Debye-Scherrer photographs and are scaled so that the strongest line has an intensity of 100.

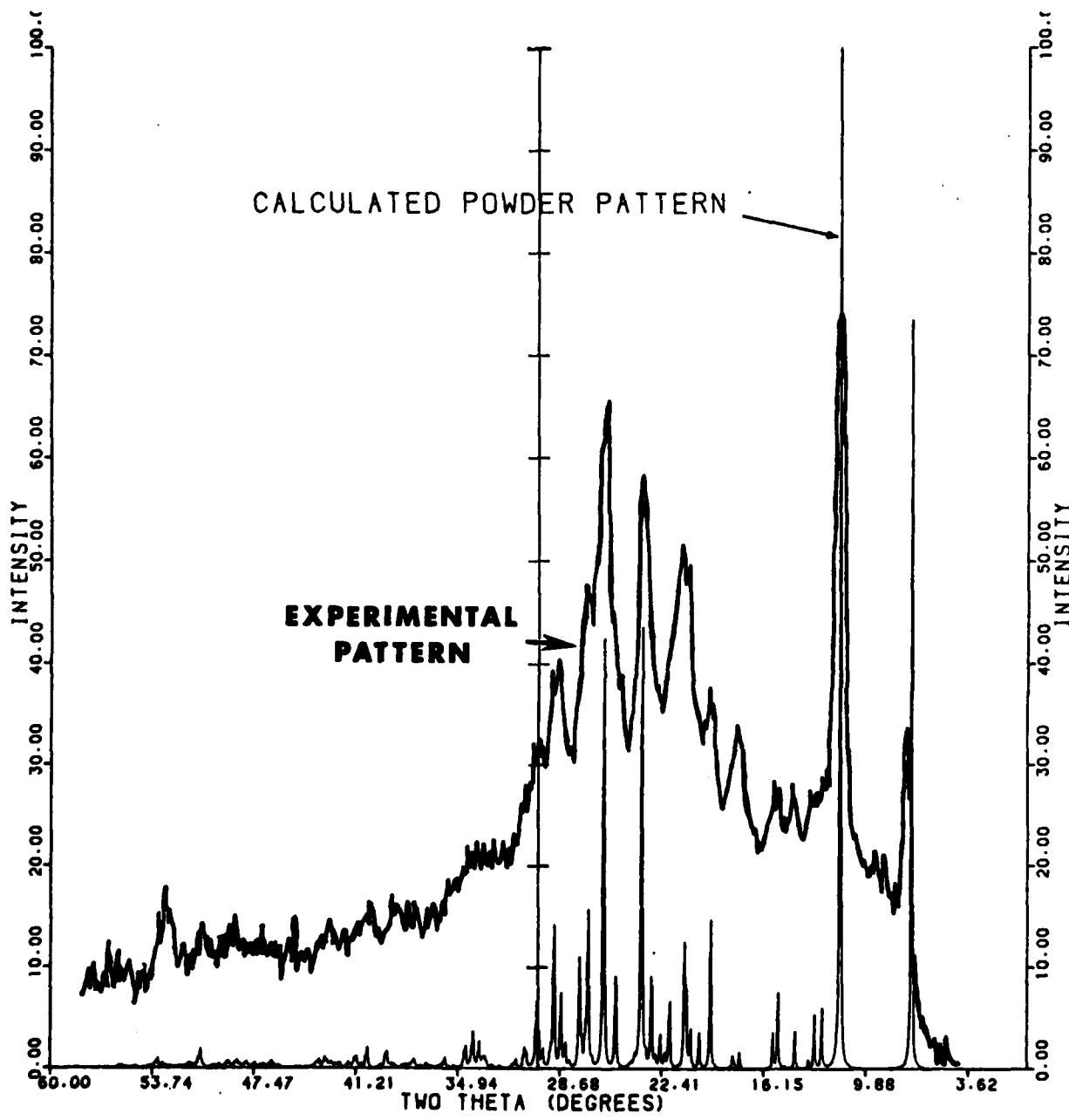


Figure 11. Comparison between the Microdensitometer Scan of a Debye-Scherrer Experimental Powder Pattern for the Ethanol-Grown Crystal and the Computed Powder Pattern using the POWD 7 Program for the Diimidazole Model Compound.

The intense 12.3\AA (12.0\AA in the sublimed pattern) reflection undoubtedly corresponds to the monomer repeat of $12.197(6)\text{\AA}$ in the model compound. The other prominent d-spacings (7.78 , 4.86 , 4.04 , 3.76 and 3.42\AA) have interpretations in terms of recurring intramolecular distances and intermolecular chain separations. It should be noted that the broad 4.86 , 3.48 , and 2.82\AA lines in the sublimed pattern appear to be fully resolved in the pattern of the ethanol grown crystals.

9. SIMULATED POWDER PATTERNS COMPUTED WITH POWD 7

The calculation of the simulated Debye-Scherrer pattern for a known crystal structure is possible with Smith and Holomany's POWD 7 Fortran Program. Figure 11 compares the experimental pattern of the diimidazole model compound with the calculated pattern on the basis of the atomic coordinates in Tables 4 and 6 as input parameters. Table 15 lists the d-spacings and intensities as well as to assign hkl values to the strongest lines. Excellent agreement is noted not only for the d-spacings, but also for the relative intensities of the lines. In addition, reducing the occupancy of the solvent water molecules from 100 to 50% does not alter significantly the simulated pattern. Thus, it would appear that the integrated intensities of the prominent lines are attributable primarily to the model compound and not to the water structure.

TABLE 15
CORRELATION BETWEEN EXPERIMENTAL AND SIMULATED POWDER
PATTERNS AND ASSIGNMENT OF BRAGG $h\bar{k}\ell$ PLANES FOR STRONGEST LINES

Experimental Pattern for Ethanol Grown Crystal		Pattern Computed with POWD 7		
$h\bar{k}\ell$	d-spacing(Å)	Intensity	d-spacing(Å)	Intensity (100% Occupancy)
0 2 0	12.31	43	12.48	63
1 1 1	7.78	100	7.73	100
1 4 1	4.96	19	4.95	1
1 2 2	4.61	22	4.58	16
2 2 1	4.19	43	4.23	12
1 4 1	3.76	52	3.77	53
1 5 1	3.42	62	3.43	52
2 4 0	3.28	32	3.31	19
2 5 0	3.07	23	3.08	16

SECTION VI

CONCLUSIONS

1. The crystal structure analysis of the diimidazole model compound has provided molecular structure information applicable to polymeric benzimidazoles in general, and in particular to rod-like benzimidazoles. The structure determination will be useful both for homopolymer structural studies and in the morphology of blends and molecular composites. With renewed interest on the part of the chemical industry aimed at the large scale production of polybenzimidazoles, this work takes on added interest since there is little published data on benzimidazoles and their interaction with water.
2. One can now begin to understand why it has not yet been possible to synthesize high molecular weight, rod-like PBI, specifically PDIAB. At low molecular weight, oligomers crystallize out of polyphosphoric acid (PPA) solution before the condensation polymerization is very far advanced, due to preferential formation of a stable hydrogen-bonded network in the presence of the excess water of condensation. This hydrogen-bonded structure is apparently more energetically favorable than the fully protonated molecular species dissolved in the solvent.
3. PBI's cannot be fully dried under normal drying conditions. Even after days of vacuum oven treatment, 5% or more water is retained in the polymer, as determined by thermogravimetric analysis. Temperatures as high as 350-450°C are required to remove the residual water, at which point the polymer may also begin to degrade. The strong affinity for water is manifested by the ability of PBI's to dry desiccant! Furthermore, the observation that crystals of the model compound grown by sublimation contain the water network is remarkable, implying that water must be carried along with the molecules during the sublimation process. A stoichiometric "limit" of bound water for PDIAB of 30% by weight is the apparent upper limit for water uptake by PBI.
4. It is now more clear why benzoxazoles (PBO) and benzothiazoles (PBT) are not water sensitive. The benzimidazoles have two types of nitrogen atoms, one that is protonated and one that possesses the lone electron

pair. In order to form a stable water network both types are apparently necessary, one functioning as a proton donor and the other as a proton acceptor. PBO's and PBT's have only lone pair electron nitrogen atoms, and in addition, the increased delocalization present in the heterocyclic rings may contribute to the lack of hydrogen bonding to water. The variation in the strength of the hydrogen bonds in PBI's probably results in the reversibility of water uptake, since some of the bonds can be more easily broken than others.

