An Interactive Program for the Interpretation of Patterson Functions and Its Uses

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Introduction

The fact that the phase of F_{hkl}[1] cannot be observed experimentally is a prominent restriction in crystal-structure analysis. A. L. Patterson approached this problem and determined that although a portion of the data is missing for a complete reconstruction of a picture of the crystal structure by Fourier methods and the F_{hkl}'s are not fully available, that the squares of the F_{hkl}'s, which do not involve their phases, are completely available. Patterson solved the problem of deriving information from these $|F_{hkl}|$'s by applying the "convolution" function of Fourier theory (4,5). Thus he derived a function in the form of a Fourier series depending on the $|F_{hkl}|$'s alone, now referred to as the Patterson function (1).

While automatic Patterson solving programs have been developed, many crystallographers prefer to interpret the Patterson function "by hand". A FORTRAN program, PATTI (PATTerson Interpreter), has been written to interactively manipulate the vectors and thus solve molecular structures from the Patterson peaks. While most of the functions carried out by PATTI are trivial in nature, the program provides a convenient mechanism for keeping track of the various vectors and trial positions. PATTI allows the user to generate trial coordinates using combinations of the Harker lines and planes and to examine these trial positions for other interactions. Subroutines are available which also allow the addition or subtraction of suspected interatomic vectors from trial positions already determined. A block diagram of PATTI is shown in Figure 1. The pro-

Subroutine name	Function
PLIST	Generates worksheet indicating possible Harker Vectors and lists various transfomations of X Y Z
HARKER	Calculates Harker symmetry operators and identifies peaks lying on Harker lines and planes
BUILD	Uses Harker planes and lines to define atomic positions (Creates test atom array)
READ20	Reads existing peaks from external tape into test atom array
WRITE20	Write test atom array onto external tape
DELXYZ	Add or subtract known vectors to existing atoms in array
LISTP	List contents of test atom array
XLIST	List Patterson peaks
DELTA	Look for vectors between test atoms
HALFX	Look for 2x 2y 2z peaks (centrosymmetric structures)
CHANGE	Manipulate coordinates in test atom array

FIGURE 1. *Block diagram showing the major subroutines and their functions in program PATTI.*

gram, written in standard FORTRAN, has been implemented on a CDC CYBER172 computer operating with the KRONOS operating system.[2]

Use of the Program

To fully test the program, a data set was obtained on a crystal of a 2:1 mixture of bis-triphenylphosphine zinc(II)bromide and triphenylphosphinetetrahydrofuran zinc(II)bromide. This complex was considered an excellent test of the potential of the program due to the presence of several heavy atoms. The compound crystallizes in space group C2/c with cell dimensions (at -160° C) of a = 35.433(20), b = 16.330(7), c = 15.391(7)Å, β = 108.70(2)°, and D_{calc} = 1.585 gm cm^{-3}. Data were collected at a low temperature (-160°C) using automated diffractometry. The diffractometer and data reduction techniques have been described previously (3).

A listing of the 25 largest peaks in the Patterson map as well as all probable Harker lines and planes through peak 50, the origin peak, are given in Table 1. There were three possible points on the Harker line at 0,Y,1/2 and eight points on the Harker plane at X,0,Z, yielding 24 trial atoms for the structure. Subroutine DELTA correctly located four trial atoms for which there were numerous interactions. A full-matrix least squares assigning bromine scattering factors to

TABLE 1. *Analysis of Patterson Peaks for Trial Structure.*

Peak Number	I	Patterson Coordinates				Atomic Interactions*	
		x	y	z			
1	51.6	.0456	0.000	.1451	H	Zn22-Br24	
2	50.0	.0627	.5000	.3398	H	Zn22-Br24	
3	49.4	0.0000	.0761	.5000	H	Zn22-Zn22	Br24-Br24
4	39.8	.1129	0.000	.1551	H	Br2 -Br2	
5	35.9	.2422	.3576	.3981		Zn1 -Zn22	
6	34.9	.2496	.4199	.3309		Br2 -Br24	
7	33.8	.0716	.3839	.2419		Br23-Br24	
8	33.8	0.0000	.2975	.5000	H	Br23-Br23	
9	33.3	-.0730	.3208	.2530		Br23-Br24	
10	33.3	-.0100	.0986	.0988		Zn22-Br23	
11	33.0	.4619	.3186	.2557		Br23-Br24	
12	32.1	-.0219	.3938	-.0924		Zn22-Br23	
13	31.9	.2491	.1413	.1695		Br2 -Br24	
14	31.7	.1751	.4574	.4110		Br2 -Br23	
15	31.2	-.0337	.1812	.2570		Br23-Br24	
16	31.2	.2140	.0455	.4204		Br2 -Br23	
17	31.0	.2323	.4546	.4991		Zn1 -Br23	
18	31.0	.4642	0.000	-.0030	H	Br23-Br23	
19	30.9	.1812	.4559	.4158		Br2 -Br23	
20	30.7	.0405	-.1076	.2455		Br23-Br24	
21	30.4	.0112	.1938	.4048		Zn22-Br23	
22	30.0	.1403	.4233	.1722		Br2 -Br24	
23	29.8	-.0445	-.0771	.3513		Zn22-Br24	
24	29.7	-.0232	.3058	.3984		Zn22-Br23	
25	29.4	.1756	.2416	-.0820		Br2 -Br23	
31	27.3	.3914	0.0000	.5085	H	Br24-Br24	
35	27.0	.4930	0.0000	.3512	H		
46	23.3	.0163	.5000	.1986	H	Zn22-Zn22	
47	23.1	.0014	0.0000	.2600	H		
48	22.8	0.0000	.2185	.5000	H	Br2 -Br2	
50	18.8	0.0000	0.0000	0.0000			