5. This work makes possible certain predictions concerning the structure of PBI polymer:

a) Fibers or films spun from concentrated dopes of high molecular weight PDIAB in PPA would be highly oriented and should exhibit three dimensional crystallinity. They would have similar or somewhat improved modulus compared to PBT, but with higher tensile strength and significantly higher lateral strength and compressive modulus, due to the formation of a hydrogen-bonded water network laterally linking polymer molecules.

b) PDIAB bulk material should have a significant energy absorption mechanism due to the hydrogen-bonded water molecules. For example, an infrared or ultraviolet laser beam would have to deposit much more energy to damage this polymer backbone than for PBT or PBO, since the loss of water would itself dissipate a great deal of absorbed energy. Similarly, PDIAB should also act as a radar absorbing material.

c) The problem of water retention in PBI's would be partially eliminated by the placement of appropriate substituents on the imidazole nitrogen atoms. This would allow PBI to be used as a structural material without the dimensional changes caused by the binding of water.

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APPENDIX - TABLE 3
OBSERVED AND CALCULATED STRUCTURE FACTORS (X10)

-12,0,L			8	17	-19	6	9	6	-10,1,L		
			9	36	-26	7	48	-50			
6	66	-52	10	67	53	8	8	22	1	6	18
						9	21	-22	2	29	5
-12,1,L			-11,4,L			-11,9,L			-11,12,L		
6	15	-10	2	32	-6	3	25	-3	4	47	60
7	9	-11	3	59	-68	4	21	-14	5	13	21
			4	4	-15	5	32	44	6	6	-5
-12,2,L			5	24	-4	6	38	-37	7	88	-78
			6	35	-29	7	91	-86	8	25	-24
6	32	-27	7	49	-48	8	9	-1	9	31	-19
7	16	6	8	59	-50	9	52	42	10	30	16
			9	9	32				11	76	69
-12,3,L			10	65	68	-10,2,L			-11,19,L		
6	45	-39	-11,5,L			3	16	30	1	6	-8
7	28	26	2	44	34	4	23	5	2	48	-32
			3	31	23	5	9	5	3	91	84
-11,0,L			4	23	-8	6	19	24	4	84	89
			5	88	97	7	9	-6	5	36	-32
4	27	37	6	6	12	8	46	49	6	143	137
6	43	36	8	57	-46	9	19	8	7	1	-13
			8	23	-6				8	29	-22
			9	52	-39	-11,11,L			9	17	24
-11,1,L			10	63	55				10	6	8
						4	16	5	11	45	-33
2	26	3	-11,6,L			5	89	-62	-10,3,L		
3	33	-34				6	9	9			
4	12	-12	2	35	-42	7	53	-54	1	2	26
5	27	13	3	6	-19	8	20	19	2	6	13
6	32	-21	4	42	-21				3	48	-32
7	15	6	5	9	-4	-11,12,L			4	61	66
8	15	5	6	31	-31				5	64	58
9	38	-44	7	128	-115	4	38	-28	6	90	-83
			8	46	-29	5	65	66	7	46	25
-11,2,L			9	11	-19	6	61	-59	8	29	-28
			10	86	75	7	21	-22	9	58	-47
2	6	2	-11,7,L			8	46	43	10	30	25
3	52	-50							11	120	131
4	11	-24	-11,13,L			-10,4,L			-10,4,L		
5	48	-48	2	51	34						
6	52	35	3	24	13	5	9	7			
7	69	56	4	6	-10	6	53	49	1	65	-77
8	34	-23	5	86	81	7	16	-30	2	58	-53
9	26	-19	6	6	-2				3	35	16
10	87	88	7	36	-26	-10,6,L			4	51	-47
			8	16	3				5	6	-6
-11,3,L			9	34	-29	2	15	-23	6	90	95
			10	1	-2	4	165	165	7	44	-44
2	19	21				6	200	202	8	68	-66
3	6	8	-11,8,L			8	32	-20	9	18	6
4	6	-24				10	58	-59	10	49	43
5	42	44	3	38	12				11	46	31
6	28	-8	4	28	-16						
7	37	-33	5	44	-44						

-18,5,L			1	41	48	5	9	9	4	21	-38
2	46	39	2	38	-13	6	18	3	6	32	28
3	35	-43	3	52	32	7	6	-8	8	137	141
4	16	19	4	77	76	8	52	-48	10	96	96
5	53	53	5	88	-79	9	35	37	12	50	-59
6	82	-87	6	8	6	10	28	-3	-9,1,L		
7	59	55	7	77	-79	-18,14,L			1	58	-67
8	41	46	8	29	-22				2	62	-53
9	21	24	9	28	-19	2	52	38	3	34	-41
10	28	-24	10	33	37	3	23	1	4	60	-59
11	3	-4	11	27	23	4	4	-13	5	69	-69
-18,18,L			-18,18,L			5	37	-43	6	42	35
-18,6,L			-18,6,L			6	54	51	7	33	39
1	118	-102	2	9	9	8	36	-48	8	1	11
2	27	-16	3	31	16	9	43	-14	9	27	-27
3	25	17	4	76	-69	-18,15,L			10	38	-21
4	92	-83	5	8	-7				11	7	26
5	8	10	6	108	117	2	27	-34	12	76	74
6	93	-94	7	43	31	3	3	-13	-9,2,L		
7	8	-19	8	53	-47	4	39	50			
8	17	5	9	58	-58	5	31	19	1	46	-36
9	52	46	10	54	-54	6	38	-28	2	144	156
10	20	-17	-18,11,L			7	24	29	3	10	1
11	74	67	-18,11,L			8	32	-34	4	27	19
-18,7,L			1	78	61	9	74	89	5	33	35
-18,16,L			2	31	-36	-18,16,L			6	46	-48
1	55	56	3	43	22				7	283	278
2	32	19	4	18	-19	-18,16,L			8	39	-36
3	54	46	5	65	-64	3	5	-16	9	93	87
4	45	47	6	29	-14	4	43	-47	10	6	-8
5	104	-113	7	28	-17	5	65	-52	11	36	-41
6	42	43	8	71	-64	6	34	26	12	26	9
7	52	-49	9	39	24	7	21	-4	-9,3,L		
8	64	66	10	14	-19	8	22	-12			
9	28	21	-18,12,L			-18,17,L			1	26	-33
10	28	-21	-18,12,L			-18,17,L			2	50	-45
11	25	10	-18,8,L			1	8	-28	3	15	-24
-18,8,L			2	49	38	4	49	38	4	159	-148
-18,8,L			3	27	-9	5	26	9	5	118	-116
1	68	-68	4	67	58	6	43	36	6	35	36
2	29	22	5	1	-16	7	13	28	7	11	3
3	65	55	6	38	34	8	37	-48	8	93	96
4	118	-113	7	43	45	-18,18,L			9	6	1
5	17	-29	8	41	-34				10	37	-38
6	23	-25	9	17	-14	-18,18,L			11	29	-14
7	55	49	10	62	-63	4	6	2	12	91	88
8	29	-34	-18,13,L			5	11	-18	-9,4,L		
9	8	-9	-18,13,L			6	44	31			
10	28	-28	-18,13,L			7	48	-38	-9,4,L		
11	78	86	1	22	-21				1	21	-21
-18,9,L			2	8	-14	-9,9,L			2	82	99
-18,9,L			3	47	38	4	48	-43	3	8	-8
-18,9,L			-18,9,L			2	192	192			

-9,4,L			-9,8,L			-9,12,L			2	34	24	
4	56	-68	1	8	17	1	42	33	3	92	-82	
5	161	154	2	5	-21	2	44	-31	4	9	-14	
6	42	-43	3	41	-39	3	62	52	5	9	22	
7	92	94	4	48	-34	4	91	77	6	73	-64	
8	154	-160	5	169	-165	5	15	27	7	70	76	
9	58	62	6	52	57	6	31	9	9	66	-64	
10	21	-4	7	15	23	7	47	-54	10	5	7	
11	37	-17	8	8	-12	8	27	36	-9,17,L			
12	29	-19	9	8	-8	9	16	-10	-9,17,L			
			10	14	-26	10	31	36	-9,17,L			
-9,5,L			11	3	12	11	18	4	1	41	23	
			12	60	54				2	23	-23	
1	15	-27				-9,13,L			3	56	55	
2	22	-13		-9,9,L					4	49	33	
3	16	-1				1	19	-14	5	27	39	
4	98	-93	1	32	31	2	8	6	6	69	63	
5	38	-15	2	39	34	3	46	-39	7	24	6	
6	33	35	3	8	8	4	68	64	8	8	25	
7	217	218	4	37	-39	5	55	-44	9	45	-41	
8	132	119	5	45	-44	6	67	-85	-9,18,L			
9	22	14	6	58	-53	7	55	55	-9,18,L			
10	33	-34	7	95	35	8	72	-71				
11	57	-55	8	24	23	9	26	-39	1	21	-7	
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			10	78	-55	11	22	2	3	9	-17	
-9,6,L			11	8	-19				4	46	35	
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5	36	39	3	22	-5	4	25	-12	-9,19,L			
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7	24	-5	5	53	39	6	11	2	-9,19,L			
8	92	-82	6	166	165	7	49	46	1	28	-24	
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			11	23	-2	-9,15,L			6	68	70	
-9,7,L				-9,11,L					7	8	-1	
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2	17	-10	1	44	42	2	29	39				
3	24	45	2	32	19	3	14	24	-9,20,L			
4	36	-28	3	58	-51	4	46	24				
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6	35	-29	5	163	-176	6	39	-17	3	7	-15	
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-9,21,L			4	149	-152	1	186	-191	-8,11,L		
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			10	68	-68	7	77	83	6	97	100
-9,22,L			11	6	-18	8	84	92	7	66	-72
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5	16	-26	-8,4,L			11	51	60	10	6	-15
6	25	-17				12	29	29	11	8	14
			1	19	2				12	21	19
-8,8,L			2	37	-46	-8,8,L					
			3	173	181						
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			10	28	-29	7	47	-50	6	154	158
-8,1,L			11	26	-16	8	140	138	7	78	81
			12	28	7	9	102	-102	8	61	-57
1	87	-105				10	9	14	9	69	68
2	34	-29	-8,5,L			11	81	-83	10	8	-9
3	216	227				12	8	-3	11	13	-12
4	52	-51	1	130	-131				-8,9,L		
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6	138	-136	3	128	126						
7	126	-127	4	149	-155	1	8	29			
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9	187	-188	6	68	59	3	44	-33	2	8	16
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11	14	26	8	26	6	5	118	-117	4	28	-26
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			10	24	-24	7	58	57	6	103	-101
-8,2,L			11	72	79	8	142	141	7	101	-102
			12	41	41	9	8	23	8	3	-1
1	22	13				10	35	-36	9	33	-48
2	55	61	-8,6,L			11	62	53	10	19	-21
3	88	89				12	24	-38	11	31	-11
4	39	43	1	31	32						
5	3	-27	2	38	-48	-8,10,L			-8,14,L		
6	29	36	3	57	60						
7	52	-47	4	77	-82	1	8	7	1	43	-34
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9	16	-8	6	205	-212	3	59	66	3	15	20
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			10	17	4	7	51	-48	7	127	130
-8,3,L			11	89	-82	8	45	51	8	8	-7
			12	22	-24	9	54	-54	9	39	34
1	51	-63				10	59	60	10	40	-31
2	22	4	-8,7,L			11	19	2			
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-8,14,L			-8,19,L			-8,24,L			2	74	77
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			2	16	-13	3	33	-34	5	219	-295
-8,15,L			3	64	69	4	58	-47	6	56	52
			4	62	55	5	6	-29	7	159	166
1	61	57	5	51	45	6	6	9	8	134	-135
2	28	36	6	37	-35				9	124	123
3	49	-19	7	51	-44	-8,25,L			10	189	-188
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7	79	-73									
8	6	-26	-8,26,L			-7,9,L			-7,4,L		
9	38	-47									
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-8,16,L			4	78	-71	8	168	176	4	36	29
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8	52	-57	1	6	26	4	14	26	13	50	-44
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11	32	-2	4	76	74	7	74	-79			
			5	18	16	8	6	14	1	55	62
-8,17,L			6	17	-9	9	67	72	2	161	-179
			7	32	-19	10	28	-37	3	43	-41
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2	21	13	9	27	15	12	6	-17	5	92	99
3	6	10				13	6	-13	6	162	166
4	88	92	-8,22,L						7	271	-275
5	122	121				-7,2,L			8	131	-134
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-8,18,L			7	6	-8	6	83	87	-7,6,L		
			8	63	45	7	425	434			
1	56	-45				8	117	126	1	86	98
2	6	-39	-8,23,L			9	38	-41	2	68	-66
3	37	-32				10	59	-61	3	6	7
4	55	-53	1	37	-39	11	5	-6	4	165	169
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7	69	-67	4	52	56				7	137	-133
8	6	7	5	32	6	-7,3,L					
9	43	47	6	15	-19						
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-7,6,L			3 78 -76			-7,14,L			1 19 -15		
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12	44	-23	9	59	54	5	6	11	6	8	-8
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-7,7,L			11 26 22			7 24 28			8 42 43		
			12	65	65	8	37	-41	9	37	24
1	11	-16				9	127	136	10	28	-21
2	122	-128	-7,11,L			10	8	-16			
3	23	-26				11	9	-20	-7,19,L		
4	213	205	1	138	-135	-7,15,L			1	21	7
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6	154	157	3	196	-199						
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8	39	28	5	157	-106	2	12	-5	4	46	46
9	166	-172	6	126	-119	3	67	58	5	74	-75
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			12	14	-26	9	25	14			
1	116	118				10	18	-19	-7,20,L		
2	132	-125	-7,12,L			11	37	35			
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9	78	-85	6	24	-16	4	8	-3	7	46	-56
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			12	24	-15	10	8	-5			
1	112	111				11	8	-8	1	35	-38
2	125	-132	-7,13,L						2	18	-20
3	75	-78				-7,17,L			3	8	41
4	175	181	1	121	-115				4	36	32
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-7,10,L			11	44	42	10	11	29	2	36	21
			12	13	-10	11	32	-33	3	6	-25
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-7,22,L			4	189	-191	2	49	42	11	119	-128
			6	187	182	3	233	-223	12	9	-13
6	75	93	8	224	-237	4	141	-145			
7	9	-11	10	30	-16	5	123	126			-6,8,L
8	9	8	12	75	75	6	83	88			
9	9	-4				7	132	-137	1	59	56
			-6,1,L			8	38	-43	2	41	48
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3	0	-10	4	195	185	13	15	13	7	88	-78
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6	9	19	7	37	41				10	42	44
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			12	32	-15	5	194	188			
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2	15	6				7	39	-59	2	38	-41
3	9	-9	-6,2,L			8	341	-331	3	54	59
4	19	5				9	116	-125	4	116	118
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			5	150	-156				9	56	-55
-7,25,L			6	87	-89	-6,6,L			10	162	167
			7	14	8				11	149	-142
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-7,26,L						9	129	119	5	168	114
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			8	292	-298	1	165	-162			
-7,27,L			9	121	-126	2	56	-59			-6,11,L
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-6,8,L			-6,4,L			8	19	22	5	222	218
						9	69	72	6	147	148
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8	115	-116	5	8	-9	6	53	49			
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-6,12,L			11	38	29	-6,20,L			6	70	69
									7	8	-6
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2	125	123				2	15	8			
3	124	-129	1	61	53	3	42	58	-6,25,L		
4	168	159	2	163	-178	4	8	-2			
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7	77	73	5	15	-33	7	16	11	3	23	9
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12	53	-52	10	72	78	-6,21,L			8	31	-25
			11	19	-2						
-6,13,L						1	4	-9	-6,26,L		
			-6,17,L			2	35	-36			
1	139	-149				3	8	21	1	8	6
2	168	98	1	15	-7	4	45	-58	2	29	-11
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8	71	-72	7	38	-39	10	28	24	-6,27,L		
9	92	89	8	49	42						
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12	8	-1				4	27	-19			
-6,19,L						5	44	-34	-6,29,L		
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				7	182	189	3	6	17				
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					9	62	-66	5	104	-101	2	89	85
1	249	-268		10	23	-18	6	47	-36	3	115	119	
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5	88	-83					10	84	85	7	94	97	
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7	88	-81					12	6	-14	9	146	159	
8	123	-122		1	114	116				10	18	14	
9	233	233		2	205	222	-5,9,L			11	31	27	
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11	23	33		4	1	4	1	14	-4				
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13	8	-11		6	75	-71	3	261	254				
				7	105	-105	4	138	130	1	283	-278	
			-5,2,L		8	117	-125	5	6	17	2	8	7
					9	83	-95	6	66	-59	3	61	-49
1	133	128		10	71	89	7	6	6	4	126	-128	
2	93	83		11	12	-9	8	115	-118	5	27	-14	
3	36	40		12	51	50	9	118	-112	6	171	163	
4	239	218		13	33	24	10	37	42	7	1	-21	
5	8	6					11	2	-4	8	78	71	
6	28	-18		-5,6,L			12	6	-8	9	54	71	
7	158	142								10	169	-162	
8	36	34		1	48	49	-5,10,L			11	56	43	
9	71	-85		3	47	43				12	36	-33	
10	55	-57		4	18	-3	1	79	-80				
11	14	-12		5	275	-269	2	96	112	-5,14,L			
12	51	-62		6	68	-76	3	129	131				
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				8	56	63	5	61	66	2	163	173	
			-5,3,L		9	22	-23	6	26	-33	3	19	19
					10	6	7	7	303	301	4	155	-158
1	188	192		11	66	69	8	38	41	5	47	56	
2	250	246		12	16	24	9	18	16	6	73	69	
3	203	-274					10	27	-1	7	144	150	
4	25	16		-5,7,L			11	22	6	8	62	58	
5	61	-45					12	6	-16	9	98	-167	
6	171	-165		1	216	212				10	26	13	
7	87	101		2	215	215	-5,11,L			11	6	14	
8	284	-261		3	300	299				12	101	-95	
9	93	101		4	298	-281	1	49	44				
10	25	-23		5	254	238	2	33	42				