*H denotes a peak lying on a Harker plane or line.

these four atoms converged to R(F) = 0.35, and a difference Fourier yielded the positions of the missing zinc atom, which lies on a crystallographic two-fold axis, and the phosphorous atoms. Subsequent Fouriers were utilized to locate the remaining non-hydrogen atoms in the two molecules, as well as one tetrahydrofuran (thf) molecule of solvation. Full-matrix refinement converged to final residuals of R(F) = 0.122 and Rw(F) = 0.090 for the 2079 observed ($I > 3\sigma(I)$) data (out of 3958 unique).

The final coordinates were input to PATTI for verification of the Patterson map, and the interactions are noted in Table 1. As can be seen, the top 25 peaks are all due (in part) to interactions between the five heavy atoms (two Zn and three Br). There are few interactions due to Zn1, since it lies in a special position in the cell and thus has half weight in the Patterson.

The two different molecules present in the crystal are shown in Figures 2 and 3, and the fractional coordinates are given in Table 2. Complete crystallographic details for the structure are available.[3]

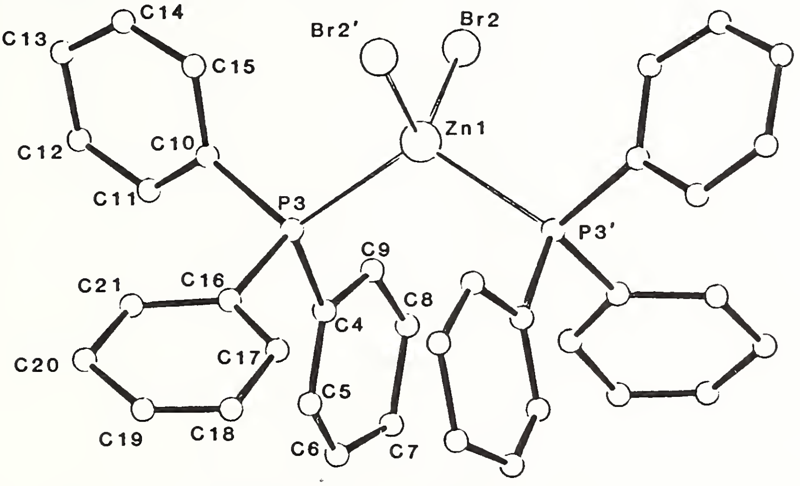

FIGURE 2. *Drawing of the* $ZnBr_2(PPh_3)_2$ *molecule. Important molecular dimensions are Zn-Br* = 2.378(6) Å; Zn-P = 2.417(13) Å; Br-Zn-Br = 113.5(4)°; P-Zn-P = 114.8(6)° and Br-Zn-P = 104.3(3)°.

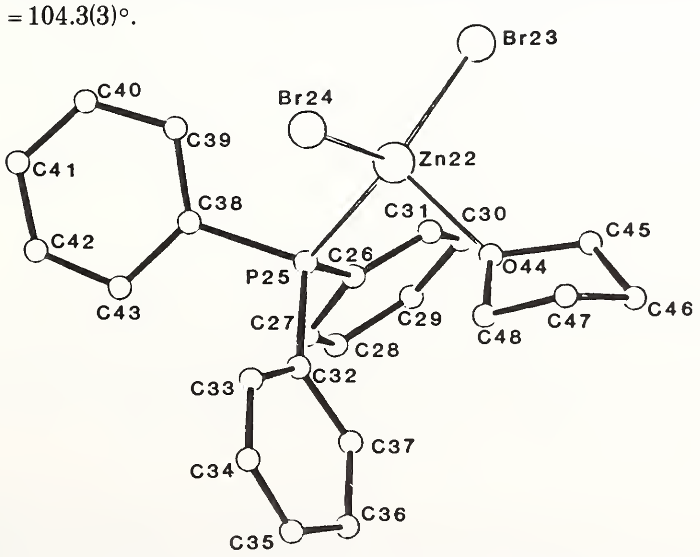

FIGURE 3. *Drawing of the* $ZnBr_2(PPh_3)(thf)$ *molecule. Important molecular dimensions are Zn-Br* = 2.359(7) Å (avg); Zn-P = 2.436(12) Å; Zn-O = 2.03(3) Å; Br-Zn-Br = 118.1(3)°; Br-Zn-P = 113.5° (avg); Br-Zn-P = 105.9°(avg) and P-Zn-O = 96.6(7)°.