-5,15,L			-5,19,L			5 115 -124			6 0 -11		
2	45	26	1	6	19	7	15	18	-5,29,L		
3	159	164	2	0	0	8	68	-77	1	21	25
4	168	-111	3	59	78	9	0	12	2	27	-19
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6	175	189	5	95	96	-5,25,L			4	35	17
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9	69	-76	8	0	-14	3	0	15	-5,30,L		
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-5,16,L			-5,20,L			6	72	88	1	0	-9
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2	31	34	2	74	-81	9	19	20	4	36	-22
3	36	-29	3	55	-52	-5,25,L			-4,6,L		
4	79	-75	4	29	-40	-5,25,L			-4,6,L		
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6	81	85	6	72	75	2	17	-9	4	244	233
7	186	185	7	88	-88	3	97	-103	6	145	149
8	0	-1	8	49	-52	4	36	37	8	223	-235
9	89	-89	9	18	-19	5	41	-41	10	17	2
10	42	-42	10	47	65	6	25	-2	12	54	-35
-5,21,L			7	0	-11	-4,1,L			-4,1,L		
-5,17,L			8	0	-17	-4,1,L			-4,1,L		
1	212	221	1	68	63	-5,26,L			1	437	-452
2	113	119	2	82	76	-5,26,L			2	58	58
3	195	184	3	57	-69	1	0	2	3	787	-667
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8	35	38	8	1	-21	6	23	14	8	48	51
9	23	-26	9	14	-4	7	0	9	9	219	223
10	0	13	-5,22,L			8	15	8	10	29	49
11	61	-76	-5,27,L			-5,27,L			11	0	-2
-5,18,L			13	74	-62	-5,27,L			-5,27,L		
1	168	184	1	81	89	1	33	-25	-4,2,L		
2	122	-138	2	82	-87	2	31	-5	-4,2,L		
3	28	37	3	67	-71	3	17	16	-4,2,L		
4	113	-113	4	0	22	4	75	85	1	309	-315
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6	97	96	6	51	-47	6	33	-21	3	478	452
7	87	-92	7	67	-83	7	0	16	4	224	217
8	16	-8	8	0	-6	-5,28,L			5	267	-272
9	56	-55	-5,23,L			-5,28,L			6	267	254
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11	36	29	2	29	31	2	0	8	8	286	-292
			3	43	-64	3	12	-45	9	120	122
			4	16	-7	4	24	-20	10	169	179
			5	61	68	5	61	68	11	20	13
						12	25	-29			

-4,3,L			-4,7,L			11 11 -24			8 195 208		
2	194	-204	1	132	135	12	9	9	9	24	-35
3	279	-262	2	342	329				10	87	-98
4	139	-135	3	215	189				11	19	-26
5	131	114	4	197	182	1	333	331			
6	360	-343	5	172	167	2	123	113			
7	25	27	6	218	-216	3	19	11	1	141	-148
8	166	171	7	124	-126	4	35	-28	2	19	26
9	45	43	8	187	196	5	196	-204	3	162	-149
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			12	26	-32	9	75	-65	7	118	112
-4,4,L						10	58	-59	8	43	45
-4,8,L						11	38	-29	9	7	-19
1	75	-79				12	37	35	10	3	12
2	487	-481	1	8	-18				11	72	72
3	188	-178	2	597	484						
4	253	240	3	279	262						
5	205	182	4	317	-316	1	58	-47			
6	67	-57	5	181	-98	2	111	100	1	34	38
7	9	-21	6	198	-185	3	282	213	2	68	-69
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9	64	67	8	66	61	5	64	-68	4	31	-34
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12	11	-6	11	69	-70	8	151	-156	7	94	-96
			12	21	7	9	8	3	8	76	79
-4,5,L						10	52	-62	9	27	-8
-4,9,L						11	45	49	10	49	63
2	237	-229				12	31	-38	11	25	19
3	63	-53	1	292	288						
4	169	-172	2	125	131						
5	146	-147	3	297	294						
6	319	-328	4	144	143	1	94	98	1	8	13
7	49	-44	5	58	-52	2	8	5	2	149	-141
8	112	111	6	12	-19	3	258	-259	3	64	-53
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12	8	-5	10	68	-63	7	55	-66	7	123	138
			11	34	29	8	54	-41	8	34	-37
-4,6,L			12	48	-36	9	29	-28	9	53	44
						10	96	-186	10	52	62
1	26	-6				11	38	41	11	8	-11
2	155	156				12	46	48			
3	463	368	1	69	-69						
4	134	-131	2	266	262						
5	216	217	3	217	-203						
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11	88	-71	9	23	24	6	147	152			
12	6	1	10	54	-52	7	189	116			

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10	22	37	2	66	80		4	24	-27	5	447	435
11	26	15	3	1	6		5	0	20	6	19	-21
			4	7	-32		6	0	-11	7	160	151
			5	105	-113		7	0	34	8	0	21
			6	21	26				9	34	-39	
1	40	-38	7	40	48	-4,29,L			10	46	50	
2	151	-164	8	17	-34				11	0	20	
3	63	76	9	30	25		1	0	13	12	0	-1
4	0	21					2	19	46			
5	32	-26	-4,24,L	3	1	9				-3,3,L		
6	217	231					4	21	-33			
7	89	94	1	70	-80		5	14	12	1	219	-223
8	13	-5	2	53	49		6	31	-15	2	23	22
9	28	-16	3	44	-47				3	209	198	
10	18	-44	4	197	209	-4,30,L			4	832	-809	
			5	62	-62				5	272	-259	
			6	70	-90		1	27	21	6	0	2
			7	64	73		2	13	-36	7	230	233
1	55	-44	8	49	-50		3	16	13	8	132	133
2	27	-29	9	0	-2		4	10	-20	9	162	-179
3	27	34					5	24	7	10	0	0
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5	0	-10				-4,31,L			12	15	-25	
6	103	-120	1	21	-6							
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8	39	-29	3	23	4		2	0	14			
9	15	23	4	100	-111		3	4	3	1	15	-5
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			6	0	-2				3	225	-223	
			7	46	-49	-3,0,L			4	25	14	
			8	27	-24				5	88	-85	
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2	237	250	-4,26,L				4	199	197	7	202	202
3	0	36					6	464	-451	8	53	-54
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6	43	-41	3	50	52		12	0	-23	11	30	-16
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9	10	25	6	25	-27				-3,5,L			
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			8	20	-20		2	224	-226	1	211	210
							3	442	433	2	35	-36
							4	237	-246	3	100	93
							5	171	167	4	685	-646
1	86	-81	1	32	22		6	68	-75	5	80	67
2	163	176	2	0	20		7	95	89	6	139	127
3	39	-37	3	0	-15		8	63	72	7	4	10
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5	14	-19	5	5	-20		10	72	-71			
6	32	-34	6	14	-35		11	7	-7			
7	83	79	7	17	-6		12	42	27			
8	39	-49										

-3,5,L			4	212	-219	2	70	-61	3	0	6
9 102 -110			5	153	141	3	26	18	4	18	-24
10 00 03			6	44	50	4	390	388	5	27	-34
11 9 6			7	6	5	5	37	32	6	31	-27
12 35 -35			8	79	82	6	31	22	7	64	50
			9	6	5	7	280	-202	8	123	-125
-3,6,L			10	38	39	8	82	-93	9	54	-62
			11	77	69	9	107	106	10	19	-16
			12	70	-77	10	23	-21	11	48	-47
1	143	139				11	0	16			
2	169	-155	-3,10,L			-3,18,L			-3,18,L		
3	198	-207				-3,14,L			-3,18,L		
4	74	-73	1	272	-248	1	26	38	1	118	113
5	399	-395	2	89	74	2	85	73	2	185	183
6	186	95	3	62	71	3	178	172	3	19	-10
7	73	76	4	229	-223	4	48	-45	4	83	84
8	17	-16	5	18	-3	5	63	54	5	64	-65
9	9	6	6	82	87	6	98	100	6	145	-140
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12	18	-1	9	77	-79	9	17	20	9	42	48
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-3,7,L			11	49	44	10	36	-44	-3,19,L		
			12	14	8	11	22	-15	-3,19,L		
1	146	-126	-3,11,L			-3,15,L			1	49	59
2	394	-387				1	86	-79	2	172	-169
3	38	21	-3,11,L			2	81	-84	3	30	28
4	104	113	1	317	-309	3	43	-37	4	83	-85
5	125	113	2	264	266	4	30	25	5	254	268
6	98	100	3	214	-214	5	33	-29	6	9	-8
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8	145	143	5	74	-81	7	172	-185	8	53	51
9	132	-124	6	103	103	8	96	-87	9	85	92
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11	94	97	8	105	-100						
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			10	56	-46	10	37	41	-3,20,L		
-3,8,L			11	22	28	11	27	-26	-3,20,L		
			12	59	-54	-3,16,L			1	203	-212
1	221	-194	-3,12,L			2	22	-15	2	167	-110
2	65	67				3	74	-72	4	24	13
3	91	-84	-3,12,L			2	87	96	5	168	-181
4	605	-592	1	75	-60	3	203	201	6	36	-43
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6	34	-46	3	311	299	5	353	348	8	13	-13
7	117	-123	4	95	89	6	83	-84	9	75	75
8	46	-52	5	12	3	7	21	9	10	16	-6
9	36	-32	6	245	254	8	21	4			
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12	0	10	9	2	1	10	9	-7	-3,21,L		
			10	13	-11	11	9	-15	1	226	-229
-3,9,L			11	0	11	-3,17,L			2	56	-51
1	17	9	-3,13,L			1	107	99	3	61	63
2	206	272				2	216	-219	4	98	89
3	490	-475	1	53	77				5	23	36

-3,21,L			1	42	-49	3	29	17	2	64	-73
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7	2	9	3	9	29	5	36	42	4	173	-176
8	53	46	4	9	29	6	285	291	5	209	204
9	38	29	5	9	-19	7	60	44	6	183	189
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			7	73	78	9	9	9	8	153	155
-3,22,L						10	123	-125	9	9	-5
-3,27,L						11	78	80	10	9	-5
1	162	-178				12	9	-16	11	78	80
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3	186	-192	2	41	49	-2,1,L			-2,5,L		
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9	36	18				6	144	-137	6	83	87
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-3,23,L						8	32	31	8	95	-97
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3	139	-156	3	36	41	11	47	-45	11	9	-3
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5	23	13	5	17	38						
6	56	-49	6	35	-44	-2,2,L			-2,6,L		
7	15	-16	7	9	14	2	316	316	1	247	244
8	46	53				3	629	-612	2	427	-436
9	18	21				4	133	136	3	113	120
-3,24,L						5	98	88	4	136	-127
						6	142	-139	5	99	103
1	9	20	2	31	13	7	69	76	6	18	9
2	9	-15	3	52	62	8	136	145	7	53	45
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4	54	54	5	9	11	10	115	-114	9	79	-74
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7	9	9	1	33	32				12	26	15
8	36	63	2	26	-29	-2,3,L					
9	9	16	3	29	11	2	138	136	-2,7,L		
			4	1	-9	3	1849	1849			
-3,25,L			5	9	-7	4	148	-142	1	57	-55
						5	524	-511	2	462	-462
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3	2	7	1	9	-8	8	54	44	5	415	-416
4	27	18	2	41	39	9	77	-74	6	200	199
5	34	35	3	9	21	10	76	-74	7	96	92
6	32	-24	4	9	-8	11	9	-8	8	42	-38
7	9	5				12	9	-9	9	114	116
8	22	7	-3,32,L						10	146	-144
-3,26,L						-2,4,L			11	52	46
			1	9	28	1	98	-98	12	14	16

-2,8,L			-2,12,L			-2,16,L			3	47	46
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2	54	-46	2	458	-444	2	93	-87	5	4	-13
3	294	-285	3	266	-243	3	32	41	6	41	51
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8	12	-15	8	77	-86	8	35	24	-2,21,L		
9	73	-79	9	37	-39	9	8	13	1	32	-52
10	48	-45	10	8	-19	10	8	5	2	58	-54
11	18	17	11	16	-1	11	29	-13	3	18	-6
12	29	38	-2,13,L			-2,17,L			4	115	118
-2,9,L			1	165	-166	1	87	91	5	28	-27
1	172	-162	2	271	-267	2	94	-84	6	34	32
2	498	487	3	247	233	3	119	103	7	8	-14
3	89	57	4	45	-47	4	78	79	8	23	11
4	165	164	5	186	189	5	79	88	9	39	16
5	257	-246	6	143	-141	6	8	-5	-2,22,L		
6	57	49	7	86	-85	7	9	21	1	8	11
7	92	103	8	113	-102	8	28	-9	2	175	100
8	232	263	9	19	-22	9	59	-51	3	8	-2
9	54	50	10	8	13	10	51	52	4	8	5
10	89	-87	11	45	51	-2,18,L			5	12	1
11	71	55	-2,14,L			1	96	88	6	64	-53
-2,10,L			2	34	29	2	47	-51	7	17	14
1	195	181	3	89	-87	3	49	47	8	35	-29
2	294	-299	3	112	133	4	95	97	-2,23,L		
3	386	-290	4	77	-72	5	192	187	1	95	101
4	168	-167	5	199	-194	6	68	55	2	145	152
5	130	-133	6	309	326	7	5	24	3	33	-35
6	58	-53	7	8	-6	8	43	-54	4	22	-19
7	0	11	8	162	-158	9	68	54	5	42	-45
8	150	-176	9	44	31	10	43	46	6	45	38
9	58	-46	10	20	-13	-2,19,L			7	12	-19
10	20	-13	11	8	-1	-2,15,L			8	36	32
11	102	96	-2,11,L			1	146	128	3	105	111
1	85	-75	2	216	-215	4	159	161	-2,24,L		
2	15	17	3	124	124	5	23	-11	1	110	120
3	87	-77	4	31	-28	6	78	-82	2	8	-8
4	126	120	5	131	128	7	39	-23	3	22	-19
5	76	-82	6	316	-324	8	48	-38	4	8	3
6	239	236	7	78	77	9	38	34	5	11	-36
7	31	-26	8	46	55	10	23	31	6	6	-16
8	32	39	9	67	-64	-2,20,L			7	26	-9
9	62	64	10	38	13	1	75	-76	8	4	11
10	33	-46	11	8	-5	2	26	-14			