TABLE 2. *Fractional Coordinates for* $ZnBr_2(PPh_3)_2.2ZnBr_2(PPh_3)$ *(thf).2thf.*

Atom	10^4x	10^4y	10^4z	Atom	10^4x	10^4y	10^4z
Zn1	5000	1902(4)*	7500	C28	5802(11)	722(25)	1807(28)
Br2	4442(1)	1103(3)	6656(3)	C29	5870(19)	1070(40)	1057(43)
P3	5164(3)	2699(8)	6347(8)	C30	6254(13)	1160(29)	1010(31)
C4	4749(10)	3456(22)	5740(23)	C31	6550(10)	918(22)	1745(24)
C5	4846(12)	4286(26)	5787(28)	C32	6865(11)	- 743(24)	3848(26)
C6	4543(15)	4766(32)	5379(34)	C33	7070(14)	-1074(30)	4653(33)
C7	4145(15)	4517(33)	5080(34)	C34	7065(11)	-1895(24)	4888(25)
C8	4047(16)	3636(36)	5042(37)	C35	6836(11)	-2411(25)	4311(27)
C9	4369(14)	3119(29)	5406(31)	C36	6608(11)	-2137(24)	3411(26)
C10	5181(11)	2041(24)	5384(26)	C37	6641(11)	-1304(25)	3206(27)
C11	5121(12)	2361(26)	4539(28)	C38	6832(12)	901(26)	4475(28)
C12	5164(15)	1910(34)	3819(36)	C39	6987(10)	1702(22)	4597(25)
C13	5332(12)	1115(28)	4030(30)	C40	6904(15)	2164(33)	5278(35)
C14	5368(14)	830(30)	4840(33)	C41	7642(13)	- 653(29)	1893(32)
C15	5328(14)	1222(30)	5580(33)	C42	6513(15)	1126(36)	5565(37)
C16	5625(10)	3300(22)	6693(24)	C43	6563(11)	605(24)	4918(26)
C17	5706(11)	3737(24)	7455(26)	O44	7579(7)	- 616(15)	2798(16)
C18	6077(12)	4243(25)	7774(28)	C45	6656(13)	1886(30)	5727(30)
C19	6302(13)	4239(29)	7260(32)	C46	7824(12)	-1482(29)	1886(30)
C20	6249(13)	3804(29)	6446(32)	C47	8056(11)	-1673(25)	2907(27)
C21	5915(10)	3335(22)	6211(23)	C48	7739(15)	-1423(32)	3260(34)
Zn22	7570(1)	449(3)	3467(3)	C49	4213(21)	3479(45)	2871(48)
Br23	7669(1)	1491(3)	2510(3)	C50	3949(21)	2868(45)	2028(50)
Br24	8047(1)	302(3)	4943(3)	C51	4047(17)	3271(34)	1228(38)
P25	6901(3)	295(7)	3560(7)	C52	4394(17)	3643(34)	1620(41)
C26	6506(11)	579(23)	2530(26)	C53	4462(21)	3728(45)	2431(53)
C27	6118(12)	477(27)	2534(29)				

*Numbers in parentheses refer to the estimated standard deviation of the least significant digit.

Results Using Other Structures

To verify the operation of PATTI, fifteen heavy atom structures of various complexity and symmetry were analyzed using the program. In only one case was the program unsuccessful, due primarily to non-crystallographic symmetry in the cell. After solution using other techniques, the correct atoms were found to indeed correspond to the Patterson peaks.

In one of the structures(2), $C_6H_6RuB_7C_2H_{11}$, the program was able to correctly locate not only the ruthenium atom, but six carbon and four boron atoms.

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Notes

1. The expression F_{hlk} represents the structure factor for the plane hkl, and is related to the observed intensity (I_{hkl}) by the expression $F_{hkl} = kI_{hkl}^{1/2}$, where k is a scale factor.
2. A FORTRAN listing of the program is available from the Molecular Structure Center at Indiana University. Address requests to JCH.

3. Complete crystallographic details for the zinc complex are available in microfiche from the Chemistry Library, Indiana University, Bloomington, Indiana, 47405. Request Molecular Structure Center Report No. 82805.

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