-2,25,L			-2,31,L			2 358 359			3 17 35		
2	93	-96	1	26	46	3	88	-94	4	65	-31
3	45	-45	2	39	9	4	121	136	5	197	-96
4	74	-82	3	14	-2	5	29	14	6	83	81
5	42	-46	4	74	69	6	121	123	7	357	-361
6	11	19	5	29	39	7	181	99	8	39	44
7	75	-63				8	52	-52	9	34	49
8	8	16	-2,32,L			9	26	5	10	31	-35
						10	94	-99	11	37	-30
						11	0	-2			
-2,26,L			1 46 -57						-1,8,L		
1	39	-44	2	9	-3	-1,4,L			1	36	13
2	177	-196	3	0	5	1	139	143	2	844	-838
3	19	13	-2,33,L			2	686	684	3	4	7
4	55	-49	1	22	36	3	51	-52	4	543	514
5	22	22	-1,8,L			4	139	136	5	197	197
6	9	7	2	323	-321	5	288	299	6	31	36
7	9	12	4	469	-471	6	89	93	7	84	-89
8	42	25	6	122	-136	7	69	66	8	52	-62
			8	19	-13	8	51	53	9	29	28
-2,27,L			9	75	81	9	75	81	10	26	11
1	46	49	10	27	-37	10	36	-15	11	0	-5
2	20	-27	-1,9,L								
3	38	-42	-1,5,L								
4	88	-91	-1,1,L			1	652	-628	1	321	-327
5	9	23	2	1272	-1318	2	116	182	2	216	-215
6	35	-42	3	29	6	3	173	-178	3	2	24
7	61	-68	3	77	74	4	31	-15	4	199	-95
-2,28,L			4	262	252	5	123	-121	5	49	-54
			5	245	-251	6	436	436	6	289	-284
1	8	-1	6	62	-56	7	7	-3	7	265	270
2	31	-46	7	111	113	8	71	-85	8	42	-40
3	9	15	8	22	-23	9	129	-146	9	8	1
4	96	-100	9	136	146	10	85	-79	10	41	26
5	8	16	10	49	-52	11	19	-23	11	27	-13
6	51	46	11	34	36	-1,10,L					
7	1	-16	-1,2,L								
-2,29,L			1	342	-349	2	327	-313	1	257	255
1	56	56	2	891	981	3	16	-23	2	26	-32
2	66	79	3	38	-28	4	213	201	3	365	-287
3	27	-29	4	267	276	5	197	191	5	52	54
4	27	-18	5	431	457	6	73	73	6	47	-34
5	35	42	6	278	-279	7	139	151	7	262	-277
6	17	-13	7	127	136	8	5	19	8	63	-62
			8	8	-7	9	84	86	9	53	55
-2,30,L			9	112	-105	10	57	54	10	8	8
			10	22	-13	11	41	-42	11	36	-6
1	25	-26	11	36	-23	-1,11,L					
2	73	-82	-1,3,L								
3	42	-29	1 567 566			1 286 -316					
4	57	68	1	489	494	2	156	-159			
5	9	-7									

-1,11,L	2 218 266	7 8 -4	5 65 63
	3 142 156	8 29 28	6 28 18
2 158 -139	4 98 -93	9 9 -27	7 20 -31
3 178 -195	5 172 -171		8 9 -3
4 120 -117	6 132 -134	-1,20,L	
5 295 290	7 0 20		-1,23,L
6 92 -05	8 56 55	1 29 44	
7 123 124	9 18 20	2 96 92	1 94 100
8 27 -16	10 32 -15	3 0 -23	2 105 -115
9 87 66		4 20 -20	3 144 -148
10 42 34	-1,16,L	5 78 -73	4 25 -16
11 33 -35		6 32 39	5 26 25
	1 79 72	7 22 10	6 9 -32
-1,12,L	2 26 10	8 0 15	7 42 36
	3 50 -46	9 43 31	8 36 -10
1 200 100	4 63 -52		
2 137 146	5 88 96	-1,21,L	-1,26,L
3 222 -221	6 85 -84		
4 152 149	7 14 -8	1 37 39	1 53 54
5 273 -266	8 39 36	2 25 -24	2 49 51
6 237 -241	9 14 -17	3 153 -163	3 54 59
7 39 31	10 62 54	4 58 66	4 29 -36
8 57 -57		5 46 52	5 27 17
9 68 71	-1,17,L	6 111 105	6 49 48
10 18 -6		7 25 5	7 16 8
11 46 -43	1 261 250	8 121 121	
	2 27 20	9 0 24	-1,27,L
-1,13,L	3 85 -76		
	4 91 -92	-1,22,L	1 0 6
1 231 -239	5 0 -4		2 72 -71
2 310 298	6 93 -92	1 121 -125	3 62 79
3 173 159	7 28 -31	2 100 100	4 0 -4
4 82 79	8 30 27	3 28 34	5 0 7
5 87 84	9 63 -58	4 41 -55	6 14 -8
6 107 -107	10 19 -7	5 53 58	7 7 11
7 25 -12		6 82 81	
8 49 56	-1,18,L	7 20 -27	-1,28,L
9 49 42		8 0 19	
10 39 38	1 93 96	9 27 -18	1 47 -64
11 36 -42	2 70 69		2 128 145
	3 56 -58	-1,23,L	3 0 14
-1,14,L	4 24 22		4 28 -18
	5 76 -86	1 60 -61	5 6 24
1 66 56	6 41 -44	2 114 -114	6 0 7
2 393 -364	7 75 69	3 102 -109	
3 213 209	8 21 2	4 54 53	-1,29,L
4 143 141	9 32 -25	5 12 -11	
5 38 52	10 45 -36	6 27 33	1 42 34
6 102 -109		7 95 92	2 24 -2
7 111 -109	-1,19,L	8 15 17	3 27 11
8 47 35			4 29 -18
9 54 48	1 81 87	-1,24,L	5 32 -25
10 6 12	2 144 146		6 0 -10
	3 135 -128	1 0 15	
-1,15,L	4 157 163	2 9 16	
	5 21 -20	3 46 50	
1 264 259	6 21 -18	4 38 -29	

-1,30,L			8 198 -212	7 129 -133	6 213 -216
2 29 -15	10	33 -25	9 46 46	8 159 158	7 196 183
3 83 -94	11	15 15	10 42 26	9 9 5	8 112 107
4 22 8			11 29 -11	10 18 19	
5 0 -14					
8,3,L					
-1,31,L				8,7,L	9,11,L
1 26 45	2	330 -350	1 619 -619	1 384 -361	
2 0 1	3	365 -357	2 148 -151	2 167 -165	
3 71 -83	4	334 354	3 476 452	3 29 42	
4 0 -9	5	142 153	4 49 51	4 45 -49	
	6	4 -26	5 331 327	5 23 28	
	7	57 -53	6 161 -157	6 189 184	
-1,32,L			7 64 -66	7 5 -6	
	8	31 -26	8 26 -13	8 48 -45	
1 17 -13	9	66 -72	9 12 -16	9 23 18	
2 0 -2	10	77 76	10 27 35	10 32 36	
3 34 -35			11 59 -44		
8,4,L				8,12,L	
-1,33,L				8,8,L	
1 0 -6	0	422 -395		0 296 -314	
2 21 -4	1	255 -257	0 540 -535	1 256 245	
	2	877 -962	1 294 -266	2 277 272	
	3	383 393	2 145 -124	3 163 -97	
8,9,L			3 358 333	4 162 164	
	4	36 36	4 87 81	5 6 7	
	5	135 -121	5 142 146	6 36 -26	
2 236 -252	6	128 -127	6 121 119	7 38 -33	
4 252 -262	7	199 -209	7 27 16	8 54 -51	
6 199 -215	8	201 204	8 17 22	9 26 17	
8 114 -114	9	0 0 -1	9 31 35	10 49 35	
10 152 -166	10	53 45	11 17 22		
	11		12 0 4		
8,1,L			11 5 3	8,13,L	
8,5,L					
1 23 -11			8,9,L		
2 0 -21	1	490 472	1 181 84		
3 271 -309	2	1136-1137	2 68 -64		
4 227 253	3	27 -19	3 68 -70		
5 267 299	4	44 -36	4 154 -145		
6 19 16	5	18 22	5 81 66		
7 56 -61	6	1 -4	6 61 -61		
8 114 114	7	21 -21	7 46 -49		
9 29 4	8	215 -226	8 58 39		
10 17 0	9	7 -12	9 0 18		
11 73 71	10	81 79	10 58 36		
	11	0 -6	11 3 4	8,14,L	
8,2,L			11 52 -38		
8,6,L				8,10,L	
0 935 886				0 436 441	
1 329 -323	0	169 148		1 316 -297	
2 286 301	1	398 -394	0 417 -432	2 50 60	
3 115 -122	2	769 -769	1 214 211	3 0 -14	
4 95 -100	3	197 197	2 0 -11	4 79 -76	
5 59 -64	4	63 59	3 106 157	5 66 59	
6 34 -46	5	100 100	4 145 136	6 52 -44	
7 56 -52	6	161 164	5 65 -55	7 39 -27	

8,14,L			8,19,L			8	8	-5	2	32	36
8	33	-26	1	68	71		8,24,L		3	6	-4
9	19	-13	2	38	33				4	5	-17
10	10	3	3	24	39	8	17	-3	5	6	6
			4	149	155	1	127	130		8,30,L	
8,15,L			5	26	3	2	72	78		11	-24
			6	58	57	3	56	-63		29	34
1	219	203	7	59	-41	4	11	6	1	61	62
2	139	133	8	62	-58	5	38	46	2	9	-26
3	68	56	9	26	14	6	28	-11	3	2	-12
4	116	-156				7	6	6	4	5	-8
5	97	-93		8,20,L		8	6	5	5	6	44
6	21	-12									
7	51	-50	8	6	-17		8,25,L			8,31,L	
8	48	49	1	38	-26						
9	58	-45	2	85	91	1	56	-70	1	67	75
10	14	11	3	9	-4	2	54	-63	2	18	17
			4	148	-141	3	1	6	3	6	2
8,16,L			5	24	-13	4	25	-38	4	40	44
			6	28	24	5	36	37			
8	73	-34	7	73	-73	6	6	4		8,32,L	
1	42	46	8	29	6	7	7	28			
2	158	134	9	21	26				9	6	-3
3	168	-160					8,26,L		1	6	6
4	171	-175		8,21,L					2	6	6
5	48	-28				8	34	-15	3	6	12
6	32	28	1	184	-98	1	84	89			
7	8	-9	2	86	84	2	26	18		8,33,L	
8	19	1	3	58	54	3	46	49			
9	49	41	4	8	22	4	46	-69	1	6	14
10	31	26	5	38	-32	5	6	6	2	14	-17
			6	6	4	6	6	25			
8,17,L			7	7	15	7	7	27		1,6,L	
			8	6	-4						
1	82	79					8,27,L		8	47	78
2	148	132		8,22,L					2	123	137
3	163	172				1	169	-127	4	39	-34
4	63	62	8	86	76	2	137	-138	6	157	172
5	46	-34	1	47	42	3	27	-19	8	34	35
6	8	-13	2	69	78	4	38	-26	10	6	13
7	79	-68	3	184	-113	5	6	19			
8	1	12	4	185	-185	6	33	29		1,1,L	
9	46	-37	5	6	6						
			6	1	6		8,28,L		8	11	-14
8,18,L			7	52	-53	9	23	1	1	58	-53
			8	35	7				2	233	-248
8	68	-67				1	6	34	3	92	-91
1	73	82		8,23,L		2	33	-44	4	215	-246
2	8	7				3	31	-33	5	48	58
3	156	-149	1	124	-137	4	6	-1	6	19	-27
4	27	-37	2	39	34	5	21	21	7	67	-71
5	55	59	3	94	99	6	6	9	8	32	46
6	23	-11	4	68	-74				9	166	167
7	8	-15	5	38	38		8,29,L		10	13	4
8	87	77	6	19	22						
9	18	14	7	18	16	1	32	-37			

1,2,L			1,6,L			1,8,L			1,9,L		
9	121	-126	9	212	-206	9	95	102	2	119	117
1	20	23	1	993	1007	1	59	-46	3	156	-157
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6	142	163	6	143	136	6	113	-105	8	58	59
7	192	-214	7	24	29	7	30	12	9	47	-46
8	8	-18	8	28	-24	8	33	-22			
9	72	-68	9	5	-6	9	49	44			
10	29	-31	10	0	3	10	44	-29			
1,15,L			1,11,L			1,20,-41			1,32,46		
1,3,L			1,7,L			1,13,-143			2,139,-143		
9	322	-325	9	367	-360	9	22	-3	3	91	89
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6	8	3	6	77	-75	6	130	122	9	6	21
7	106	104	7	46	-36	7	198	189			
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9	96	-101	9	36	-17	9	22	-6			
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1,16,L			1,21,-217			1,10,100			1,53,-44		
1,4,L			1,8,L			1,3,-14			3,4,14		
9	69	54	9	420	-422	9	38	37	4	4	14
1	1937	1946	1	504	-493	1	99	-112	5	152	154
2	61	-56	2	26	-8	2	0	-2	6	38	9
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5	64	-65	5	38	33	5	85	90	9	40	-34
6	45	-39	6	51	46	6	46	35			
7	60	-65	7	118	-119	7	28	30			
8	67	-60	8	9	3	8	8	3			
9	76	-77	9	43	32	9	48	-39			
10	5	15	10	0	-3						
1,17,L			1,11,37			1,24,37			4,222,-218		
1,5,L			1,9,L			5,33,-37			5,33,-37		
9	51	-43	9	32	31	1	63	-48	6	61	53
1	2138	2174	1	401	389	2	19	17	7	28	-8
2	738	707	2	696	-564	3	7	-9	8	69	-62
3	52	-56	3	267	-266	4	81	-73	9	13	-23
4	332	324	4	56	60	5	139	-136			
5	58	60	5	32	-25	6	122	113			
6	30	31	6	80	-65	7	27	21			
7	204	-209	7	16	-5	8	36	41			
8	29	-25	8	9	-22	9	70	58			
9	33	26	9	8	4						
10	0	9	10	21	5						
1,14,L			1,10,L			5,46,-64			4,68,73		
1,18,L			5,243,-245			5,46,-41					

1,18,L			8	48	32	4	24	17	10	24	-5	
			1	51	-58	5	0	-11				
6	9	2	2	121	127				2,2,L			
7	44	37	3	10	12		1,29,L		8	136	156	
8	25	-24	4	23	-27				1	129	-121	
9	6	-28	5	81	74	8	117	-129	2	377	-350	
1,19,L			6	24	18	1	0	-11	3	228	235	
			7	28	-15	2	37	32	4	25	36	
8	242	251	1,24,L			3	28	31	5	66	-69	
1	68	74				4	21	12	6	35	-35	
2	193	261	9	9	11	5	51	-46	7	34	-34	
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4	111	-125	2	134	-139	9	34	-52	9	9	8	
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6	15	26	4	33	24	11	27	25	2,3,L			
7	21	-26	5	2	18	12	0	-8	8	456	-530	
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			7	0	18	14	0	4		2	45	41
1,28,L			1,25,L			1,31,L			3	37	-47	
8	169	176	8	88	-94	9	66	-76	4	151	-150	
1	26	23	1	38	-51	10	38	7	5	58	-51	
2	166	-178	2	46	-46	11	28	-25	6	26	29	
3	73	-74	3	48	38	12	0	-9	7	57	58	
4	63	62	4	14	15	1,32,L			8	45	46	
5	51	-53	5	0	3				9	33	21	
6	9	14	6	36	-22	10	36	-52	10	35	31	
7	8	4	7	0	4	11	0	9	2,4,L			
8	44	-34				12	38	-5	1,21,L			
1,21,L			1,26,L			1,33,L			6	1128-1397		
8	31	36	8	36	43	1,33,L			1	237	246	
1	63	-56	1	5	-9	9	48	-38	2	261	239	
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3	132	149	3	36	39	11	0	7	4	129	128	
4	67	68	4	20	22	2,0,L			5	44	-49	
5	37	-38	5	20	-17				6	44	38	
6	7	3	6	21	-22	12	369	-487	7	44	46	
7	0	-6				13	61	-47	8	33	38	
8	41	-33	1,27,L			14	72	-87	9	3	9	
						1,22,L			10	64	54	
1,22,L			8	91	-102	6	12	16	2,5,L			
			1	27	18	7	178	-176				
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1	31	-20	3	45	45				1	33	-33	
2	149	-199	4	23	-1	9	474	598	2	34	-33	
3	2	-11	5	28	-38	10	122	121	3	547	514	
4	0	-4	6	17	-8	3,220,-245			4	96	-92	
5	27	22	1,28,L			4	83	-99	5	52	-42	
6	45	46				5	117	-141	6	74	-72	
7	20	-11	8	44	-42	6	21	-34	7	0	-8	
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1,28,L			2	0	2	8	79	83	9	0	3	
			3	23	32	9	27	17				

2,5,L			2,10,L			3 151 157			2,19,L		
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2,6,L			2	943	919	7	28	-21	2	42	-34
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1	236	223	5	137	-129	2,15,L			5	29	22
2	79	-71	6	67	-72	2,11,L			6	22	3
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5	196	-174	9	0	-14	1	25	28			
6	14	-22				2	62	-53	2,20,L		
7	75	72	2,11,L			3	197	-200	9	114	117
8	43	-36	4	205	-197	5	88	84	1	73	-89
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2,7,L			3	122	-117	8	22	19	4	33	26
			4	68	-59				5	9	8
8	44	-16	5	39	-36	2,16,L			6	6	11
1	16	-2	6	121	117				7	4	-12
2	289	277	7	66	49	9	9	4	2,21,L		
3	96	-85	8	13	-6	1	75	-59	2,12,L		
4	24	17	9	10	0	2	27	-27	4	67	-61
5	122	108				3	68	78	9	39	-19
6	28	3	2,10,L			5	74	71	1	16	-24
7	39	26				6	26	-21	2	18	-15
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9	2	0	1	28	11	8	42	29	4	8	2
			2	97	-159				5	6	5
2,8,L			3	71	53	2,17,L			6	27	22
			4	43	-38				7	6	-10
8	346	338	5	93	-95	2,16,L			2,22,L		
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3	8	-4	8	4	-9	2	64	-72	1	41	-36
4	6	5	9	61	-52	3	205	-216	2	26	28
5	146	-129				4	112	-125	3	44	-54
6	191	-98	2,11,L			5	2	3	4	28	35
7	81	77				6	47	44	5	51	-46
8	8	-17	8	233	-219	7	44	49	6	15	-12
9	8	1	1	13	0	8	27	-9	7	4	-5
			2	197	-189	2,18,L			2,23,L		
2,9,L			3	298	-295						
			4	135	-133	2,19,L					
8	134	-129	5	119	119	9	244	-252	9	43	44
1	66	-56	6	26	23	1	0	-1	1	73	77
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6	196	98	2,14,L			6	46	37	6	6	-12
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6	54	-47	2	31	24	1	8	18	6	185	95
						2	151	-144			
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						4	125	-99	8	22	15
8	23	-22	0	25	12	5	88	-84	9	53	44
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			8	24	-2	1	42	-34	5	43	33
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						5	139	-128			
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1	28	-11	3	175	163	8	37	-28	9	148	-148
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			7	31	-25				4	146	137
			8	14	11	0			5	139	127
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9	24	-22				2	82	88	7	8	-13
1	8	-11				3	185	-161	8	31	16
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1	25	-6	6	91	-182				4	289	-196

3,12,L			3,17,L			1 18 -22			3 16 18		
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3,13,L			5	0	1	3,23,L			2	52	54
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9	103	-103	3,19,L			2	15	22			
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1	19	-7									
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4,4,L											
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9	268	-249							5	22	-29
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4,26,L			3	121	138	3	42	48	5	18	-1		
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4	24	-2	1 8 16	3 12 -1	5 8 -10	
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			6,15,L		8 14 9	
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2	37	-41	2 45 -38	8 56 -55	3 19 -21	
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5	35	-23	6,23,L	3 34 -46		
				4 17 5		7,10,L
			6,16,L	5 19 21		
0	115	116	8 21 26		8 88 -88	
1	24	-12	1 64 -63		1 78 -66	
2	26	32	2 12 14	7,4,L		
3	44	-38		8 35 41	2 19 -16	
4	24	-8	0 25 9	1 196 192	3 1 -26	
5	8	1	1 34 17	2 81 -71	4 3 -16	
			6,24,L	3 62 48		
				4 8 8		7,11,L
0	5	1	2 13 2	5 8 8		
				5 0 0		
			6,17,L	8 17 -24		
			6,25,L		1 64 55	
0	53	-68	8 28 -26	7,5,L	2 17 -18	
1	46	42	1 8 -4	8 84 -89	3 13 -3	
2	38	34		1 56 -63	4 24 -17	
3	46	24	6,26,L	2 118 192		7,12,L
4	16	-8		3 39 -36		
			8 2 -1	4 27 23	8 46 -49	
			6,18,L	5 8 -1	1 88 -76	
0	8	11	8 38 -26		2 8 7	
1	39	36	6,27,L	7,6,L	3 68 -63	
2	93	91	8 8 -12	8 115 116	4 1 1	
3	71	-52		1 58 -54		
4	3	8	7,8,L	2 26 26	7,13,L	
				3 8 8		
			6,19,L	4 8 -9	8 26 -7	
				5 28 -6	1 59 65	
0	34	26	4 53 56		2 57 -49	
1	78	82		7,7,L	3 24 -14	
2	62	61			4 59 -39	
3	39	36		8 22 29		

7,14,L			7,23,L			8,6,L			8,14,L		
1	41	30	0	8	3	0	23	-30	0	30	25
2	25	10	1	44	-42	1	55	50	1	8	-11
3	9	-16				2	37	37	2	31	-26
4	47	25	7,24,L			3	9	2	8,15,L		
7,15,L			0	25	4	8,7,L			0	21	25
0	50	-44	8,8,L			0	92	97	1	36	-27
1	15	15				1	9	-18	2	31	-43
2	10	-22	0	45	53	2	26	-4			
3	29	-14	2	113	-116	3	6	16	8,16,L		
			4	49	-35						
7,16,L			8,8,L			0	6	-1			
0	24	-35	8,1,L			0	91	-91	1	43	-26
1	43	32	0	33	27	1	24	19	2	12	6
2	40	47	1	62	56	2	43	46	8,17,L		
3	23	12	2	99	-100	3	8	-7			
			3	29	-23				0	25	16
7,17,L			4	39	-22	8,9,L			1	46	-36
0	29	-22	8,2,L			0	73	70	8,18,L		
1	31	-20				1	35	26			
2	42	24	0	8	-6	2	33	16	0	32	27
3	0	-12	1	20	-18	3	27	2	1	39	-27
			2	33	47						
7,18,L			3	10	-8	8,18,L			8,19,L		
			4	41	-41						
0	25	-21	8,3,L			0	39	26	0	8	-14
1	21	10				1	38	-11	1	23	-19
2	45	-31	2	25	-23	2	20	11			
3	7	-1	3	29	-28	3	8	-11	8,20,L		
			1	25	-23						
7,19,L			2	74	-78	8,11,L			0	8	-1
			3	23	8						
0	19	-7	4	56	-33	0	18	-5	8,21,L		
1	8	1				1	57	50			
2	47	37	8,4,L			2	31	27	0	8	22
						3	8	12			
7,20,L			0	123	121				9,8,L		
			1	60	59	8,12,L					
0	0	-27	2	50	62				0	112	-104
1	0	-3	3	24	17	0	15	-15	2	0	4
2	0	-15	4	36	-17	1	38	48			
						2	14	8	9,1,L		
7,21,L			3	10	1						
			8,5,L								
0	34	13	0	77	-76	8,13,L			0	25	38
1	0	14	1	23	-8				1	70	59
2	30	-20	2	5	1	0	27	-9	2	24	2
			3	0	-23	1	49	41	9,2,L		
7,22,L			4	14	2	2	0	-4	0	93	-89
									1	106	104
0	0	-14							2	3	-14
1	0	-6									

9,3,L			9,8,L			9,14,L			10,3,L		
1	75	-74	9	19	4	9	27	17	9	9	-18
2	38	34	1	11	34	1	9	-18			
			2	9	1				10,4,L		
9,4,L			9,9,L			9,15,L			9	7	5
0	29	-25	9	49	-39	9	22	7			
1	64	74	1	17	16				10,5,L		
2	42	34	2	18	5	9,16,L			9	9	-18
9,5,L			9,10,L			9	25	26			
0	25	-26	9	23	-23	9,17,L			10,6,L		
1	28	13	1	9	12	9	3	-5	9	1	10
2	39	19							10,7,L		
9,6,L			9,11,L			10,8,L			9	8	3
0	9	-4	9	65	-61	9	48	-55			
1	9	36	1	9	-19				10,8,L		
2	46	19				10,1,L			9	18	6
9,7,L			9,12,L			9	13	19			
0	21	-29	9	49	-32				10,9,L		
1	6	-7	1	9	-16	10,2,L			9	17	5
2	9	8				9	27	5			
9,13,L			9	19	-24				10,10,L		
			1	13	12				9	17	28

-1,15,L	3 135 -120	1 8 15
1 264 259	4 157 163	2 9 16
	5 21 -20	3 46 56
	6 21 -18	4 38 -29

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END

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